

## BITERTANOL (144)

### EXPLANATION

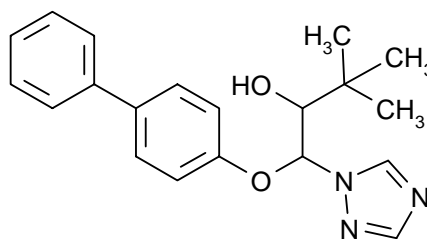
Bitertanol is an effective fungicide used preventively or curatively for the control of certain diseases in fruits and vegetables, e.g. scab and *Monilia laxa* in stone fruit, and as seed treatments against *Fusarium spp.*, *Septoria*, *Tilletia caries* etc.

Bitertanol was originally evaluated in 1983 for toxicology and 1984 for residues. The compound was identified as a candidate for periodic re-evaluation at the 1996 CCPR (ALINORM 97/24, Annex 1) and scheduled for consideration by the FAO Panel of the 1999 JMPR at the 1997 CCPR (ALINORM 97/24A para 91, Appendix III).

The present Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP and residue trials from the manufacturer. Additional information on GAP and national MRLs was provided by Australia, Germany, Poland and the Netherlands, and on GAP by the UK.

### IDENTITY

ISO Common name:	bitertanol
Chemical name:	
IUPAC:	1-(biphenyl-4-yloxy)-3,3-dimethyl-1-(1 <i>H</i> -1,2,4-triazol-1-yl)butan-2-ol (two diastereoisomers)
CA:	$\beta$ -([1,1'-biphenyl]-4-yloxy)- $\alpha$ -(1,1-dimethylethyl)-1 <i>H</i> -1,2,4-triazole-1-ethanol 2 diastereoisomers, A (1 <i>RS</i> , 2 <i>SR</i> ) and B (1 <i>RS</i> , 2 <i>RS</i> ), approximately 70:30
Manufacturer's code number:	BAY KWG 0599
CAS number:	55179-31-2
CIPAC number:	386
Synonyms:	Baycor, Sibutol
Structural formula:	



Molecular formula:  $C_{20}H_{23}N_3O_2$

Molecular mass: 337.4 g/mol

## PHYSICAL AND CHEMICAL PROPERTIES

A detailed chemical and physical characterization of the active ingredient is given in Table 1.

Test materials:

- A Bitertanol diastereoisomer A, batch KRJ 061080 (purity 99.4 %)
- B Bitertanol diastereoisomer B, batch KRJ 071080 (purity 99.7 %, data from 1981)
- C Bitertanol diastereoisomer B, (high-melting form), batch KRJ 120387 (purity 99.15 %)
- D Bitertanol diastereoisomer B, (low-melting form), batch KRJ 071080 (purity 97.4 %, data of 1989)
- E Bitertanol, batch 940309ELB03 (purity 96.7 % (diastereoisomer A 77.7%, diastereoisomer B 19.0%))
- F Bitertanol, batch APF 13028501 (purity 98.7 %)

Table 1. Physical and chemical properties of bitertanol.

Property	Characteristics	Test material	Reference																																												
Physical state, colour	white to grey powder		Bayer AG, 1998																																												
Odour	weak, characteristic		Bayer AG, 1998																																												
Vapour pressure	Diastereoisomer A: 2.2 x 10 <sup>-10</sup> Pa at 20 °C 8.0 x 10 <sup>-10</sup> Pa at 25 °C diastereoisomer B: 2.5 x 10 <sup>-9</sup> Pa at 20 °C 7.5 x 10 <sup>-9</sup> Pa at 25 °C	A  B	Herrmann, 1981a  Herrmann, 1981b																																												
Melting point	Diastereoisomer A: 138.6 °C diastereoisomer B (high-melting form): 147.1 °C (after heat treatment) diastereoisomer B (low-melting form): 125.8 °C (after heat treatment)	A, C, D	Krohn, 1989																																												
Partition coefficient n-octanol/ water	Diastereoisomer A: log Pow = 4.04 at 20 °C, pH 2-9 diastereoisomer B: log Pow = 4.15 at 20 °C, pH 2-9	E	Krohn, 1996																																												
Solubility in water	Diastereoisomer A: 2.7 mg/l at 20°C diastereoisomer B: 1.1 mg/l at 20°C sum of A + B: 3.8 mg/l at 20°C	E	Krohn, 1996																																												
Solubility in organic solvents (at 20 °C, in g/l)	<table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th style="text-align: center;">A</th> <th style="text-align: center;">B</th> <th style="text-align: center;">A + B</th> </tr> </thead> <tbody> <tr> <td>n-heptane</td> <td style="text-align: center;">0.30</td> <td style="text-align: center;">0.14</td> <td style="text-align: center;">0.44</td> </tr> <tr> <td>xylene</td> <td style="text-align: center;">16</td> <td style="text-align: center;">1.8</td> <td style="text-align: center;">18</td> </tr> <tr> <td>dichloromethane</td> <td></td> <td></td> <td style="text-align: center;">&gt;250</td> </tr> <tr> <td>2-propanol</td> <td style="text-align: center;">41</td> <td style="text-align: center;">26</td> <td style="text-align: center;">67</td> </tr> <tr> <td>1-octanol</td> <td style="text-align: center;">35</td> <td style="text-align: center;">18</td> <td style="text-align: center;">53</td> </tr> <tr> <td>polyethylene glycol</td> <td style="text-align: center;">65</td> <td style="text-align: center;">56</td> <td style="text-align: center;">120</td> </tr> <tr> <td>acetone</td> <td style="text-align: center;">127</td> <td style="text-align: center;">74</td> <td style="text-align: center;">200</td> </tr> <tr> <td>ethyl acetate</td> <td style="text-align: center;">92</td> <td style="text-align: center;">59</td> <td style="text-align: center;">150</td> </tr> <tr> <td>acetonitrile</td> <td style="text-align: center;">51</td> <td style="text-align: center;">28</td> <td style="text-align: center;">79</td> </tr> <tr> <td>dimethyl sulfoxide</td> <td></td> <td></td> <td style="text-align: center;">&gt;250</td> </tr> </tbody> </table>		A	B	A + B	n-heptane	0.30	0.14	0.44	xylene	16	1.8	18	dichloromethane			>250	2-propanol	41	26	67	1-octanol	35	18	53	polyethylene glycol	65	56	120	acetone	127	74	200	ethyl acetate	92	59	150	acetonitrile	51	28	79	dimethyl sulfoxide			>250	E	Krohn, 1996
	A	B	A + B																																												
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Relative density	data on the pure active ingredient not available; technical material: 1.19 20°C/4°C		Mobay Chemical Corporation, 1984e																																												
Hydrolysis rate	0.25 mg/l and 2.5 mg/l bitertanol in sterile aqueous buffer (pH 4, 7, 9) at 25°C and 40°C: no degradation after 30 days		Nichol and Thornton, 1979																																												
Photochemical degradation	half-life in aqueous solution under natural sunlight approximately 11 days		Sietsema, 1983																																												
Dissociation constant	Bitertanol does not show basic or acidic properties in water. It is not possible to specify a dissociation constant in aqueous solution.	E	Stupp, 1996																																												

Property	Characteristics	Test material	Reference
Temperature of decomposition or sublimation	Diastereoisomers A and B thermally stable at room temperature.	F	Klusacek, 1986
Volatility	Henry's law constant at 20 °C (calculated) Diastereoisomer A: $2.3 \times 10^{-10}$ [hPa x m <sup>3</sup> /mol] diastereoisomer B: $5.3 \times 10^{-9}$ [hPa x m <sup>3</sup> /mol]		Krohn, 1992

## Formulations

### Bitertanol

300 EC	emulsifiable concentrate containing 300 g/l bitertanol
500 SC	suspension concentrate containing 500 g/l bitertanol
25 WP	wettable powder containing 250 g/kg bitertanol

### Combinations of bitertanol with other pesticides

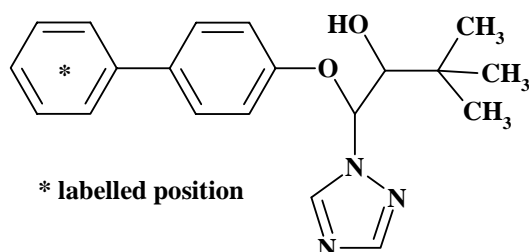
39.8 DS	powder for dry seed treatment containing 37.55 bitertanol + 2.3% fuberidazole
535.9 FS	flowable concentrate for seed treatment containing 33.8% bitertanol + 2.1% fuberidazole
199 FS	flowable concentrate for seed treatment containing 187.5 g/l bitertanol + 11.5 g/l fuberidazole
286 FS	flowable concentrate for seed treatment containing 188 g/l bitertanol + 23 g/l fuberidazole + 75 g/l triadimenol
325 FS	flowable concentrate for seed treatment containing 75 g/l bitertanol + 250 g/l anthraquinone
337.5 FS	flowable concentrate for seed treatment containing 37.5 g/l bitertanol + 125 g/l anthraquinone + 175 g/l imidacloprid
375 FS	flowable concentrate for seed treatment containing 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
398 FS	flowable concentrate for seed treatment containing 375 g/l bitertanol + 23 g/l fuberidazole
398.5 FS	flowable concentrate for seed treatment containing 375.2 g/l bitertanol + 23.3 g/l fuberidazole
10 LA	lacquer containing 10 g/l bitertanol + 10 g/l 8-hydroxyquinoline sulfate
236.1 LS	solution for seed treatment containing 140 g/l bitertanol + 8.6 g/l fuberidazole + 87.5 g/l imidacloprid
298 LS	solution for seed treatment containing 280 g/l bitertanol + 18 g/l fuberidazole
55 WP	wettable powder containing 5% bitertanol + 50% captan
68.75 WP	wettable powder containing 7.5% bitertanol + 60% captan + 1.25% triadimenol
72.5 WP	wettable powder containing 12.5% bitertanol + 60% captan

## METABOLISM AND ENVIRONMENTAL FATE

### Animal metabolism

#### Rat biokinetics

Bitertanol uniformly labelled with <sup>14</sup>C in the second ring of the biphenyl moiety was administered orally



to male and female rats at a dose level of 10 mg/kg (Klein, 1988a). Radioactivity was determined in the excreta and plasma as a function of time and the individual organs and tissues as well as the carcass were finally assayed for total radioactivity. Male rats were also administered the same dose

intraduodenally after bile fistulation and radioactivity was assayed in the excreta, including the bile, and in the body at death. A summary of the biokinetic data is given in Table 2.

After oral administration most of the radioactivity was absorbed. After intraduodenal administration of 10 mg/kg to the bile-fistulated male rats the recovered radioactivity in the urine, bile, and body excluding the gastrointestinal tract accounted for about 81%. Absorption commenced immediately, and the plasma concentration increased from 25 to 75% of the peak value within one to two hours, depending on the sex.

The radioactivity was almost completely excreted with the urine and faeces within the 72-hour test period. More than 90% of the recovered radioactivity was excreted with the faeces, and only about 7% with the urine. On average, the residual radioactivity in the body excluding the gastrointestinal tract at death amounted to about 0.5% of the administered dose, and that in the gastrointestinal tract to about 0.1%.

From the results of the bile fistulation experiment it could be concluded that most of the faecally eliminated radioactivity was first absorbed and then eliminated into the gut lumen with the bile, mainly after entering the enterohepatic circulation.

Table 2. Recovery of radioactivity as percentage of the administered dose (Klein, 1988a).

Sample	Route and sex		
	Oral, male	Oral, female	Intraduodenal, male
Bile			77.00
Urine	7.74	6.21	3.76
Faeces	92.16	85.77	14.19
GI-Tract	0.10	0.15	0.02
Body exc. GI-Tract	0.46	0.58	0.46
Recovery	100.46	92.71	95.42

The radioactivity was rapidly distributed from the intravascular space to the peripheral tissues. The maximum dose-normalized concentration of radioactivity in the plasma was reached after three to eight hours. The terminal elimination of radioactivity from the plasma was determined by linear regression analysis, which showed a half-life of about 26 hours.

Table 3 shows the radioactivity levels determined in the individual organs and tissues after oral doses at the end of the test period (72 hours); the highest concentrations were found in the liver and kidneys.

Table 3. Dose-normalized concentrations of total radioactivity in organs and tissues of rats 72 h after single oral doses of 10 mg/kg (Klein, 1988a).

Sample	Male rats			Female rats		
	P <sup>1</sup> , mean	cv, %	n	P <sup>1</sup> , mean	cv, %	n
Erythrocytes	0.00451	7	5	0.00409	19	5
Spleen	0.00227	15	5	0.00321	21	5
GI-Tract	0.01025	35	5	0.01369	46	5
Liver	0.07322	12	5	0.09844	26	5
Kidneys	0.03713	10	5	0.03623	39	5
Testicles	0.00082	17	5			
Ovaries				0.00658	45	5
Uterus				0.00235	37	5
Muscle	0.00070	10	5	0.00075	12	5
Bone	0.00075	5	5	0.00073	19	5
Heart	0.00162	16	5	0.00166	17	5
Lung	0.00551	20	5	0.00785	28	5

Sample	Male rats			Female rats		
	P <sup>1</sup> , mean	cv, %	n	P <sup>1</sup> , mean	cv, %	n
Brain	0.00052	19	5	0.00155	44	5
Skin	0.00164	10	5	0.00240	16	5
Carcase	0.00104	10	5	0.00141	16	5
Fat	0.00091	26	4	0.00114	37	5
Plasma	0.00187	16	5	0.00184	26	5
Body excl. GI-Tract	0.00511	13	5	0.00649	20	5

<sup>1</sup> (radioactivity measured per g sample)/(radioactivity administered per g body weight)

### Rat metabolism

The biotransformation of bitertanol was also studied by Klein (1988b, 1991). Metabolites were determined in the faeces, urine and bile, as well as in the liver, kidneys and perirenal fat at various times after dosing.

It was shown that metabolism commenced immediately after absorption from the lumen of the gastrointestinal tract. The parent compound was not detected in either urine or bile. The only metabolite identified in the bile was *p*-hydroxybitertanol. Excretion of the unchanged parent compound in the urine was unlikely owing to its lipophilic character. Metabolic degradation in the organs was also rapid: the bitertanol level in the liver fell from about 15 to 2% of the total organ radioactivity within eight hours. The main metabolite in the liver was also *p*-hydroxybitertanol, with smaller amounts of *p*-hydroxybitertanol acid, *p*-hydroxybitertanol alcohol, and bitertanol acid. The kidneys showed almost identical results: the percentage of total organ radioactivity fell from about 14 to 2.5% within eight hours. The major metabolite in the kidneys was again *p*-hydroxybitertanol, amounting to about 30 to 50% of the organ radioactivity. The other metabolites found in the liver were also present in the kidneys at similar levels.

The total radioactivity in the fat samples was too low to permit reliable quantification or identification of possible metabolites. This was mainly owing to the small amount of fat available in the young adult test animals.

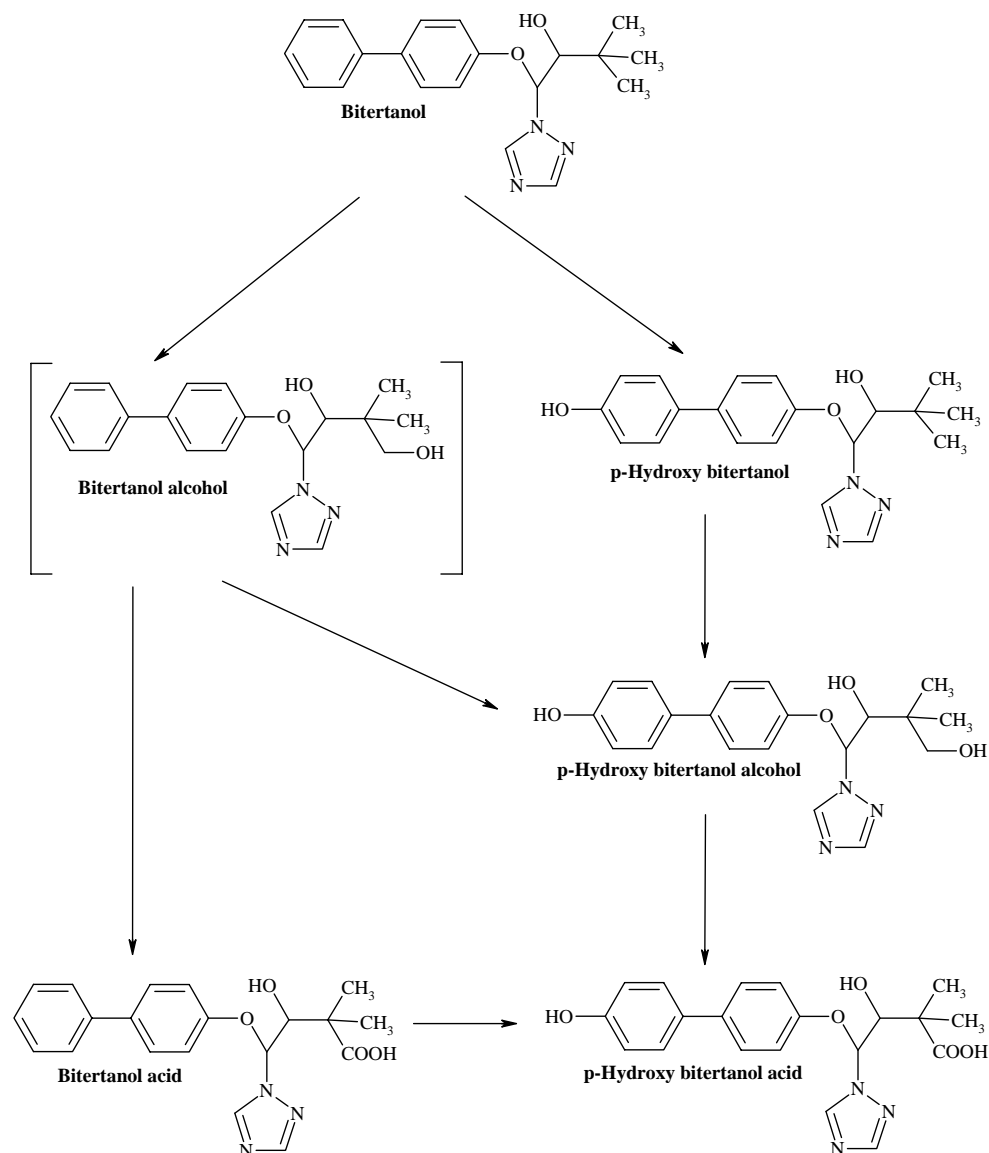
The presence of the parent compound in the faeces of orally treated rats can probably be explained by the unabsorbed fraction of administered radioactivity, amounting to approximately 15% of the dose. The main metabolite in the liver and kidneys, *p*-hydroxybitertanol, could also be identified in the faeces. The amounts of the other biotransformation products found in the organs were probably too low for detection in the excreta. The distribution of the identified metabolites in the faeces, liver and kidneys is shown in Table 4.

Table 4. Identified compounds in faeces, liver and kidneys as % of total <sup>14</sup>C at various times after oral administration of 10 mg/kg bitertanol (Klein, 1988b, 1991).

Compound	Faeces		Liver				Kidneys			
	male at 48 h	female	Male at				Male at			
			40 min	2 h	4 h	8 h	40 min	2 h	4 h	8 h
bitertanol	16.7	13.0	15.2	6.6	2.6	1.9	14.2	6.0	4.5	2.5
<i>p</i> -OH-bitertanol	2.1	2.2	33.2	38.0	23.2	25.0	32.4	35.1	46.9	48.9
<i>p</i> -OH-bit. alcohol			5.2	3.8	7.4	7.4	3.2	3.0	2.8	2.6
bitertanol acid			5.4	4.5	1.7	1.3	2.9	2.3	2.2	4.0
<i>p</i> -OH-bit. acid			3.5	3.0	---	---	3.0	---	2.2	---
Total identified			62.5	55.7	34.8	35.5	55.6	46.3	58.9	57.9

Proposed metabolic pathways of bitertanol in rats are shown in Figure 1.

Figure 1. Proposed metabolic pathways of bitertanol in rats after oral administration of 10 mg/kg (Klein, 1991).



The absorption, excretion, and metabolism of [U-*phenyl*-<sup>14</sup>C]bitertanol was investigated in rats under various dosing conditions as follows (Puhl and Hurley, 1983)

- Group A: single intravenous radiolabelled dose at 100 mg/kg
- Group B: single oral radiolabelled dose at 100 mg/kg
- Group C: fourteen daily oral unlabelled doses chemical followed by a single oral radiolabelled dose in each case at 100 mg/kg
- Group D: single oral radiolabelled dose at 1000 mg/kg

The absorption of radioactivity was found to depend on the dose. Its elimination was mainly in the faeces with urinary radioactivity representing only 4-11% of the dose. Seven days after dosing, 0.2-0.4% of the dose remained in the body. Bitertanol was extensively metabolized, with similar metabolite profiles in the various groups. The relative levels of metabolites were also similar, except that the animals receiving the highest oral dose eliminated much more unchanged parent compound than the others. A total of 14 metabolites plus bitertanol, representing a total of 38-76% of the recovered radioactivity were identified or characterized (Table 5). The metabolic reactions included ring hydroxylation and di-

hydroxylation, aryl *O*-methylation, aliphatic hydroxylation, aliphatic oxidation to the tertiary carboxylic acid, and ether cleavage.

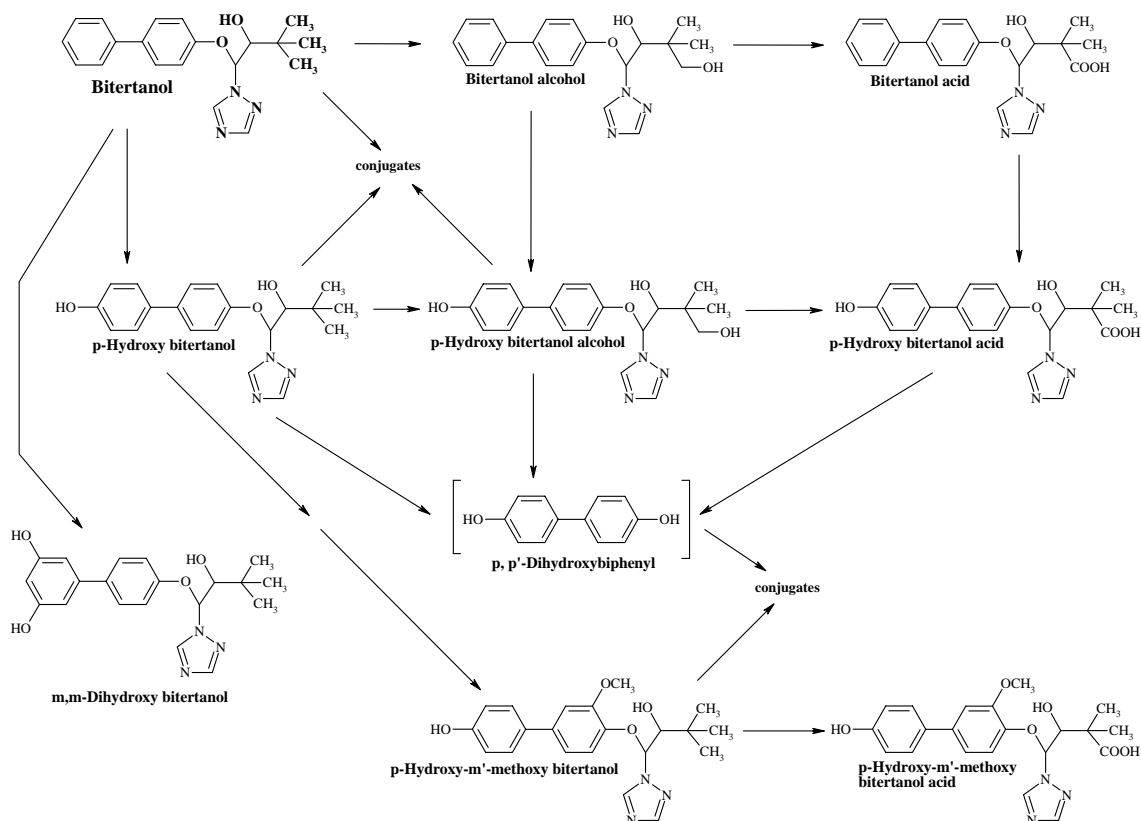
Table 5. Identified compounds in the excreta of rats (Puhl and Hurley, 1983).

Compound	% of recovered radioactivity							
	100 mg/kg i.v.		100 mg/kg oral		100 mg/kg oral		1000 mg/kg oral	
	Single dose		Single dose		Multiple doses		Single dose	
	Male	female	male	female	male	female	male	female
bitertanol	1.8	1.4	8.5	4.3	6.8	2.9	55.3	59.1
<i>p</i> -hydroxybitertanol	8.6	7.5	7.2	6.6	4.6	5.5	3.9	3.0
<i>p</i> -hydroxybitertanol alcohol	4.2	3.1	5.6	5.1	6.3	3.3	1.7	1.6
bitertanol acid	4.9	2.5	3.1	3.4	4.2	3.5	1.3	1.3
<i>p</i> -hydroxybitertanol acid	11.6	9.1	6.6	10.2	5.6	9.2	4.7	4.2
<i>m,m</i> -dihydroxy bitertanol	3.8	8.4	5.2	9.9	6.4	9.0	2.1	3.3
<i>p</i> -hydroxy- <i>m'</i> -methoxybitertanol	3.2	1.9	5.1	2.1	0.2	0.1	1.7	0.9
bitertanol alcohol	1.5	1.2	1.6	1.0	1.0	1.2	0.7	0.3
<i>p</i> -hydroxy- <i>m'</i> -methoxybit. acid	1.6	---	1.0	---	1.1	---	0.6	---
Conjugates*	2.6	3.6	2.1	2.5	2.0	3.3	1.5	1.8
Total	43.8	38.7	46.0	45.1	38.2	38.0	73.5	75.5

\*Glucuronide or sulfate

The metabolic reactions in rats under these conditions are shown in Figure 2.

Figure 2. Reaction pathways involved in metabolism of bitertanol in rats after oral administration of 100 and 1000 mg/kg doses (Puhl and Hurley, 1983).



The absorption, excretion, and metabolism of [U-*phenyl*-<sup>14</sup>C]bitertanol was investigated in male and female rats after a single oral dose of 100 mg/kg (Puhl *et al.*, 1979).

The results were similar to those found later and described above. The administered radioactivity was completely eliminated within 7 days. About 92% of the dose was found in the faeces and about 8% in the urine. The liver and kidneys showed the highest tissue residue levels. The unchanged parent compound constituted 8-11% of the excreted radioactivity. Chemical and spectral examination of some of the other components indicated that bitertanol underwent mono- and dihydroxylation of the biphenyl ring and hydroxylation at the *tert*-butyl group. In this early report structures were not identified.

### Ruminant metabolism

The metabolism and excretion of [U-*phenyl*-<sup>14</sup>C]bitertanol was investigated in a dairy cow after oral administration of 0.2 mg/kg bw. The excretion and tissue levels were described by Obrist *et al.* (1981) and the complete data including the metabolism results were given by the same authors in a second report (1983). In the first experiment, a single oral dose of 0.2 mg/kg bw was administered to a lactating dairy cow. Of the recovered radioactivity, 82.8% was in the faeces, 9.3% in the urine, and 0.2% in the milk. The residues in the milk did not exceed 0.009 mg/kg as bitertanol. The main metabolic pathway involved monohydroxylation of the phenyl ring. Minor reactions included hydroxylation and oxidation of the *tert*-butyl group, ring dihydroxylation, aryl *O*-methylation, ether cleavage, and conjugation. Thus, the major metabolites in the urine, faeces and milk were the diastereoisomers of *p*-hydroxybitertanol and their conjugates. The identified residues in the faeces and urine together represented about 75% of the excreted radioactivity (Table 6). The blood levels peaked at 0.013 mg/kg (bitertanol equivalents) 12.5 hours after dosing.

Table 6. Compounds identified in fractions of urine, faeces and milk after oral administration of [U-*phenyl*-<sup>14</sup>C]bitertanol to a dairy cow at 0.2 mg/kg bw (Obrist *et al.*, 1981, 1983).

Compound	<sup>14</sup> C as % of excreted		<sup>14</sup> C as % of total milk residue
	Urine	Faeces	Milk
bitertanol	0.2	12.3	35.2
<i>p</i> -hydroxybitertanol	2.2	39.2	48.8
<i>p</i> -hydroxy- <i>m'</i> -methoxy bitertanol	0.3	0.2	---
bitertanol alcohol	0.4	3.6	8.5
<i>p</i> -hydroxybitertanol alcohol	0.5	6.7	2.1
bitertanol acids	0.8	---	---
<i>p</i> -hydroxybitertanol acid	0.5	---	---
<i>p</i> -hydroxybiphenyl	0.7	2.6	2.9
<i>p,p'</i> -dihydroxybiphenyl	3.5	1.2	---
polar metabolites	---	15.3	---
Unextractable	---	4.1	---

In a subsequent experiment, the same animal was treated with five daily doses of 0.2 mg/kg bw [U-*phenyl*-<sup>14</sup>C]bitertanol, and killed 12.5 hours after the last dose. Tissue residues were 0.82 mg/kg (bitertanol equivalents) in the liver, 0.11 mg/kg in the kidneys, 0.03 mg/kg in fat and 0.01 mg/kg in muscle. The recovered radioactivity in the milk did not exceed 0.2% of the applied <sup>14</sup>C, and multiple dosing did not result in increased residues (the final residue was 0.008 mg/kg as compared with a maximum of 0.009 mg/kg in the single-dose experiment). Prominent metabolites in the tissues included *p*-hydroxybitertanol, bitertanol alcohol, *p*-hydroxybitertanol alcohol, and *p,p'*-dihydroxybiphenyl. The results are summarized in Table 7.



Table 7. Compounds identified in fractions of tissues from a dairy cow taken 12.5 hours after five daily oral doses of [U-phenyl-<sup>14</sup>C]bitertanol, 0.2 mg/kg bw per dose (Obrist *et al.*, 1981, 1983).

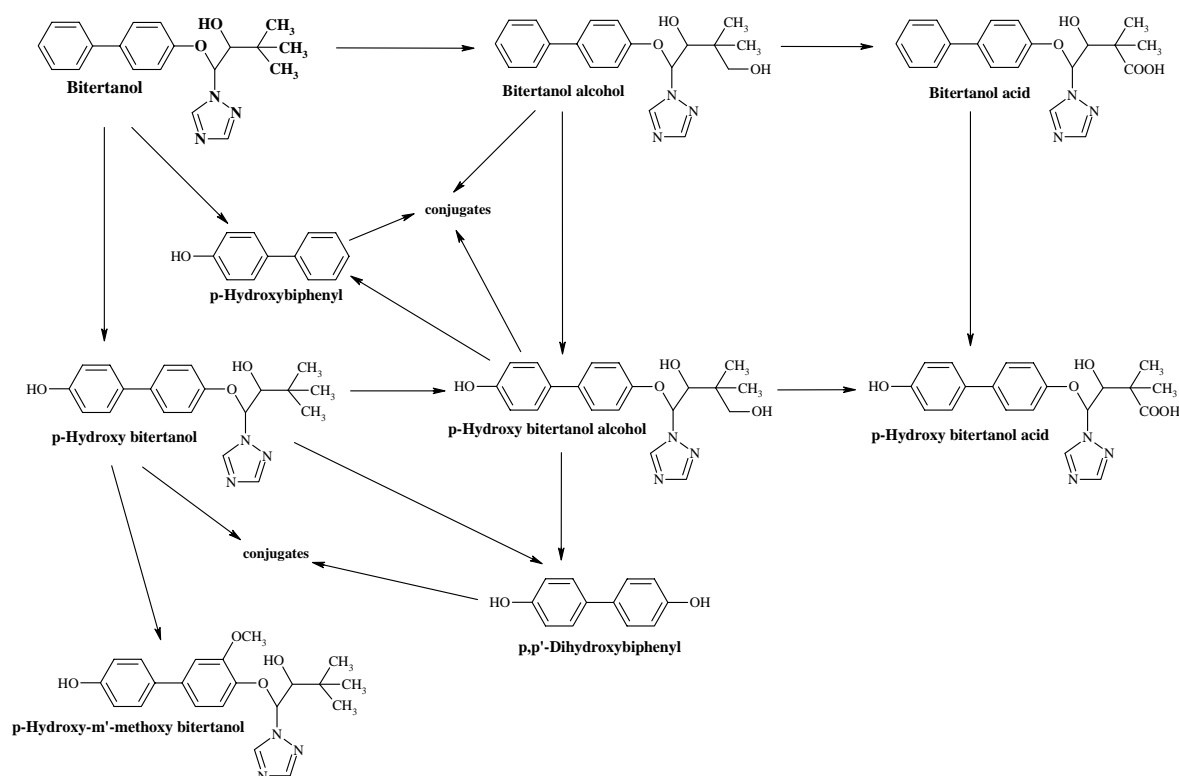
Compound	<sup>14</sup> C, % of total residue					
	Liver A*	Liver B*	Kidneys A*	Kidneys B*	Muscle	Fat
Bitertanol	6.8	6.8	5.7	5.7	13.6	25.0
<i>p</i> -hydroxybitertanol	24.5	39.6	17.6	19.5	37.7	18.6
<i>p</i> -hydroxy- <i>m</i> '-methoxy bitertanol	3.1	4.1	2.7	2.7	---	---
Bitertanol alcohol	0.9	0.9	4.8	4.8	14.0	7.1
<i>p</i> -hydroxybitertanol alcohol	2.1	2.7	5.4	5.4	12.4	9.2
<i>p</i> -hydroxybiphenyl	---	0.8	4.0	2.3	3.6	7.9
<i>p,p'</i> -dihydroxybiphenyl	---	1.0	4.2	2.8	5.3	11.7
Unextractable	30.5	30.5	33.0	33.0	< 0.1	9.2

A\* The residue remaining from the methanol extract after evaporation was partitioned between hexane and acetonitrile.

B\* The residue remaining from the methanol extract after evaporation was solubilized with a sodium acetate buffer and incubated with glucosylase. After extraction of the incubate with dichloromethane/acetonitrile (2:1), the residue in the organic phase was partitioned between hexane and acetonitrile.

The metabolic reactions in the dairy cow are shown in Figure 3.

Figure 3. Major reaction pathways in metabolism of bitertanol in the dairy cow (Obrist *et al.*, 1983).



### Poultry metabolism

The metabolism and excretion of [U-phenyl-<sup>14</sup>C]bitertanol were investigated in 3 groups of laying hens (Obrist and Puhl, 1986).

Group A: Five birds given a single oral dose at 2.5 mg/kg bw for determination of excretion pattern.

Group B: Ten birds given a single oral dose at 2.5 mg/kg bw for determination of blood levels.

Group C: Three birds given 5 daily doses at 8.0 mg/kg bw (equivalent to 90 ppm in feed) for investigation of tissue residues.

Group A showed the elimination of 98% of the dose with the excreta and 0.2% in the eggs over a period of four days. The major metabolites in the excreta were the diastereoisomers of *p*-hydroxybitertanol and their conjugates. The proportion of totally identified radioactivity in the excreta was 86%, and 84% of the egg residue was identified. The total radioactive residues in the tissues were 0.1 mg/kg as bitertanol four days after dosing. Blood levels peaked 0.5-1 hour after administration. Analyses of tissues collected 45 minutes after the last of five daily doses resulted in identification of 81% of the liver residue and 86-92% of the residues in the other tissues.

It can be concluded that bitertanol is intensively metabolized and rapidly excreted by laying hens. The major metabolic pathway involves hydroxylation of the phenyl ring followed by sulfuric or glucuronic acid conjugation. Minor metabolic reactions include hydroxylation of the *tert*-butyl group, dihydroxylation of the biphenyl ring system, *O*-methylation and conjugation. Metabolites are not retained by the tissues, as shown by the low residues ( $\leq 0.1$  mg/kg) four days after a single dose. The distribution of the identified compounds in the edible tissues and eggs is shown in Tables 8 and 9 respectively.

Table 8. Identified compounds in edible tissues taken 45 minutes after the last of five daily doses of [U-*phenyl*- $^{14}\text{C}$ ]bitertanol to three laying hens at 8.0 mg/kg bw (Obrist and Puhl, 1986).

Compound	$^{14}\text{C}$ , % of total residue				
	Liver	Kidneys	Muscle	Fat	Skin
bitertanol	34.7	27.2	67.8	78.2	74.9
<i>p</i> -hydroxybitertanol, free	14.7	27.7	23.2	12.1	13.2
<i>p</i> -hydroxybitertanol, conjugated <sup>1</sup>	25.4	24.8	1.5	---	4.2
<i>p</i> -hydroxybitertanol alcohol glucuronide	0.4	0.9	---	---	---
	0.2	---	---	---	---
Bitertanol alcohol glucuronide	1.2	1.8	---	---	---
	0.8	1.1	---	---	---
<i>p</i> -hydroxybiphenyl	0.2	0.2	---	---	---
<i>p,p'</i> -dihydroxybiphenyl	0.7	0.2	---	---	---
dihydroxybitertanol	0.9	---	---	---	---
hydroxymethoxybitertanol	1.7	2.2	---	---	---
polar metabolites	4.4	4.4	0.5	---	---
Unextracted	7.2	1.9	2.6	6.8	5.3

<sup>1</sup>Sulfate, glucuronide, others

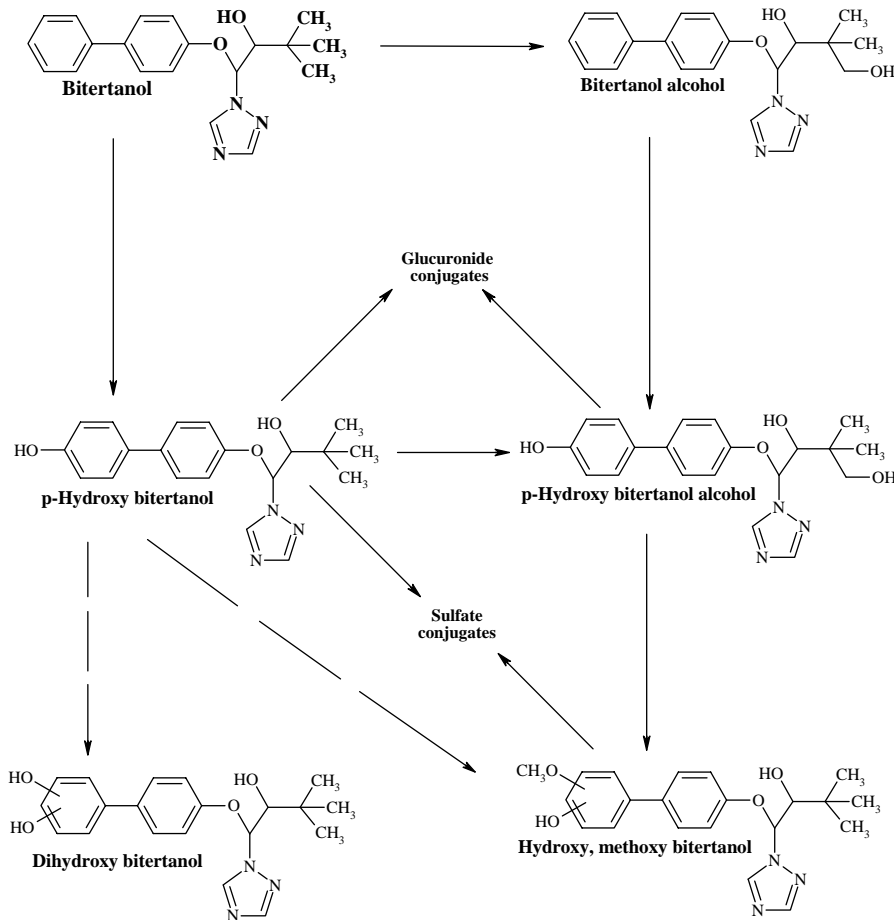
Table 9. Identified compounds in eggs after the administration of single or multiple oral doses of [U-*phenyl*- $^{14}\text{C}$ ]bitertanol to laying hens (Obrist and Puhl, 1986).

Compound	$^{14}\text{C}$ , % of total residue in eggs	
	Single dose 2.5 mg/kg bw	Multiple doses 5 x 8.0 mg/kg bw
bitertanol	54.8	36.6
<i>p</i> -hydroxybitertanol, free	6.3	6.4
<i>p</i> -hydroxybitertanol, conjugated <sup>1</sup>	21.6	37.9
<i>p</i> -hydroxybitertanol alcohol	0.4	0.3
bitertanol alcohol	0.6	0.5
<i>p,p'</i> -dihydroxybiphenyl	---	1.3
hydroxymethoxybitertanol	0.6	1.0
polar metabolites	0.5	1.2
Unextracted	8.4	6.7

<sup>1</sup>Sulfate, glucuronide

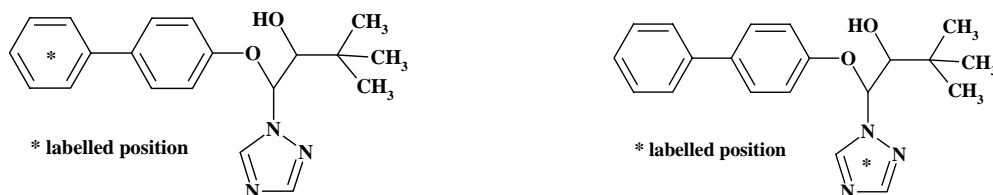
The metabolic reactions in poultry are shown in Figure 4.

Figure 4. Metabolism of bitertanol in poultry (Obrist and Puhl, 1986).



### Plant metabolism

The metabolism of bitertanol was investigated in apples, peanuts and cotton after spray application and in spring wheat after seed dressing with biphenyl- and triazole-labelled compounds. The labelled positions are shown below.



The two diastereoisomers are referred to as forms I and II in these studies. Form I is defined as the isomer having the lower  $R_f$  value on silica gel TLC with ethyl acetate as mobile phase.

**Apples.** [U-phenyl- $^{14}\text{C}$ ]bitertanol as a 50% WP was applied to apple surfaces at a concentration corresponding to 0.015% ai (Puhl and Hurley, 1981a). The compound was slowly metabolized with a half-life of approximately 150 days. The two diastereoisomers were metabolized at similar rates. After 21 and 49 days 90 and 86% respectively of the total apple residue was identified. Bitertanol

constituted 83% at 49 days while the keto-analogue of bitertanol (BUE 1662) and 4-hydroxybiphenyl together contributed 3%. The overall bitertanol isomer ratio changed little with time indicating similar rates of metabolism for the two isomers. Only 2% of the radioactive residue remained in the aqueous fractions, while 9.8% remained unextracted. After 49 days only 5% of the residue had penetrated into the pulp. The authors provide ample evidence from the literature that the unextracted radioactivity is not bioavailable to mammals after ingestion since it is probably associated with high molecular weight materials which are not readily digestible.

The results with the triazole-labelled active ingredient were very similar (Pither and Stevenson, 1987a). After spray application of a 50% WP formulation to apples, bitertanol was metabolized only very slowly. The degradation was less than 5% after 49 days (mature harvest) with very little penetration of the radioactivity into the pulp. 9.1% of the recovered radioactivity was detected in the washed peel. Most of the radioactivity associated with the peel and pulp fractions was extractable with organic solvents: only 2.5 and 0.3% of the total radioactive residue was unextractable from the peel and pulp samples respectively, and 95.6% of the recovered residue was identified as unchanged bitertanol.

Peanuts. The metabolism of [*U-phenyl*-<sup>14</sup>C]bitertanol in peanuts was investigated after spray application and after root uptake from a nutrient solution.

After spray application to peanut plants at 560 g/ha bitertanol was slowly metabolized with an estimated half-life of 141 days (combined isomers). There was a significant difference in the degradation rate of the two isomers: bitertanol I was absorbed and metabolized with a half life of about 100 days and bitertanol II with a half life of about 300 days. Fractionation of shoot tissues 28 days after treatment of young plants showed that 96.5% of the radioactivity was organosoluble, of which 86.2% was bitertanol and 4.3% was tentatively identified by mass spectrometry as the 6-*O*-malonyl-β-D-glucoside of bitertanol I. Several other metabolites each represented less than 1% of the residue. Only 0.6% of the radioactivity was found in the aqueous and 2.9% in the solid fractions. The root residues were low as compared with those in the shoots, indicating that there was little basipetal movement of radioactivity. Nuts and shells harvested 2.5 months after a single foliar application both contained residues of 0.066 mg/kg bitertanol equivalents, corresponding to 0.008% of the total plant residue. The mature plants contained 75.1% bitertanol, 5.8% 6-*O*-malonyl-β-D-glucoside, and 19.1% unidentified radioactivity in organo- and water-soluble or unextractable fractions.

Administration of bitertanol by root uptake from a nutrient solution resulted in the absorption of 43.7% of the available compound in 7 days. The isomers were absorbed equally, but again isomer I was metabolized more rapidly than isomer II. 6-*O*-malonyl-β-D-glucoside was observed in all the experiments. Bitertanol does not appear to be translocated from old to new growth, nor to volatilize from the leaf surface.

Wheat. The metabolism and distribution of bitertanol in spring wheat after seed treatment was investigated in two trials with phenyl- and triazole-labelled test compounds applied at 75 g ai/100 kg seed (Brennecke, 1986). Samples were collected at three intervals after sowing, the third sample being taken at harvest.

The percentages of the recovered radioactivity at these sampling times were 0.3-2.8% in the aerial plant parts (forage, grain, glumes, straw), 29.4-70.1% in the roots (including seed), 12.1-41.5% in the top soil layer (0-5 cm), and 0.2-2.3% in the 5 to 10 cm soil layer. Losses of radioactivity varied between 17.3 and 31.8%. The total <sup>14</sup>C at harvest from the phenyl label was 0.26 mg/kg as bitertanol in straw, 0.08 mg/kg in grain, 20 mg/kg in roots, and 0.13 mg/kg in the top soil layer. From the triazole label the corresponding residues were 0.64 mg/kg in straw, 0.53 mg/kg in grain, 24 mg/kg in roots, and 0.20 mg/kg in the top soil layer.

Owing to the very low levels of radioactivity in many extracts, characterization and identification were possible only to a limited extent. The organic extracts of the top soil layer (59% biphenyl label, 83% triazole label) and the roots (66.5% biphenyl label, 74% triazole label) contained almost exclusively unchanged parent compound. The metabolites detected in the grain from the triazole label treatment were triazolylalanine (50-66%, 0.12–0.16 mg/kg), triazolylacetic acid (22-34%, 0.04-0.07 mg/kg) and 2-hydroxy-3-(1*H*-1,2,4-triazol-1-yl)propionic acid in traces (<1%, <<0.01 mg/kg). In straw these metabolites were present at lower concentrations than in grain (<0.01-0.03 mg/kg). Unchanged parent compound (approx. 6% or 0.038 mg/kg) and bitertanol benzoic acid (BUE 2684, 5.3%) were also identified.

The high levels of unextractable radioactivity in forage (about 70%) and straw (about 61%) were reduced by acid or enzymatic hydrolysis, but 52 and 40% of the radioactivity was still bound to forage and straw respectively, probably to the lignin fraction.

Cotton. Cotton plants in the early bloom stage were sprayed twice with triazole-labelled bitertanol at 250 g/ha. The spray interval was 14 days (Pither and Stevenson, 1987b).

In the mature plants 63 days after the second application, 91% of the recovered radioactivity was associated with the foliage and 5.5% with the calyx fraction; 1.3%, 1 and 1% was found in the lint, seed and hull respectively. Most of the recovered residue was identified as the unchanged bitertanol isomers I and II, amounting to a total of 79% of the mature harvest residue. The relative concentrations of the bitertanol isomers remained constant throughout the study period. Trace amounts of bitertanol benzoic acid (BUE 2684) were identified at the interim sampling period of 35 days. Two further unknown metabolites were observed, collectively accounting for 1.3 and 0.3% of the 35-day and 63-day samples respectively.

#### Confined rotational crop study

[U-*biphenyl*-<sup>14</sup>C]bitertanol was applied eight times as a foliar spray to a target crop of peanuts at 0.56 kg ai/ha per application. The peanuts were removed 31 days after the last application and part of the soil was planted with rotational crops of wheat, kale or mustard, and sugar beets. The remainder of the soil was planted with these rotational crops either 118 or 364 days after the final application. The rotational crops were analysed for radioactive residues at intervals up to harvest (Puhl *et al.*, 1982).

The radioactive residues in harvest samples of leafy vegetables (kale and mustard) ranged from 0.10 mg/kg as bitertanol (118-day rotation) to 0.02 mg/kg (364-day rotation). Harvest samples of sugar beet roots contained residues of 0.38 mg/kg (118-day rotation) to 0.01 mg/kg (364-day rotation), while residues in wheat heads ranged from 0.23 mg/kg (31-day rotation) to 0.01 mg/kg (364-day rotation).

Owing to the low residue concentrations, only limited identification was possible. Bitertanol was present in the 31-day wheat crop, as was bitertanol benzoic acid (BUE 2684). Organosoluble residues in harvest samples used for food or fodder were all below 0.05 mg/kg. Insoluble and water-soluble residues may have partly resulted from incorporation of soil-generated <sup>14</sup>CO<sub>2</sub> into natural plant constituents.

The metabolic pathways of bitertanol in plants are shown in Figure 5 and the distribution of radioactive compounds in the crops and crop parts is shown in Table 10.

Figure 5. Proposed metabolic pathways of bitertanol in plants.

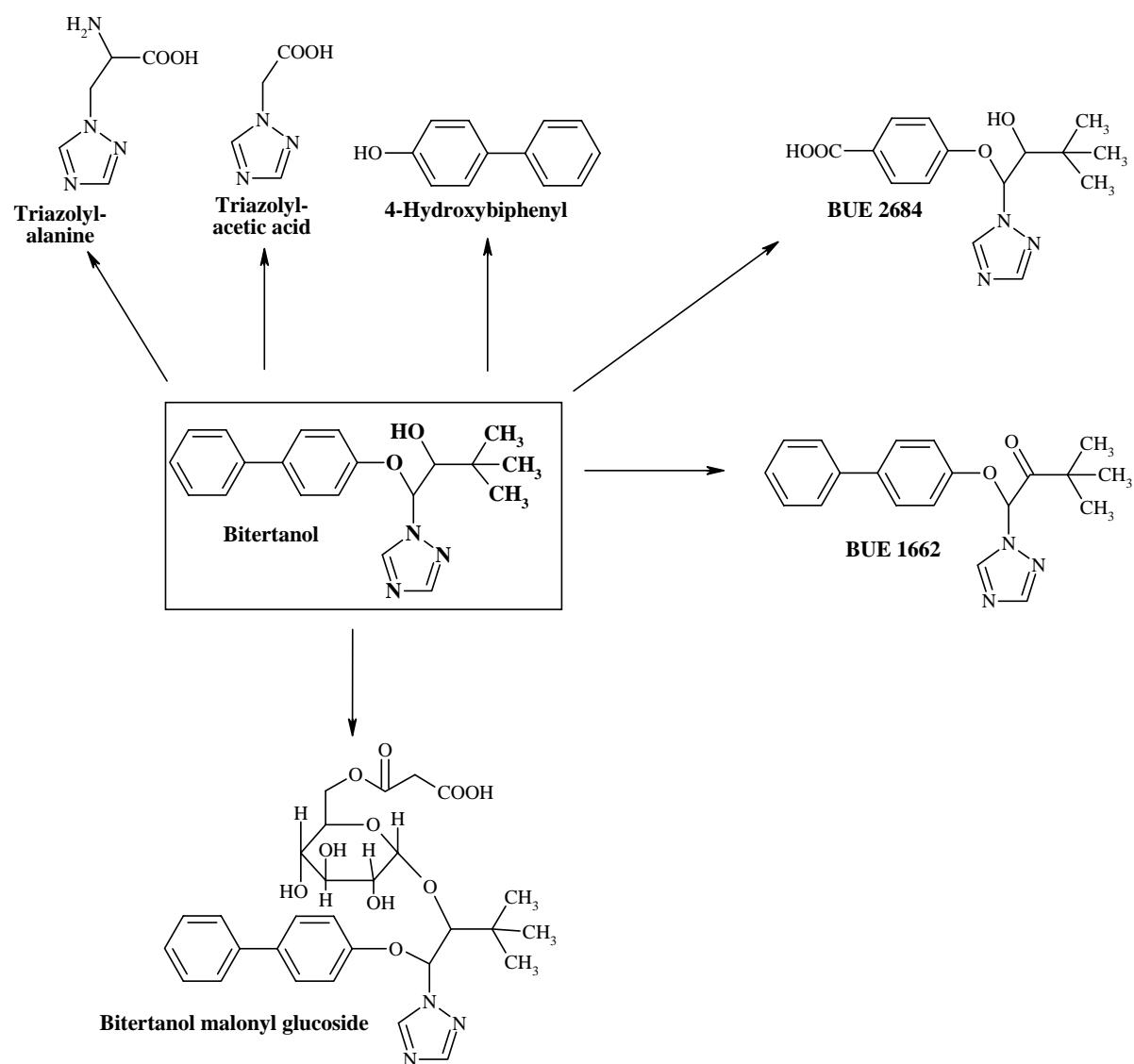


Table 10. Distribution of radioactive compounds in crops and crop parts after application of bitertanol.

Reference	Crop	Application rate, kg ai/ha <sup>①</sup> or conc., % <sup>•</sup>	Sample	Label	Days after application	TRR as bitertanol, mg/kg	Bitertanol, % of TRR	BUE 1662, % of TRR	4-OH-biphenyl, % of TRR	BUE 2684, % of TRR	TA, % of TRR	TAA, % of TRR	Malonyl glucoside, % of TRR	Unknown, % of TRR	Unextracted, % of TRR +
Puhl and Hurley, 1981a	Apple	0.015 <sup>•</sup>	Fruit	Biphenyl	0	0.27	82.8 <sup>④</sup>	3.0 <sup>④a</sup>						4.4 <sup>④</sup>	9.8 <sup>④</sup>
					7	0.36									
					14	0.28									
					35	0.27									
					42	0.21									
					49	0.27									
Pither and Stevenson, 1987a	Apple	0.015 <sup>•</sup>	Fruit	Triazole		nr	95.6 <sup>④</sup>						1.9 <sup>④</sup>	2.5 <sup>④</sup>	
Puhl and Hurley, 1981b	Peanut	0.56 <sup>①</sup>	Shoots	Biphenyl		nr	93.4						2.4	3.3	0.9
			Roots			86.2						4.3	6.6	2.9	
Brennecke, 1986	Wheat	75 g ai/100 kg <sup>⑤</sup>	Forage	Biphenyl		0.13 <sup>⑦</sup>									70.4 <sup>⑦</sup>
			Grain		0.08 <sup>⑥</sup>								90.6 <sup>⑥</sup>		
			Glumes		0.30 <sup>⑥</sup>								79.3 <sup>⑥</sup>		
			Straw		0.26 <sup>⑥</sup>								61.2 <sup>⑥</sup>		
			Roots		20.35 <sup>⑥</sup>	66.5 <sup>⑥</sup>							31.4 <sup>⑥</sup>		
			Soil 0-5 cm		0.13 <sup>⑥</sup>	59.0 <sup>⑥</sup>							38.0 <sup>⑥</sup>		
Soil 5-10 cm	< 0.01 <sup>⑥</sup>								45.3 <sup>⑥</sup>						
Brennecke, 1986	Wheat	75 g ai/100 kg <sup>⑤</sup>	Forage	Triazole		0.42 <sup>⑦</sup>	9.4 <sup>⑦</sup>								19.7 <sup>⑦</sup>
			Grain		0.53 <sup>⑥</sup>				50-66 <sup>⑥</sup>	22-34 <sup>⑥</sup>			5.7 <sup>⑥</sup>		
			Glumes		0.29 <sup>⑥</sup>								10.0 <sup>⑥</sup>		
			Straw		0.64 <sup>⑥</sup>	5.9 <sup>⑥</sup>			5.3 <sup>⑥</sup>				46.2 <sup>⑥</sup>		
			Roots		23.92 <sup>⑥</sup>	73.6 <sup>⑥</sup>							15.9 <sup>⑥</sup>		
			Soil 0-5 cm		0.20 <sup>⑥</sup>	83.4 <sup>⑥</sup>							14.3 <sup>⑥</sup>		
Soil 5-10 cm	< 0.01 <sup>⑥</sup>								45.0 <sup>⑥</sup>						
Pither and Stevenson, 1987b	Cotton	0.25 <sup>①</sup>	Leaves	Triazole		91	78.8			0.2 <sup>—</sup>					15.2
			Calyx		5.5										
			Lint		1.3										
			Seed		1										
			Hull		1										

nr: not reported

±: not extractable by drastic procedures

⑦: at 36 or 49 days

BUE 1662: keto analogue of bitertanol

④: 49 days after application; a: sum of BUE 1662 and 4-OH-biphenyl

|: at harvest (63 days)

BUE 2684: bitertanol benzoic acid

⑤: seed dressing

—: at interim sampling (35 days)

TA: triazolylalanine

⑥: at harvest (95 or 100 days)

TAA: triazolylacetic acid

## Environmental fate in soil

### Photolysis

In a model experiment, bitertanol was spotted on two HPTLC plates, one of which was irradiated for six weeks while the other was shielded for the same period (Wilmes, 1980). With an error margin of the densitometric analyses of  $\pm 10\%$  photolytic degradation could not be reliably established, but the data suggest a slight degradation.

[U-*biphenyl*- $^{14}\text{C}$ ]bitertanol was applied to a silt loam soil and irradiated continuously with simulated sunlight for 35 days at  $25^\circ\text{C}$  and 55% relative humidity (Sietsema, 1982). Interim samples were taken at 7, 14, 21, and 28 days. At the end of the test period 91.5% of the extractable radioactivity from the irradiated samples was unchanged bitertanol as determined by thin-layer chromatography. No other discrete spots of radioactivity were visible in any of the chromatograms. 96.6% of the extractable radioactivity from the dark samples was from bitertanol. More than 90% of the  $^{14}\text{C}$  in the irradiated and non-irradiated samples was extractable throughout the experiment. It is concluded that photodecomposition plays little part in the degradation of bitertanol on soil surfaces.

### Adsorption/desorption

The adsorption of bitertanol by loam, silty clay and sand from solutions at initial concentrations of 1.6-13.6 mg/ml was studied by Puhl and Hurley (1979a). The results, which conformed well to the Freundlich equation, indicated that the compound is strongly adsorbed to soil, with  $K_{\text{OC}}$  values computed from the results of about 2000. Desorption was also determined. The results are shown in Tables 11 and 12.

Freundlich equation:  $\log x/m = \log K + 1/n \log C$

x = bitertanol adsorbed,  $\mu\text{g}$   
 m = mass of adsorbing soil, g  
 C = concentration in solution,  $\mu\text{g/ml}$   
 K, n = constants

Table 11. Adsorption of bitertanol to soils after equilibration for 24 hours (Puhl and Hurley, 1979a).

Soil	Freundlich constants			C, $\mu\text{g/ml}$		Biteranol on soil, $\mu\text{g/g}$ at equilibrium	% adsorbed
	K	1/n	r, % <sup>1</sup>	initial	at equilibrium		
Kansas loam	35.8	0.791	99.6	1.57	0.08	1.49	95
				3.33	0.17	3.16	95
				6.55	0.42	6.13	94
				13.60	1.17	12.43	91
Hagerstown silty clay	19.6	0.883	99.9	1.57	0.22	1.35	86
				3.33	0.50	2.83	85
				6.55	1.08	5.47	84
				13.60			
Florida sand	39.9	0.957	99.7	1.57	0.14	1.43	91
				3.33	0.36	2.97	89
				6.55	0.62	5.93	91
				13.60	1.40	12.20	90

<sup>1</sup>r = correlation coefficient describing the degree of conformity of the data with the Freundlich equation



Table 12. Desorption of bitertanol from soils (Puhl and Hurley, 1979a).

Soil	initial conc.	Freundlich constants			Bitertanol adsorbed to soil, µg/g		% desorbed
	[mg/kg]	K	1/n	r, % <sup>1</sup>	after adsorption	after 4 desorptions	
Kansas Loam	0.16	2.18	0.225	95.1	1.49	1.43	4
	0.33	2.43	0.111	95.9	3.16	3.04	4
	0.66	7.62	0.282	97.5	6.13	5.86	4
	1.36	10.16	0.233	82.3	12.43	11.69	6
Hagerstorm silty clay	0.16	1.47	0.196	90.5	1.35	1.24	8
	0.33	2.58	0.191	93.8	2.83	2.59	8
	0.66	4.81	0.242	92.6	5.47	4.91	10
	1.36						
Florida sand	0.16	1.83	0.222	95.9	1.43	1.34	6
	0.33	2.91	0.198	79.7	2.97	2.79	6
	0.66	4.58	0.155	93.9	5.93	5.62	5
	1.36	7.69	0.116	94.0	12.20	11.61	5

<sup>1</sup>r = correlation coefficient describing the degree of conformity of the data with the Freundlich equation

In a recent study the adsorption/desorption of the possible soil degradation product bitertanol benzoic acid (BUE 2684) by loamy sand, sand, silty loam and silty clay was investigated at concentrations ranging from 0.01 to 5.0 mg/l. The percentage of the test compound adsorbed varied between 5.4 and 40.8%. The results indicated that the compound is highly mobile in soil since the  $K_{OC}$  values computed from the results were very low, from 6.06 to 15.37. In desorption experiments between 17.9 and 90.7% of the adsorbed bitertanol benzoic acid was desorbed (Burhenne, 1996).

### Mobility

The distribution of [U-*phenyl*-<sup>14</sup>C]bitertanol in soil after the seed treatment of winter wheat was investigated in a study under simulated winter climate conditions. When the plants reached the 3-leaf stage, only 0.32% of the applied radioactivity was recovered in the shoot while more than 99% remained in the soil, caryopsis and roots. Autoradiography demonstrated that the radioactivity was confined to the soil directly adjacent to the seed and did not move into deeper soil layers (Thielert and Kuck, 1992).

The leaching characteristics of aged [U-*phenyl*-<sup>14</sup>C]bitertanol residues were studied in a sandy loam (Dutch polder) soil and a loamy sand (BBA standard soil 2.1) (Brennecke, 1983a). After fortification with bitertanol at a concentration of 10 mg/kg, the soils were incubated at 9°C and 22°C for 30 days and 105 days. The soil concentration corresponded to an exaggerated application rate of approximately 15 kg ai/ha. The proportion of the applied radioactivity mineralized to <sup>14</sup>CO<sub>2</sub> after the ageing periods ranged from 2.1 to 68%. Leaching was induced in the soil columns containing the aged bitertanol residues by percolating water equivalent to 200 mm of rainfall for 48 hours. The application of simulated rainfall to the columns packed with the sandy loam soil was continued for an additional 72 hours, equivalent to 500 mm of precipitation.

The radioactivity in the leachates collected from the sandy loam soil accounted for only 0.2 to 0.6% of the applied dose after 48 hours of rainfall, and 1.0 to 2.8% after 120 hours. The leachates from the loamy sand contained 0.5 to 3.3% of the applied dose after 48 hours of simulated rainfall. In the total of 19 leaching experiments only one leachate sample from the loamy sand contained a higher proportion of the applied radioactivity (38.9%). It consisted almost quantitatively of bitertanol benzoic acid (BUE 2684); unchanged bitertanol was not found. Analysis of the soil columns after leaching showed that 84.2 to 86.0% of the radioactivity remaining in the soil was retained in the upper 5 cm layer. The overall average recovery of the radioactivity was 98.4%.

No essential differences in leaching characteristics were observed between the bitertanol residues aged at 22°C and those aged at 9°C in either soil. Prolongation of ageing from 30 days to 105 days reduced the radioactivity in the leachate (0.2-0.5% of the AR) from both soils because by

this time bitertanol had already been largely degraded to CO<sub>2</sub> (51 to 68%). The results show that aged bitertanol residues have only a limited tendency to leach into deeper soil layers (Tables 13 and 14).

Table 13. Radioactivity balance for aged [U-*phenyl*-<sup>14</sup>C]bitertanol residues in soil (Brennecke, 1983a).

	Temp., °C	Duration of ageing, days	Radioactivity in soil, %	<sup>14</sup> CO <sub>2</sub> , %
NL polder soil	22	30	84.5	12.1
	22	105	50.0	51.4
	9	30	101.3	2.1
Standard soil 2.1	22	30	57.8	31.0
	22	105	34.4	68.0
	22	30	58.9	40.5
	9	30	88.3	5.0

Table 14. Leaching of aged [U-*phenyl*-<sup>14</sup>C]bitertanol residues after simulated rainfall (Brennecke, 1983a).

	Temp., °C	Duration of ageing, days	Leachate, ml	Radioactivity in leachate, %	
				*	**
NL polder soil (48 hours rainfall)	22	30	385	0.6	0.7
	22	105	410	0.2	0.5
	9	30	407	0.2	0.2
Standard soil 2.1 (48 hours rainfall)	22	105	368	0.5	1.7
	22	30	397	1.0	1.8
	9	30	410	3.3	3.5
NL polder soil (120 hours rainfall)	22	30	965	2.8	3.1
	22	105	1023	1.0	2.1
	9	30	1013	1.1	1.2

\* Applied radioactivity (AR) = 100 %

\*\* Radioactivity in soil (AR-<sup>14</sup>CO<sub>2</sub>) = 100 %

Bitertanol was spotted on TLC plates coated with six different types of soil ranging from non-adsorptive sand to fine clay (Obrist and Thornton, 1979). Development of the plates with distilled water showed that bitertanol could be classified as being of low mobility.

### Degradation

A laboratory study of aerobic degradation was conducted with [U-*phenyl*-<sup>14</sup>C]bitertanol on four agricultural soils: sand, loamy sand, silt loam and silt (Fent, 1997). The application rate corresponded to 560 g ai/ha and the soils were incubated for 120 days. Samples were taken after 0, 3, 7, 14, 22, 30, 60, 90, 100, and 120 days.

The test substance was rapidly degraded with initial half-lives <1 day to 9 days. At the end of the test period the degradation curve flattened, giving DT-90 values of 15 to 102 days. The main product after 120 days was <sup>14</sup>CO<sub>2</sub>, representing 50 to 64% of the applied radioactivity. Bitertanol benzoic acid (BUE 2684) was the only other identified product, detected only in trace amounts, less than 0.3% of the applied radioactivity, in two of three extracts after concentrating them. Less than 4.2% of the AR remained unidentified. Unextracted residues, which were bound to the stable humin fraction, increased within the first 22 days to about 30-50% of the applied <sup>14</sup>C. After that period the unextractable residues decreased slightly in all the soils, indicating that a part of the bound residues became bioavailable again and thus subject to mineralization. The recovery ranged from 90.6 to 110% of the applied radioactivity. The results are shown in Tables 15 and 16.

Table 15. DT-50 and DT-90 values of bitertanol in soils (Fent, 1997).

Soil	DT-50, days	DT-90, days
BBA 2.1 (sand)	4.97	54.90
BBA 2.2 (loamy sand)	9.23	101.9
Laacher Hof (silt loam)	4.00	44.15
Höfchen (silt)	0.56	15.30

Table 16. Distribution of radioactivity, as % of that applied, after aerobic incubation of [U-*phenyl*-<sup>14</sup>C]bitertanol on four different soils (Fent, 1997).

Days	Bitertanol	BUE 2684	<sup>14</sup> CO <sub>2</sub>	Unidentified	Unextracted	Total
Soil BBA 2.1						
0	109.2	0.0	0.0	0.1	0.8	110.1
3	99.8	0.0	1.1	0.5	4.5	105.9
7	81.0	0.0	4.5	1.1	11.9	98.5
14	42.7	0.0	10.4	1.8	25.2	80.1
22	22.6	0.0	43.6	2.1	30.5	98.8
30	14.0	0.0	52.0	1.5	29.8	97.3
60	8.6	0.0	54.1	1.5	26.4	90.6
90	6.9	0.0	64.7	1.5	25.9	99.0
100	6.5	0.0	59.0	1.3	24.8	91.6
120	5.2	0.0	63.6	1.1	23.2	93.1
Soil BBA 2.2						
0	104.4	0.0	0.0	0.1	0.0	104.5
3	87.4	0.0	1.5	2.9	10.7	102.5
7	55.3	0.2	11.2	4.2	24.6	95.5
14	32.6	0.0	12.8	2.6	34.2	82.2
22	26.8	0.0	32.5	3.8	38.1	101.2
30	20.0	0.0	37.3	2.0	39.5	98.8
60	13.8	0.0	42.1	1.9	37.0	94.8
90	10.6	0.0	48.3	1.9	38.8	99.6
100	10.9	0.0	48.0	1.8	38.4	99.1
120	9.8	0.0	51.3	1.4	36.7	99.2
Soil Laacher Hof						
0	108.0	0.0	0.0	0.1	0.8	108.9
3	80.5	0.3	2.4	1.5	16.8	101.5
7	50.5	0.0	7.6	1.6	31.0	90.7
14	21.1	0.0	23.7	2.1	41.8	88.7
22	10.0	0.0	43.2	1.5	43.6	98.3
30	8.6	0.0	44.2	1.6	43.0	97.4
60	4.9	0.0	51.7	1.2	38.8	96.6
90	3.6	0.0	54.0	1.2	38.7	97.5
100	3.4	0.0	53.1	1.2	39.8	97.5
120	3.2	0.0	56.4	1.0	36.8	97.4
Soil Höfchen						
0	104.3	0.0	0.0	0.1	1.1	105.5
3	59.9	0.0	3.4	3.5	25.2	92.0
7	29.4	0.0	18.0	2.7	41.1	91.2
14	13.5	0.0	29.4	2.8	46.2	91.9
22	6.9	0.0	40.1	2.5	48.8	98.3
30	6.2	0.0	43.3	2.0	45.7	97.2
60	4.2	0.0	47.2	1.8	44.2	97.4
90	3.0	0.0	51.0	1.6	42.6	98.2
100	2.9	0.0	51.6	1.4	42.6	98.5
120	3.0	0.0	50.4	1.3	41.2	95.9

Brennecke (1986) investigated the degradation and distribution of bitertanol in soil after seed treatment of spring wheat with the phenyl- and triazole-labelled compound at 75 g ai/100 kg seed (metabolism in wheat was also studied). The recovered radioactivity at the different sampling times

ranged from 12.1 to 41.5% in the 0-5 cm soil layer and from 0.2 to 2.3% in the 5-10 cm layer. The total radioactive residue at harvest amounted to 0.13 mg/kg as bitertanol in the top soil layer for the phenyl label and 0.2 mg/kg for the triazole label. The radioactive residue in the organic soil extracts consisted almost exclusively of unchanged bitertanol.

Brennecke (1982a) studied the aerobic degradation of [U-*phenyl*-<sup>14</sup>C]bitertanol in loamy sand and sandy loam after application of an exaggerated rate corresponding to about 15 kg ai/ha. The study was conducted at 22°C and at 9°C, and samples were taken up to 92 days at the higher temperature and up to 180 days at the lower temperature.

Bitertanol was rapidly degraded at 22°C, with half-lives of 17 days in the loamy sand and 30 days in the sandy loam. At 9°C the half-life in the loamy sand was 70 days, in the sandy loam 179 days. <sup>14</sup>CO<sub>2</sub> was the main product. The results are shown in Table 17.

Table 17. Results of aerobic incubation of [U-*phenyl*-<sup>14</sup>C]bitertanol with two soils (Brennecke, 1982a).

Temperature, °C Days after application	Sandy loam		Loamy sand	
	9 180	22 92	9 180	22 92
Recovery, %	101.8	98.1	94.9	92.8
<sup>14</sup> CO <sub>2</sub> , % of recovered <sup>14</sup> C	19.4	49.1	53.0	68.0
Unextracted, % of recovered <sup>14</sup> C	27.7	38.5	29.6	24.4

In only one of the five experiments (loamy sand, 22°C) bitertanol benzoic acid (BUE 2684) was found as an intermediate in the formation <sup>14</sup>CO<sub>2</sub> in amounts between about 6 and 19%. An unknown product was also observed in amounts of ≤1%. These compounds were found at 7, 14 and 30 days, but not thereafter. In repeat experiments at 22°C and 9°C, no accumulation of the two compounds was observed; together they accounted for less than 2% of the <sup>14</sup>C. Neither compound was detected in the sandy loam soil, but an additional product was identified at both temperatures as the keto analogue of the parent compound (BUE 1662) at levels of 0.7 to 1.7%. It was not found in the loamy sand.

Puhl and Hurley (1979b) studied the aerobic soil degradation of [U-*phenyl*-<sup>14</sup>C]bitertanol after application of 1.5 and 15 kg ai/ha to silt loam. The results corroborated those of Brennecke (1982a). Bitertanol was degraded in silt loam with a half-life of 14 days at the simulated field use rate of 1.5 kg/ha. The half-life at the exaggerated rate of 15 kg ai/ha was 20 days.

After incubation of the low-dose samples for 121 days, 8.4% of the applied radioactivity was organosoluble, the main constituent being bitertanol (6% of the applied <sup>14</sup>C); 0.8% was water-soluble, 45.0% was unextracted and 45.8% was evolved as <sup>14</sup>CO<sub>2</sub> (Table 18). No other compounds were identified, whereas at the higher dose the two diastereoisomers of bitertanol benzoic acid (BUE 2684) were formed. Fractionation of the soil organic matter after 121 days showed that the previously unextracted radioactivity was distributed rather evenly in the humic acid, fulvic acid, and humin fractions at levels of 12.4%, 12.8 and 19.8% respectively.

An interesting difference between the 1.5 and 15 kg ai/ha samples was the presence of significant amounts of water-soluble radioactivity after 14 and 29 days in the high-dose samples. After acidification and extraction most of this radioactivity was identified as being due to bitertanol benzoic acid (BUE 2684).

Table 18. Distribution of radioactivity as % of that applied after aerobic incubation of [U-*phenyl*-<sup>14</sup>C]bitertanol with silt loam (Puhl and Hurley, 1979b).

Period, days	Bitertanol	<sup>14</sup> CO <sub>2</sub>	Bitertanol benzoic acid	Not identified	Unextracted
1.5 kg ai/ha					
0	98.6	---	---	1.2	0.2
3	90.7	0.8	---	3.9	4.6
7	67.8	7.1	---	4.6	20.5
14	46.8	15.4	---	6.6	31.2
30	22.9	29.7	---	4.8	42.6
59	12.7	40.8	---	4.1	42.4
91	8.5	42.8	---	2.8	45.9
121	6.0	45.8	---	3.2	45.0
15 kg ai/ha					
0	98.3	---	---	1.6	0.1
7	86.4	2.3	---	4.0	7.3
14	61.0	12.0	6.5	4.0	16.5
29	28.7	25.8	8.6	5.4	31.5

Degradation under anaerobic conditions was also investigated and found to be slower (Table 19). Bitertanol was stable in sterilized soil.

Table 19. Comparative distribution of radioactivity in soil samples incubated with [U-*phenyl*-<sup>14</sup>C]bitertanol under aerobic and anaerobic conditions (Puhl and Hurley, 1979b).

Conditions	Days	<sup>14</sup> C, % of applied			
		Bitertanol	<sup>14</sup> CO <sub>2</sub>	Not identified	Unextracted
aerobic	30	22.9	29.7	4.8	42.6
	59	12.7	40.8	4.1	42.4
	91	8.5	42.8	2.8	45.9
anaerobic	28	20.8	33.0	6.2	40.0
	60	19.5	30.5	5.4	44.6

Takase and Yoshimoto (1980) studied the degradation of bitertanol in upland soil under laboratory and field conditions in Japan. In the laboratory the degradation half-life was 12 days in alluvial soil and 30 days in volcanic ash. In the field, bitertanol was applied 4 times at intervals of 7 or 10 days to peanut fields of the same soils at 500 g ai/ha. The computed half-lives were 14.6 days in the alluvial soil and 2.5 days in the volcanic ash, demonstrating the rapid degradation of bitertanol in soil.

## ENVIRONMENTAL FATE IN WATER/SEDIMENT SYSTEMS

### Hydrolysis

Wilmes (1981) investigated the hydrolysis of bitertanol. Degradation was only observed in the presence of Fe<sup>3+</sup>. In an aqueous solution containing 50 mg/l bitertanol, 1% FeCl<sub>3</sub> and 20% ethanol to facilitate dissolution of the compound, the half-life was approximately 6 weeks at 70°C. No hydrolytic degradation was observed in distilled water, buffered solutions (pH 3-10) or 1% solutions of CuCl<sub>2</sub>, NaHCO<sub>3</sub> or CaCl<sub>2</sub>.

Nichols and Thornton (1979) investigated hydrolysis in sterile aqueous buffer solutions at pH 4, 7, and 9 maintained at 25°C and 40°C at concentrations of 0.25 and 2.5 mg/l. No degradation was apparent after 30 days. Recoveries ranged from 85 to 108%. The ratio of the isomers remained constant and temperature had no noticeable effect. Bitertanol was evidently stable under the test conditions.

### Photolysis in water

Hellpointner (1991) determined the quantum yield of the direct photodegradation of bitertanol in water in polychromatic light. From UV absorption data and the kinetic results of two photodegradation experiments in a carousel irradiation reactor the quantum yield was calculated to be 0.0697, and the half-life of direct photodegradation was calculated by two different simulation models to range from one month to one year for the periods of main use, indicating that direct photodegradation in water contributes little to the overall elimination of bitertanol in the environment.

Sietsema (1983) irradiated aqueous solutions of [*triazole*-<sup>14</sup>C]bitertanol in a carousel device with an Ace photoreactor. The half-life was 37.7 to 52.2 h under these conditions, which could be extrapolated to about 11 days for the half-life of bitertanol under natural sunlight. The major photolysis products identified were 1,2,4-triazole, 4-hydroxybiphenyl, and a high molecular weight polymer. Several minor products, each accounting for << 10% of the total radioactivity, were also observed. The isomeric form I of bitertanol was photolysed slightly faster than form II.

Wilmes (1980, 1981) irradiated bitertanol dissolved in a mixture of acetonitrile and water (1:1). The initial degradation half-life was 1.2 hours with or without the addition of 2% acetone as a sensitiser. Several batches of technical grade bitertanol were examined under these conditions, with resulting half-lives of 2.2 to 2.8 h. A large number of degradation products were formed at low concentrations, 1,2,4-triazole and 4-hydroxybiphenyl being major components.

As a conclusion, bitertanol can be readily degraded by light but such degradation is likely to be reduced under environmental conditions since very little light of effective wavelengths (<290 nm) is available in water.

### Aquatic degradation

Fritz (1990) investigated the degradation of [U-*phenyl*-<sup>14</sup>C]bitertanol in two aquatic micro-ecosystems containing sediment. The samples originated from a recultivated gravel pit away from agricultural areas in Lienden (oligotrophic) and a drainage ditch in a fruit orchard in Ijzendoorn (eutrophic). The test compound was added to the water at a concentration of 1.0 mg/l which corresponded to an application rate of 1 kg ai/ha, assuming a water depth of 10 cm. The incubation was conducted at 22°C in the dark and lasted for 120 days.

A high proportion of the applied radioactivity was taken up by the sediment, reaching a maximum of 69 to 91% after 25 days. At the end of the test period of 120 days the total amount of radioactivity in the sediment had decreased to about 38 to 44% (Table 20). The unextractable radioactivity in the sediment of both systems amounted to about 35% on average after 120 days.

Table 20. Distribution of radioactivity as % of that applied in water/sediment after addition of [U-*phenyl*-<sup>14</sup>C]bitertanol (Fritz, 1990).

Incubation, time	<sup>14</sup> CO <sub>2</sub>		Surface water incl. dissolved <sup>14</sup> CO <sub>2</sub>		Sediment		Total <sup>14</sup> C	
	Lienden	Ijzendoorn	Lienden	Ijzendoorn	Lienden	Ijzendoorn	Lienden	Ijzendoorn
2-3 hours	---	---	38.5	32.5	61.4	71.5	99.9	104.0
7 days	0.3	0.1	37.2	12.6	55.9	80.3	93.4	93.0
25 days	1.8	0.6	24.9	7.4	68.9	90.8	95.6	98.8
53 days	11.3	3.1	23.8	6.9	59.5	87.2	94.6	97.2
82 days	36.2	37.0	9.9	3.1	43.4	52.5	89.5	92.6
120 days	47.3	46.2	5.6	1.8	38.4	43.5	91.3	91.5

Bitertanol was rapidly degraded. Only about 2 to 3% of the parent compound was detected in the surface water of both systems after 53 days and was no longer detectable in the water phase after 82 days. The isomeric ratio was not affected. The sediment contained 24 to 59% of the applied

bitertanol after 53 days. This decreased to 3 to 4% at the end of the test period of 120 days. The degradation half-life of bitertanol in both waters varied between 24 and 27 days. Small amounts ( $\leq 1\%$ ) of bitertanol benzoic acid were detected in the surface water, and traces (0.4-0.8%) of the keto analogue (BUE 1662) in the sediment. Mineralization was extensive: after 120 days nearly half of the applied radioactivity was detected as  $^{14}\text{CO}_2$ . Bitertanol did not accumulate in the sediment. The results are shown in Table 21 and the degradation pathways in Figure 6.

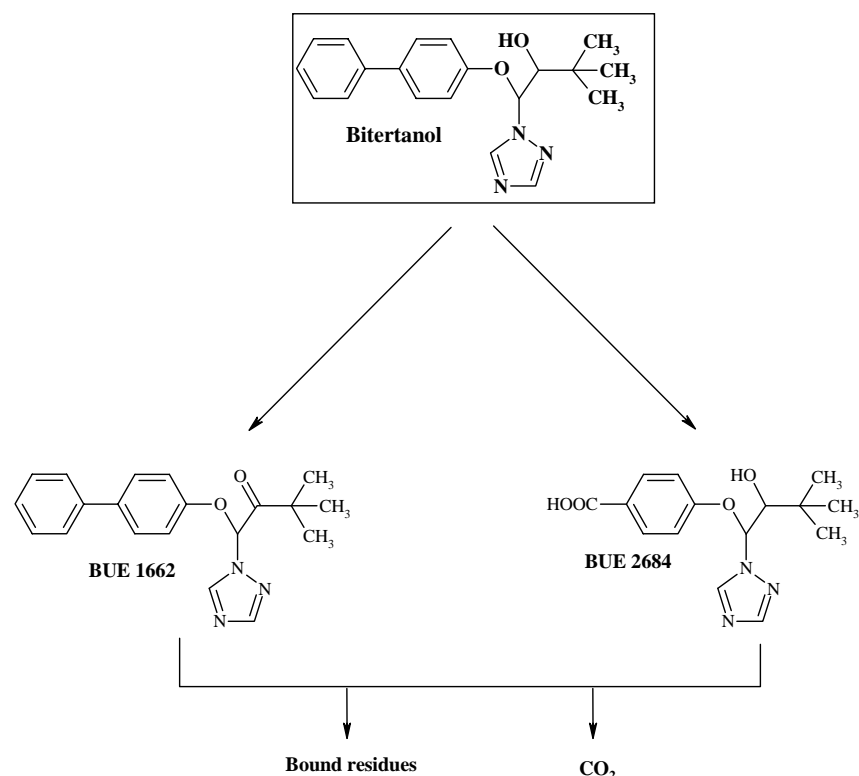
Table 21. Distribution of [U-*phenyl*- $^{14}\text{C}$ ]bitertanol and its degradation products in water/sediment systems as a function of the incubation period (Fritz, 1990).

Incubation period, days	$^{14}\text{C}$ , % of applied											
	Total $^{14}\text{C}$ in water or extracted from sediment		Bitertanol		Bitertanol benzoic acid BUE 2684		Keto analogue BUE 1662		$^{14}\text{CO}_2$ <sup>1</sup>		Not identified	
	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.
	Surface water											
0	38.5	32.5	37.4	31.3	n.d. <sup>1</sup>	n.d.	n.d.	n.d.	---	---	1.1	1.2
7	37.2	12.6	35.4	11.8	< 0.1	0.2	n.d.	n.d.	0.6	0.2	1.5	0.8
25	24.9	7.4	16.4	4.1	0.5	0.5	n.d.	n.d.	2.1	0.8	8.1	3.0
53	23.8	6.9	2.9	1.6	n.d.	1.0	< 0.1	< 0.1	22.8	4.3	9.8	3.9
82	9.9	3.1	n.d.	n.d.	0.3	0.2	n.d.	n.d.	39.7	37.8	6.3	2.3
120	5.6	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	48.9	46.7	4.0	1.3
	Sediment											
0	55.0	59.4	53.3	57.2	n.d.	n.d.	n.d.	n.d.	---	---	1.7	2.2
7	48.5	69.3	46.5	66.7	n.d.	n.d.	n.d.	n.d.	0.3	0.2	2.0	2.6
25	57.0	75.6	53.9	71.9	n.d.	n.d.	n.d.	0.4	0.4	0.5	3.1	3.3
53	26.8	63.5	23.5	58.8	n.d.	n.d.	0.4	0.8	0.6	0.3	2.9	3.9
82	12.6	12.5	10.3	10.2	n.d.	n.d.	0.1	0.2	0.2	0.2	2.2	2.1
120	5.3	6.1	3.2	4.0	n.d.	n.d.	< 0.1	0.1	0.1	0.1	2.1	2.0

n.d. not detected

<sup>1</sup> $^{14}\text{CO}_2$  in surface water includes that in the  $\text{CO}_2$  trap

Figure 6. Proposed pathways of bitertanol degradation in water/sediment systems (Fritz, 1990).



## METHODS OF RESIDUE ANALYSIS

### Regulatory analytical methods

DFG method S 19 was validated for bitertanol in plant materials (Specht and Thier, 1989). Recoveries were 80-100% and the limit of determination (LOD) was 0.5 mg/kg. DFG method 613 was validated for bitertanol in plant materials, soil and water by Brennecke (1987). Recoveries were between 82 and 114%. Limits of determination were 0.01-0.05 mg/kg for plant materials, 0.05 mg/kg for soil and 0.005 mg/l for water.

A multi-residue method for non-fatty and fatty foods was provided by the government of The Netherlands (Olthof, 1999a). The residues are extracted with acetone/water or ethyl acetate. There is no clean-up for plant materials but animal products are cleaned up by gel-permeation chromatography (GPC), HPLC or liquid-liquid partitioning (LLP). Determination is by gas chromatography with an ion trap detector (ITD) or nitrogen-phosphorus detector (NPD). The LOD was reported as 0.05 mg/kg for both non-fatty and fatty foods and recoveries were generally between 90 and 100%.

DFG multi-residue method W 5 was applied to bitertanol in water (Brennecke and Vogeler, 1987) with recoveries between 91 and 114%. The LOD was 0.005 mg/l. A thin-layer separation with UV detection and automated multiple development (Burger, 1988) was applied to bitertanol in ground and drinking water with recoveries between 85 and 116%. The LOD was 0.05 µg/l.

Animal materials have been analysed by gas chromatography with an NPD after clean-up by gel-permeation chromatography and mini-silica gel column chromatography (Specht and Tillkes, 1980a). An enforcement method for the determination of bitertanol residues in bovine and poultry tissues, milk and eggs (Sandie and Coffman, 1985) was based on gas chromatography with nitrogen-specific detection (NPD). Samples were extracted with acetone and methylene chloride and cleaned up by various procedures. Recoveries ranged from 79 to 103% for tissues (0.5 mg/kg fortification), 87



to 89% for milk (0.1 mg/kg fortification), and 66% at 0.01 mg/kg to 104% at 0.05 mg/kg for eggs. The lowest fortification levels were 0.5, 0.1 and 0.01 mg/kg respectively.

### Specialized methods

The following specialized methods were used for the analysis of the plant and animal samples in the supervised trials.

Thornton, 1977 (method F 107). This method was applied to the determination of bitertanol in apples. Samples were macerated in acetone and the filtered raw extract partitioned with dichloromethane. The dichloromethane phase was purified by column chromatography on Florisil. The analyte was determined by gas chromatography with a phosphorus/nitrogen selective flame ionization detector. Recoveries were between 86 and 108% at fortification levels of 0.05 and 0.5 mg/kg. The LOD was 0.05 mg/kg.

The method was also validated for bananas. Recoveries from banana peel and pulp ranged from 56 to 85% at a fortification level of 0.05 mg/kg, and from 86 to 114% at 0.1 mg/kg (Becker, 1980). Further determinations of recoveries from the pulp and peel of green and ripe bananas at a fortification level of 0.05 mg/kg gave recoveries of 82 to 90% from green and 70 to 88% from ripe bananas. Ripe peel was also fortified at incremental rates from 0.02 to 0.1 mg/kg, giving recoveries of 100 to 120% (Disher, 1982). The LOD for all banana commodities was 0.01 mg/kg.

Specht and Tilkes, 1980b (method 00029, formerly F 136). This method was developed for the determination of bitertanol in plant materials. After extraction with acetone and liquid-liquid partitioning with dichloromethane the organic phase is purified by gel-permeation chromatography and the analyte determined by GLC with an NPD. Recoveries were between 74 and 112% at fortification levels between 0.02 and 2.4 mg/kg. The LOD was 0.02 mg/kg.

The method was modified by including a silica gel clean-up before, or in bananas and peaches after, gel-permeation chromatography (Specht and Tilkes, 1982 [modification M003], 1981a,b, modification M004/006). It was validated with several plant materials with recoveries between 80 and 107% at fortification levels between 0.01 and 5.0 mg/kg. The LOD was 0.05 mg/kg. A further modification gave an LOD of 0.01 mg/kg for banana fruit and peel (Brennecke, 1983b, modification M003/E013).

Another modification with changes to sample weights and details of the gel-permeation chromatography (Brennecke, 1981a, modification M009) gave a recovery of 97% from peaches at 0.05 mg/kg.

For black currants and beans the clean-up had to be further improved (Brennecke, 1981a, modification M009). Interferences were removed by acetonitrile/n-hexane partition, acetonitrile/water/dichloromethane partition and column chromatography on silica gel as well as gel-permeation chromatography. Recoveries were between 93 and 110% at fortification levels between 0.05 and 0.5 mg/kg. The LOD was 0.05 mg/kg.

Recovery data for several crops are reported in the following supplements to method 00029: E001 - barley (Brennecke, 1983c), E002 - cucumbers (Brennecke, 1981b), E003 - oat forage (Brennecke, 1982b), E005 - oat grain and straw (Brennecke, 1982c), E006 - peaches and gooseberries (Brennecke, 1982d), E007 - rye forage (Brennecke, 1983d), E008- rye grain and straw (Brennecke, 1982e).

Brennecke, 1985 (method 000031, formerly F223). Bitertanol is extracted from plant material with acetone for samples with high water content and with an acetone/water mixture for samples with low water content. Clean-up is by column chromatography on silica gel and gel-permeation chromatography on Bio Beads S-X 3 polystyrene gel, and determination by gas chromatography with

a nitrogen-specific thermionic detector. Recoveries ranged from 80 to 105% and LODs from 0.01 to 0.05 mg/kg. In supplement E003 the method was validated for nectarines (Möllhoff, 1986), and in E006 for tea (Brennecke, 1995).

Brennecke, 1988a,b (method 00003, formerly F281, modification M002). Sample from plants and their processed commodities are extracted with acetone (acetone/water for dry materials) and the filtered extracts applied to a disposable extraction column after evaporation of the acetone. Bitertanol is eluted with a mixture of cyclohexane and ethyl acetate and determined by HPLC with fluorescence detection. Recoveries over a range of 0.002 to 20 mg/kg were between 65 and 105%. The LOD was 0.02 mg/kg for raw and processed plant commodities and 0.002 mg/kg for beverages.

In modifications M004 and M006 (Bachmann, 1994a,b) and M006/E003 (Nüßlein, 1995) the aliquot is taken from the filtered raw extract instead from the aqueous phase after evaporation of the acetone. Extracts of bananas and peach juice are removed from the macerate by suction instead of filtration. Recoveries were between 79 and 100% at fortification levels between 0.01 and 1 mg/kg. The LOD was 0.01 mg/kg for banana fruit and peel and peach juice, and 0.02 mg/kg for peach fruit.

Method 00003 was also validated for cherry jam (modification E001, Köhler, 1989) and tomato preserve, paste and juice (modification E002, Krebber, 1991).

Allmendinger, 1998 (modification of method 00462). An LC-MS-MS method was developed for the determination of bitertanol and fuberidazole in wheat forage, grain and straw. The purpose of the modification was to extend the method to new sample materials which required an additional clean-up (extraction on Chem-Elut). The mean recoveries of bitertanol were 80 to 99%. The LOD was 0.05 mg/kg.

Leimkuehler *et al.*, 1983 (method F218). The method was developed to quantify bitertanol and its metabolites in bovine tissues, milk, poultry tissues and eggs. Samples are extracted with acetone, methanol or hexane and hydrolysed with acid to release 1,2,4-triazole. The triazole is converted to triazolylpinacolone which is determined by gas chromatography with an NPD. Several clean-up steps are required including partitioning, ion-exchange chromatography and high-performance liquid chromatography. Recoveries, determined at 0.05 and 0.1 mg/kg with all samples and also at 0.5 and 2.0 mg/kg with bovine liver, were between 60 and 120%. The LOD was 0.01 mg/kg.

## **Stability of residues in stored analytical samples**

### Plant materials

The storage stability of bitertanol on dry beans, green beans, apples, peaches and cherries was determined (Mobay Chemical Corporation, 1983a,b, 1984a,b; Köhler, 1993). Samples were spiked with bitertanol at 0.1 and 1.0 mg/kg (dry beans), 0.2 mg/kg (cherries), and 0.5 mg/kg (green beans). The stability of incurred residues was determined in apples and peaches. Frozen samples were stored at temperatures below -20°C.

Bitertanol was stable (recoveries 85-87%) in green beans, apples and peaches for at least as long as the study lasted, 406, 1262 and 797 days respectively. Recoveries from dry beans were  $\geq 80\%$  for 10-12 months but only 50-60% after 14 or 15.5 months. (In the residue trials on plants with a low water content, cereal grains and bananas, no samples were stored for more than a year). The recovery from cherries was generally  $>70\%$ , and  $\geq 80\%$  of the recovery from concurrent analyses of freshly fortified samples, showing that residues of bitertanol were stable in cherries for the tested times of storage.

In summary, bitertanol residues were found to be stable in green and dry beans for more than 1 year, in peaches and cherries for at least 2 years, and in apples for at least 3.5 years. The results are shown in Table 22.

Table 22. Storage stability of bitertanol in plant commodities.

Sample	Fortification, mg/kg	Storage period, days	Recovery, %		Reference Report no.
Dry beans	0.1	0	100		Mobay, 1983a 84252
		255	80		
		314	80		
		416	60		
	1.0	0	100		
		48	95		
		303	89		
		362	100		
464	54				
Green beans	0.5	0	-		Mobay, 1984a 84571
		61	91		
		151	88		
		406	87		
Apples	-	0	100		Mobay, 1984b 84264
		1262	85		
Peaches	-	0	100		Mobay, 1983b 84222
		797	87		
			% remaining	Concurrent recovery	
Cherries	0.2	0	94	101	Köhler, J., 1993 RA-212/93
		35	89	-	
		59	79	-	
		88	76	92	
		179	60	-	
		401	61	78	
		731	79	83	

### Animal products

Leimkuehler (1983) determined the storage stability of radiolabelled bitertanol and *p*-hydroxybitertanol in the liver, kidneys, muscle and fat from the metabolism study on a dairy cow (Obrist *et al.*, 1983). The samples were held in cold storage (-18° to -23°C) for approximately 2 years. The results showed no significant loss of bitertanol or *p*-hydroxybitertanol residues in any of the four tissues over the two year period. The Meeting noted the very low level of the residues in kidneys, muscle and fat.

Table 23. Storage stability of residues in animal products.

Sample	Storage period, days	Recovery in stored sample		Reference Report no.
		Bitertanol	<i>p</i> -hydroxybitertanol	
Liver	0	0.056 mg/kg = 100 %	0.325 mg/kg = 100 %	Leimkuehler, 1983 84126
	825	89 %	110 %	
Kidneys	0	0.006 mg/kg = 100 %	0.021 mg/kg = 100 %	
	825	83 %	110 %	
Muscle	0	0.001 mg/kg = 100 %	0.004 mg/kg = 100 %	
	825	100 %	225 %	
Fat	0	0.008 mg/kg = 100 %	0.006 mg/kg = 100 %	
	825	150 %	233 %	

### **Definition of the residue**

On the evidence of metabolism studies with foliar spray treatments of apples, cotton and peanuts, the residue of concern is bitertanol *per se*.

After seed treatment of wheat at a commercial application rate, the metabolites detected in the grain at harvest (from the triazole ring label) were conjugates of 1,2,4-triazole, triazolylalanine (50-66% of the total  $^{14}\text{C}$ , 0.12-0.16 mg/kg) and triazolylacetic acid (22-34% of total  $^{14}\text{C}$ , 0.04-0.07 mg/kg). The parent compound was not detectable in the grain. The presence of free 1,2,4-triazole was excluded by chromatographic comparison with the authentic reference compound.

As 1,2,4-triazolylalanine is a plant metabolite of several pesticides that contain a 1,2,4-triazole moiety, being formed by its conjugation with serine, the conjugate was evaluated by the 1989 JMPR for toxicology and residues. The 1989 Meeting concluded that residues of 1,2,4-triazolylalanine arising from the use of triazole fungicides do not present a toxicological hazard.

The metabolism studies on rats, a dairy cow and laying hens indicate that bitertanol and the metabolite *p*-hydroxybitertanol (free and conjugated) are the main residue components in animal tissues, milk and eggs.

As bitertanol has no acidic or basic properties in aqueous solution, the partition coefficient will not be influenced by the pH. The octanol-water partition coefficients ( $\log P_{\text{OW}} = 4.04$  diastereoisomer A, 4.15 diastereoisomer B) indicate that bitertanol is fat-soluble.

The Meeting concluded that the following residue definitions are appropriate.

For compliance with MRLs. For plant and animal products: bitertanol.

For estimations of dietary intake. For plant products: bitertanol. For animal products: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

## USE PATTERN

Information on GAP was received from the manufacturer and the governments of Australia, Germany, The Netherlands, Poland and the UK. The major registered uses of bitertanol on food crops are shown in Tables 24 (foliar spray) and 25 (seed treatment).

Table 24. Registered uses of bitertanol as foliar sprays or pruning paint.

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Apple	Austria	25 WP	F	Foliar spray	0.19-0.25	0.013-0.017	2-3	21
	Australia	10 LA <sup>1</sup>	F	Pruning paint	undiluted			14
	Belgium	25 WP	F	Foliar spray	0.19-0.38	0.013-0.025	42	
		500 SC	F	Foliar Spray	0.19-0.38	0.013-0.025		42
	France	25 WP	F	Foliar spray		0.019-0.025	14	
	Germany	25 WP	F	Foliar spray	0.19	0.013		1-5
	Greece	25 WP	F	Foliar spray	0.25-0.5	0.013-0.025	14	
	Italy	25 WP	F	Foliar spray	0.23-0.3	0.019-0.025		21
	Netherlands	25 WP	F	Foliar spray	0.2-0.34	0.02	2-5	14
	Poland	25 WP	F	Foliar spray	0.29-0.38	0.029-0.08	2-3	14
		72.5 WP <sup>2</sup>	F	Foliar spray	0.28	0.03-0.06		14
	Portugal	500 SC	F	Foliar spray	0.19	0.019	21	
	South Africa	68.75 WP <sup>3</sup>	F	Foliar spray	0.09-0.26	0.008		1-2
	Spain	25 WP	F	Foliar spray	0.25-0.38	0.025-0.038	15	
	Switzerland	55 WP <sup>4</sup>	F	Foliar spray	0.2-0.25	0.01 – 0.015		1-4
	Turkey	25 WP	F	Foliar spray	0.25	0.013	14	

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Banana	Cameroon	300 EC	F	Foliar spray	0.15	1.5-3		
	Belize	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Costa Rica	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Dominican Republic	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Guatemala	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Honduras	300 EC	F	Foliar spray	0.15	0.02-0.2		0
	Nicaragua	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Panama	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Philippines	300 EC	F	Foliar spray via air plane	0.15-0.20	0.5-0.65		0
	Taiwan	300 EC	F	Foliar spray	0.12	0.4		6
Barley, winter	Germany	25 WP	F	Foliar spray	0.375	0.094	1	NS <sup>5</sup>
Beans	Australia	300 EC	F	Foliar spray	0.15		3	3
Cherries	Austria	25 WP	F	Foliar spray	0.56	0.038	1-2	A <sup>6</sup>
	Belgium	25 WP	F	Foliar spray	0.56	0.038	2-3	A
		500 SC	F	Foliar spray	0.56	0.038	2-3	A
	Germany	25 WP	F	Foliar spray	0.56	0.038	3	21
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Netherlands	25 WP	F	Foliar spray	0.19	0.013	2-3	21
	Poland	25 WP	F	Foliar spray	0.38	0.038-0.08	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	14
	Switzerland	55 WP <sup>4</sup>	F	Foliar spray	0.2	0.01		21
Courgette	Netherlands	500 EC	G	Foliar spray	0.15- 0.45 or 0.9	0.03	3-9	3
Cucumber	Belgium	300 EC	G	Foliar spray	0.6	0.03		3
		500 SC	G	Foliar spray	0.6	0.03		3
	Italy	25 WP	G	Foliar spray	0.19-0.22	0.019-0.025	2-3	14
	Netherlands	300 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3
		500 EC						
Melons	Netherlands	300 EC 500 EC	G <sup>7</sup>	Foliar spray	0.15- 0.45 or 0.9	0.03	3-9	3
Nectarine	France	300 EC	F	Foliar spray		0.03	usp <sup>7</sup>	14
		25 WP	F	Foliar spray		0.019-0.025		14
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	South Africa	300 EC	F	Foliar spray	0.14-0.36	0.012		35
	Spain	25 WP	F	Foliar spray	0.38-0.56	0.025-0.038	1-3	15
Peach	France	25 WP	F	Foliar spray		0.019-0.025		14
		300 EC	F	Foliar spray		0.03	usp <sup>7</sup>	14
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	South Africa	300 EC	F	Foliar spray	0.14-0.36	0.012		35
	Spain	25 WP	F	Foliar spray	0.38-0.56	0.025-0.038	1-3	15
Pear	Austria	25 WP	F	Foliar spray	0.19-0.25	0.013-0.0175	2-3	21
	Belgium	25 WP	F	Foliar spray	0.19-0.38	0.013-0.025		42
		500 SC	F	Foliar spray	0.19-0.38	0.019-0.025		42
	France	25 WP	F	Foliar spray		0.013-0.025		14
	Germany	25 WP	F	Foliar spray	0.19	0.013	1-5	14
	Greece	25 WP	F	Foliar spray	0.25-0.5	0.013-0.025		14
	Italy	25 WP	F	Foliar spray	0.23-0.3	0.019-0.025		21
	Netherlands	25 WP	F	Foliar spray	0.2-0.3	0.02	2-5	14
	Poland	72.5 WP <sup>2</sup>	F	Foliar spray	0.28	0.03-0.06	2-3	14
	Portugal	500 SC	F	Foliar spray	0.19	0.019		21
	South Africa	68.75 WP <sup>3</sup>	F	Foliar spray	0.09-0.26	0.008	1-2	14
	Spain	25 WP	F	Foliar Spray	0.25-0.38	0.025-0.038		15
	Switzerland	55 WP <sup>4</sup>	F	Foliar spray	0.2-0.25	0.01-0.015	1-4	21
	Turkey	25 WP	F	Foliar spray	0.25	0.013		14

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Pepper, sweet	Netherlands	500 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3
Plums	Belgium	25 WP	F	Foliar spray	0.56	0.038	2-3	A
		500 SC	F	Foliar spray	0.56	0.038	2-3	A
	France	25 WP	F	Foliar spray		0.019-0.025		14
		300 EC	F	Foliar spray		0.03	nsp <sup>7</sup>	14
	Greece		F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Poland	25 WP	F	Foliar spray	0.38	0.038-0.08	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	Switzerland	55 WP <sup>2</sup>	f	Foliar spray	0.2	0.01		21
Tomato	Belgium	300 EC	G	Foliar spray	0.6	0.03		3
		500 SC	G	Foliar spray	0.6	0.03		3
	Netherlands	500 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3

<sup>1</sup>10 LA :10 g/l bitertanol + 10 g/l 8-hydroxyquinoline sulfate

<sup>2</sup>72.5WP :12.5 % bitertanol + 60 % captan

<sup>3</sup>68.75 WP: in-can mixture: 7.5 % bitertanol + 60% captan + 1.25 % triadimenol

<sup>4</sup>55 WP : in-can mixture: 5 % bitertanol + 50% captan

<sup>5</sup>NS : PHI controlled by stage of growth at time of application. PHI in days not stated

<sup>6</sup>A : not applicable, as treatments during the growth stage of flowering only are registered

<sup>7</sup>nsp : number of treatments not specified. Label: use at the blossom and during the season, avoid repeated applications.

F : field; G: greenhouse

Table 25. Registered uses of bitertanol for seed treatment.

Crop	Country	Form.	Bitertanol content	kg ai/100 kg seed
Field pea	Poland	FS	33.8%	0.08
Lupin	Poland	FS	33.8%	0.08
Barley	France	FS	75 g/l	0.015
	Netherlands	DS	37.5%	0.056
	Sweden	LS	280 g/l	0.07
	UK	FS	188 g/l	0.038
Oats	Austria	FS	375 g/l	0.038-0.075
	France	FS	75 g/l	0.015
		FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.056
		DS	37.5%	0.056
	UK	FS	190 g/l	0.057
		FS	187.5 g/l	0.056
	UK	FS	375 g/l	0.056
		LS	140 g/l	0.056
	Netherlands	DS	37.5%	0.056
Poland	FS	33.8%	0.05	
Sweden	LS	280 g/l	0.056-0.07	
Rye	Austria	FS	375 g/l	0.038-0.075
	Denmark	LS	280 g/l	0.028-0.042
	France	FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.056
		DS	37.5%	0.056
	UK	FS	190 g/l	0.057
		FS	187.5 g/l	0.056
	UK	FS	375 g/l	0.056
Netherlands	DS	37.5%	0.056	
Poland	FS	33.8%	0.05	

Crop	Country	Form.	Bitertanol content	kg ai/100 kg seed
	Sweden	LS	280 g/l	0.056
Triticale	Denmark	LS	280 g/l	0.028-0.042
	UK	FS	187.5 g/l	0.056
		FS	375 g/l	0.056
	Poland	FS	33.8%	0.07
Wheat	Austria	FS	375 g/l	0.038-0.075
	Belgium	FS	190 g/l	0.038
		FS	75 g/l	0.015
		FS	37.5 g/l	0.015
		DS	37.5%	0.038
	Denmark	LS	280 g/l	0.028-0.042
	France	FS	75 g/l	0.015
		FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.075
		DS	37.5%	0.075
		FS	190 g/l	0.076
	UK	FS	187.5 g/l	0.056
		LS	140 g/l	0.056
		FS	375 g/l	0.056
		LS	280 g/l	0.056
		FS	188 g/l	0.038
	Netherlands	DS	37.5%	0.056
Poland	FS	33.8%	0.07	
Sweden	LS	280 g/l	0.056-0.07	

## RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 26 to 33 (foliar sprays) and Tables 34 to 38 (seed treatments).

Table 26. Residues of bitertanol from supervised trials on apples and pears.

Table 27. Residues of bitertanol from supervised trials on cherries.

Table 28. Residues of bitertanol from supervised trials on plums.

Table 29. Residues of bitertanol from supervised trials on nectarines.

Table 30. Residues of bitertanol from supervised trials on peaches.

Table 31. Residues of bitertanol from supervised trials on bananas.

Table 32. Residues of bitertanol from supervised trials on greenhouse tomatoes.

Table 33. Residues of bitertanol from supervised trials on greenhouse cucumbers.

Table 34. Residues of bitertanol from supervised trials on spring barley (seed treatment).

Table 35. Residues of bitertanol from supervised trials on oats (seed treatment).

Table 36. Residues of bitertanol from supervised trials on rye (seed treatment).

Table 37. Residues of bitertanol from supervised trials on spring wheat (seed treatment).

Table 38. Residues of bitertanol from supervised trials on winter wheat (seed treatment).

Where residues were not detected they are recorded in the Tables as below the limit of determination (LOD). Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although all trials included control plots, no control residues are recorded in the Tables except where they exceeded the LOD. Results are not corrected for recovery.

Most trials were carried out in Europe. In view of the different European climatic conditions, the residue trials were evaluated according to the common practice of the European Community (EC, 1998), complying with the critical GAP of northern and/or southern Europe. For the evaluation of the residue trials the regions of equal climatic conditions were defined as follows.

Northern and Central Europe: Sweden, Norway, Denmark, the UK, Ireland, northern and central France, Belgium, The Netherlands, Germany and Poland.

Southern Europe and the Mediterranean: Spain, Portugal, southern France, Italy and Greece.

#### Foliar spray uses

Apples and pears. (Table 26). The use of bitertanol on pome fruit is widely registered throughout Europe and in South Africa.

Trials in northern Europe on apples and pears were carried out in Germany, with both high-volume and low-volume atomizing spraying. With a water rate of 1500 or 2000 l/ha the spray concentration was 0.019 or 0.025 kg ai/hl, and with a water rate of 300, 500 or 750 l/ha the concentration was 0.05, 0.06 or 0.09 kg ai/hl. The application rate related to area was 0.28, 0.38 or 0.5 kg ai/ha. The number of treatments was 8 in 7 trials, 10 in 3 trials, and 12 in 2 trials. The spraying intervals ranged from 7 to 14 days. Except for the first treatment in 4 trials, all treatments were after flowering.

Eight residue trials on apples in southern Europe were in Italy, Spain and southern France. The spray concentrations were either 0.025 or 0.038 kg ai/hl and the water volumes 800-1500 l/ha. Thus the bitertanol applied per hectare was 0.25-0.46 kg. There were 5 applications in all the trials. The treatments were carried out during the stages of (1) bud to leaf development, (2) emergence of inflorescence to flowering, (3) end of flowering, (4) fruit development (fruit about final size), and (5) early to advanced maturity of fruit. In all but one of the trials samples were collected after a pre-harvest interval of 14 days.

In 7 trials in South Africa, apple trees received 6 or 7 high-volume sprays (1800-3500 l/ha) at a concentration of 0.013 kg ai/hl, corresponding to 0.23-0.44 kg ai/ha. Two other trials were at 0.88 kg ai/ha. The spraying intervals were generally 9-14 days.

Table 26. Residues of bitertanol from supervised trials on apples and pears.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10340-82 Germany, 1982	Williams Christ pear	500 SC	0.19	375	0.0125	12		0	1.4
								7	1.3
								10	0.69
								14	1.1
								21	0.82
10306-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0	1.2
								7	0.81
								10	0.75
								14	0.91
								21	0.47
10307-82 Germany, 1982	Williams Christ pear	25 WP		250	0.0125	12		0	0.69
								7	0.28
								10	0.2
								14	0.2
								21	0.23
10310-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0	1.7
								7	1.2
								10	0.98
								14	0.97
								21	0.57



Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10311-82 Germany, 1982	Williams Christ pear	25 WP		250	0.0125	12		0	0.63
								7	0.42
								10	0.34
								14	0.25
								21	0.25
10341-82 Germany, 1982	Williams Christ pear	500 SC		250	0.0125	12		0	0.98
								7	0.55
								10	0.28
								14	0.3
								21	0.33
10302-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0	1.4
								7	1.2
								10	1.5
								14	0.92
								21	0.85
10303-82 Germany, 1982	Fruehe aus Trevoux pear	25 WP	0.19	375	0.0125	12		0	1
								7	0.5
								10	0.43
								14	0.62
								21	0.57
								28	0.43
10322-83 Germany, 1983	Fruehe aus Trevoux pear	500 SC	0.19	375	0.0125	12		0	1.32
								7	1.63
								10	0.98
								14	0.59
								21	0.53
								28	0.65
10323-83 Germany, 1983	Williams Christ pear	500 SC	0.19	1500	0.0125	12		0	0.88
								7	0.48
								10	0.36
								14	0.22
								21	0.17
10301-86 Germany, 1986	Alexander Lucas pear	25 WP	0.19	1500	0.0125	12		0	1.2
								7	1.1
								10	1.2
								14	0.93
								21	0.62
10311-86 Germany, 1983	Alexander Lucas pear	500 SC	0.19	1500	0.0125	12		0	1
								7	1.1
								10	0.89
								14	0.92
								21	0.45
10300-78 Germany, 1978	Jonathan apple	25 WP	0.5	2000	0.0125	10	fruit diameter 62 mm	0	1.0
								4	0.92
								14	0.69
								21	<u>0.70</u>
10301-78 Germany, 1978	Cox Orange apple	25 WP	0.5	2000	0.025	10	fruit diameter 63 mm	0	1.2
								4	1.2
								7	0.64
								14	0.66
								21	<u>0.86</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10303-78 Germany, 1978	James Grieve apple	25 WP	0.5	2000	0.025	8	fruit diameter 67 mm	0 4 7 14 21	1.1 0.85 1.2 <u>0.62</u> 0.61
10305-79 Germany, 1979	Golden Delicious apple	25 WP	0.38	1500	0.025	10	87	0 7 10 14 21	1.5 1.8 1.7 <u>1.8</u> 1.0
10313-80 Germany, 1980	Jonathan apple	25 WP	0.38	750 (1500) <sup>1</sup>	0.05 (0.025) <sup>1</sup>	12	fruit diameter 60 mm	0 7 10 14 21	0.27 0.19 0.15 <u>0.13</u> 0.12
10304-83 Germany, 1983	Golden Delicious apple	25 WP	0.28	500 (1500)	0.06 (0.02)	12	8 weeks before harvest	0 7 14 21 28	0.63 0.42 <u>0.25</u> 0.2 0.16
10300-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 56 mm	0 7 10 14 21	0.55 0.6 0.3 <u>0.55</u> 0.3
10301-84 Germany, 1984	Jonathan apple	25 WP	0.28	1500	0.019	8	fruit diameter 59 mm	0 7 10 14 21	0.4 0.2 0.1 <u>0.08</u> 0.05
10302-84 Germany, 1984	James Grieve apple	25 WP	0.28	300 (1500)	0.09 (0.018)	8	85	0 7 10 14 21	1 0.6 0.6 <u>0.23</u> 0.2
10303-84 Germany, 1984	Golden Delicious apple	25 WP	0.28	300 (1500)	0.09 (0.018)	8	85	0 7 10 14 21	1.1 0.8 0.7 <u>1.0</u> 0.8
10304-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 52 mm	0 7 10 14 21	0.2 0.1 0.09 <u>0.09</u> 0.05
10305-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 52 mm	0 7 10 14 21	0.16 0.12 0.09 <u>0.13</u> 0.07

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2010/93 303267 Italy, 1993	Perleberg apple	25 WP	0.38	1500	0.025	5	81	0	0.24
								3	0.18
								7	0.19
								10	0.14
								14	<u>0.24</u>
			21	0.07					
RA-2010/93 303283 Spain, 1993	Golden apple	25 WP	0.30	800	0.038	1	81	0	0.62
			0.33	890	0.038	1	21	0.23	
			0.38	1000	0.038	3			
RA-2010/93 303291 Spain, 1993	Golden apple	25 WP	0.37	987	0.038	1	81	0	0.37
			0.44	1174	0.038	3	3	0.48	
			0.46	1227	0.038	1	6	0.49	
							11	0.31	
							14	<u>0.36</u>	
			21	0.36					
RA-2104/96 606944 Spain, 1996	Starking apple	500 SC	0.25	1000	0.025	3	85	0	0.22
			0.33	1300	0.025	1	3	0.24	
			0.38	1500	0.025	1	7	0.21	
							10	0.24	
							14	0.15	
			21	<u>0.18</u>					
RA-2104/96 606960 Spain, 1996	Golden apple	500 SC	0.25	1000	0.025	3	85	0	0.37
			0.33	1300	0.025	1	3	0.32	
			0.38	1500	0.025	1	7	0.35	
							10	0.26	
							14	<u>0.34</u>	
			21	0.19					
RA-2104/96 606979 Italy, 1996	Granny Smith apple	500 SC	0.26	1020	0.025	1	79	0	0.29
			0.24	977	0.025	1	14	<u>0.09</u>	
			0.34	1455	0.023	1	21	0.06	
			0.36	1450	0.025	1			
			0.37	1480	0.025	1			
RA-2104/96 606987 Italy, 1996	Red Chief apple	500 SC	0.24	952	0.025	1	79	0	0.22
			0.25	1002	0.025	1	14	<u>0.08</u>	
			0.38	1536	0.025	1	21	0.05	
			0.38	1532	0.025	1			
			0.36	1437	0.025	1			
RA-2104/96 606995 South France, 1996	Golden Delicious apple	500 SC	0.25	1000	0.025	3	85	0	0.31
			0.38	1500	0.025	2	14	<u>0.23</u>	
							21	0.19	
311/88195/V 144 South Africa, 1981	Star Crimson apple	25 WP	0.23	1800	0.013	7	--	0	1.1
							7	0.68	
							14	0.66	
							22	0.36	
							29	0.31	
				36	0.18				

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
311/88161/V 16A South Africa, 1981	Starking apple	25 WP	0.38	3000	0.013	7	--	0	0.83
								9	0.77
								19	0.36
								26	0.50
								34	0.46
42	0.23								
311/88161/V 16B South Africa, 1981	Golden Delicious apple	25 WP	0.38	3000	0.013	7	--	0	1.0
								9	0.55
								19	0.25
								26	0.26
								34	0.36
42	<0.05								
311/88352/W 26A South Africa, 1982	Golden Delicious apple	25 WP	0.88	3500	0.025	7	--	0	1.6
								5	0.88
								13	0.58
								19	1.1
								27	0.36
34	0.24								
311/88352/W 26B South Africa, 1982	Golden Delicious apple	25 WP	0.44	3500	0.013	7	--	0	1.9
								5	0.66
								13	0.50
								19	0.52
								27	0.26
34	0.17								
311/88352/W 26C South Africa, 1982	Golden Delicious apple	25 WP	0.44	3500	0.013	6	--	0	1.8
								8	0.92
								16	0.56
								22	0.54
								30	0.61
37	0.44								
44	0.11								
311/88352/W 29A South Africa, 1982	Starking apple	25 WP	0.875	3500	0.025	7	--	0	1.5
								5	1.2
								13	1.1
								19	0.51
								27	0.4
34	0.34								
311/88352/W 29B South Africa, 1982	Starking apple	25 WP	0.44	3500	0.013	7	--	0	0.75
								5	0.61
								13	0.71
								19	0.25
								27	0.27
34	0.24								
311/88352/W 29C South Africa, 1982	Star Crimson apple	25 WP	0.44	3500	0.013	6	--	0	1.8
								8	1.1
								16	0.45
								22	0.36
								30	0.31
37	0.18								
44	0.16								

<sup>1</sup>kg ai/hl calculated for 1500 l water/ha

Cherries (Table 27). The use of bitertanol on cherries is widely registered throughout Europe.

In Germany 14 residue trials on sour cherries were carried out with high- and low-volume spraying. The spray concentrations were 0.08, 0.15, or 0.19 kg ai/hl (low-volume atomizing spraying, water volumes 250-500 l/ha) and 0.025 or 0.038 kg ai/hl (high-volume spraying, water volume 1500 l/ha). The rate per area was either 0.38 or 0.56 kg ai/ha. Four trials were with 3 treatments and 10 trials with 5. The spray intervals were generally 7-14 days. In 8 trials all treatments were after flowering; in the others one treatment was applied before and/or during flowering and the others after flowering. In all trials with 5 applications, cherries were sampled at the GAP PHI of 21 days.

Two trials were conducted in northern and 4 in southern France, all on sweet cherries, with 2 treatments at a spray concentration of 0.03 kg ai/hl corresponding to 0.3 kg ai/ha (water volume 925-1000 l/ha) and a PHI of 7 days. Samples were also collected on days 3, 10, and 14. The interval between the 2 treatments was 13-15 days. The applications were carried out during the development and maturity of the fruit.

Table 27. Residues of bitertanol from supervised trials on cherries.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
10300-82 Germany, 1982	Schattenmorelle (sour)	25 WP	0.38	250 (1500) <sup>2</sup>	0.15 (0.025) <sup>2</sup>	3 (3) <sup>1</sup>	81	fruit without stone	0	1.2
									14	0.27
									28	0.1
									35	0.06
									42	0.05
10301-82 Germany, 1982	Schattenmorelle	25 WP	0.38	250 (1500)	0.15 (0.025) <sup>2</sup>	3 (3) <sup>1</sup>	79	fruit without stone	0	3.2
									14	0.34
									28	0.07
									35	0.07
									42	<0.05
10302-82 Germany, 1982	Schattenmorelle	25 WP	0.38	250 (1500) <sup>2</sup>	0.15 (0.025) <sup>2</sup>	3 (3) <sup>1</sup>	77	fruit without stone	0	11
									14	2.3
									28	0.68
									35	0.36
									42	0.58
10303-82 Germany, 1982	Schattenmorelle	25 WP	0.38	250	0.15	3 (3) <sup>1</sup>	77	fruit without stone	0	4.0
									14	0.65
									28	0.21
									35	0.12
10312-86 Germany, 1986	Schattenmorelle	500 SC	0.56	1500	0.038	5 (3) <sup>1</sup>	71	fruit without stone	0	14
									7	5.9
									14	3.6
									21	0.48
									28	<u>0.85</u>
10313-86 Germany, 1986	Schattenmorelle	500 SC	0.56	1500	0.038	5 (4) <sup>1</sup>	77	fruit without stone	0	6.2
									7	0.8
									14	0.96
									21	0.35
									28	<u>0.68</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
10315-86 Germany, 1986	Schattenmorelle	500 SC	0.56	300 (1500) <sup>2</sup>	0.19 (0.038) <sup>2</sup>	5 (4) <sup>1</sup>	77	fruit without stone	0	8.9
									7	1.8
									14	2.0
									21	<u>0.83</u>
28	0.63									
10311-87 Germany, 1987	Schattenmorelle	500 SC	0.56	1500	0.038	5 (5) <sup>1</sup>	77	fruit without stone	0	1.0
									7	0.61
									14	0.24
									21	0.2
28	0.19									
10313-87 Germany, 1987	Schattenmorelle	500 SC	0.56	300 (1500) <sup>2</sup>	0.19 (0.038) <sup>2</sup>	5 (5) <sup>1</sup>	77	fruit without stone	0	2.8
									7	1.2
									14	0.84
									21	0.44
28	0.37									
10314-87 Germany, 1987	Schattenmorelle	500 SC	0.56	300 (1500) <sup>2</sup>	0.19 (0.038) <sup>2</sup>	5 (3) <sup>1</sup>	81	fruit without stone	0	7.1
									7	3.4
									14	0.8
									21	<u>0.52</u>
28	0.49									
0206-89 Germany, 1989	Heimanns Rubin (sour)	500 SC	0.38	1500	0.025	5 (5) <sup>1</sup>	81	fruit without stone	0	0.93
									7	0.38
									14	0.25
									21	0.31
28	0.30									
0207-89 Germany, 1989	Schattenmorelle	500 SC	0.38	1500	0.025	5 (4) <sup>1</sup>	85	fruit without stone	0	1.5
									7	0.98
									14	0.85
									20	<u>0.19</u>
								whole fruit, calculated	7	0.81
									14	0.77
20	0.17									
0209-89 Germany, 1989	Schattenmorelle	500 SC	0.38	500 (1500) <sup>2</sup>	0.08 (0.027) <sup>2</sup>	5 (5) <sup>1</sup>	81	fruit without stone	0	1.1
									7	0.84
									14	0.46
									21	0.39
28	0.44									
0210-89 Germany, 1989	Schattenmorelle	500 SC	0.38	500 (1500) <sup>2</sup>	0.08 (0.027) <sup>2</sup>	5 (4) <sup>1</sup>	83	fruit without stone	0	1.9
									7	0.52
									14	0.36
									21	<u>0.36</u>
								28	0.24	
								whole fruit, calculated	7	0.43
									14	0.31
									21	0.32
28	0.22									

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
RA-2113/96 0746-96 N. France, 1996	Sunburst (sweet)	500 SC	0.3	1000	0.03	2	83	fruit with stone	0	0.33
									3	0.20
									7	0.22
									10	0.14
									14	0.15
RA-2113/96 0747-96 N. France, 1996	Marmotte (sweet)	500 SC	0.28	925	0.03	1	87	fruit with stone	0	0.31
			0.3	1000	0.03	1			3	0.26
									7	0.14
									10	0.29
									14	0.13
RA-2113/96 0680-96 S. France, 1996	Napoleon (sweet)	500 SC	0.3	1000	0.03	2	81	fruit with stone	0	0.95
									3	0.57
									7	0.46
									10	0.36
									14	<u>0.37</u>
RA-2113/96 0681-96 S. France, 1996	Van (sweet)	500 SC	0.3	1000	0.03	2	77	fruit with stone	0	0.53
									3	0.21
									7	0.13
									10	0.06
									14	<u>0.08</u>
RA-2113/96 0682-96 S. France, 1996	Belge (sweet)	500 SC	0.3	1000	0.03	2	77	fruit with stone	3	0.40
									7	0.38
									10	<u>0.17</u>
									14	0.15
RA-2113/96 0683-96 S. France, 1996	Starking- son (sweet)	500 SC	0.3	1000	0.03	2	83	fruit with stone	0	0.43
									3	0.24
									7	<u>0.15</u>
									14	0.14

<sup>1</sup>(no. of treatments): applications after flowering

<sup>2</sup>kg ai/hl calculated for 1500 l water/ha

Plums (Table 28). The use of bitertanol in plums is registered in Belgium, France, Italy, Poland, Portugal and Switzerland.

Twelve trials in Germany were with 5 applications, at about 7- or 14-day intervals, with both high- and low-volume (atomizing) spraying. Water volumes were 1000 l/ha at a concentration of 0.038 kg/hl or 1500 l/ha at a concentration of 0.025 or 0.038 kg ai/hl, giving rates of 0.38 or 0.56 kg ai/ha. Water volumes of 300 l/ha at 0.125 kg ai/hl or 500 l/ha at 0.075 kg ai/hl both gave 0.38 kg ai/ha. In 6 trials all applications were after flowering with spray intervals of about 7 or 14 days. In the other six trials 2 applications were during and shortly after flowering.

In southern Europe four residue trials were in France and one in Portugal, with 3 applications at a concentration of 0.03 kg ai/hl. With a water volume of 1000 l/ha this corresponded to 0.3 kg ai/ha. The treatments were during fruit development and fruit maturity at intervals of 13-14 days.

Table 28. Residues of bitertanol from supervised trials on plums.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg									
			kg ai/ha	Water l/ha	kg ai/hl														
10328-81 Germany, 1981	Bühler- früh- zwetsche	300 EC	0.56	1500	0.038	5 (5) <sup>1</sup>	fruit colouring	fruit without stone	0	2.7									
									7	1.3									
									10	2.2									
									14	1.4									
									21	<u>1.8</u>									
								whole fruit, calculated	0	2.6									
									7	1.2									
									10	2.1									
									14	1.3									
									21	1.7									
10329-81 Germany, 1981	Haus- zwetsche	300 EC	0.56	1500	0.038	5 (5) <sup>1</sup>	85	fruit without stone	0	2.2									
									7	1.5									
									10	1.5									
									14	<u>0.89</u>									
									21	0.72									
								whole fruit, calculated	0	2.1									
									7	1.4									
									10	1.4									
									14	0.85									
									21	0.69									
10330-81 Germany, 1981	Ortenauer	300 EC	0.38	1000	0.038	5 (5) <sup>1</sup>	85	fruit without stone	0	1.1									
									7	1.0									
									10	0.59									
									14	<u>0.59</u>									
									21	0.24									
10356-81 Germany, 1981	Haus- zwetsche	300 EC	0.38	1000	0.038	5 (5) <sup>1</sup>	85	fruit without stone	0	1.8									
									7	1.5									
									10	1.6									
									14	0.83									
									21	<u>1.4</u>									
								whole fruit, calculated	10	1.5									
									14	0.79									
									21	1.3									
									0230-88 Germany, 1988	Haus- zwetsche	500 SC	0.38	1500	0.025	5 (4) <sup>1</sup>	88	fruit without stone	0	0.39
																		7	0.32
14	<u>0.33</u>																		
21	0.22																		
0232-88 Germany, 1988	Haus- zwetsche	500 SC	0.38	1500	0.025	5 (3) <sup>1</sup>	88	fruit without stone										0	0.21
									7	0.17									
									14	<u>0.21</u>									
									21	0.21									
									28	0.11									



Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
0233-88 Germany, 1988	Auerbacher	500 SC	0.38	300 (1500) <sup>2</sup>	0.125 (0.025) <sup>2</sup>	5 (3) <sup>1</sup>	75	fruit without stone	0	0.07
									7	0.07
									14	<u>0.04</u>
									21	<0.02
28	<0.02									
0234-88 Germany, 1988	Hauszwetsche	500 SC	0.38	300 (1500) <sup>2</sup>	0.125 (0.025) <sup>2</sup>	5 (3) <sup>1</sup>	76	fruit without stone	0	1.7
									7	1.1
									14	0.92
									21	0.92
28	<u>0.94</u>									
0220-89 Germany, 1989	Auerbacher	500 SC	0.38	1500	0.025	5 (3) <sup>1</sup>	77	fruit without stone	0	0.31
									7	0.19
									14	0.13
									21	<u>0.16</u>
28	0.07									
0221-89 Germany, 1989	Hauszwetsche	500 SC	0.38	1500	0.025	5 (5) <sup>1</sup>	88	fruit without stone	0	0.72
									7	0.45
									14	<u>0.58</u>
									21	0.33
								28	0.40	
								whole fruit, calculated	0	0.69
									7	0.43
									14	0.55
21	0.31									
28	0.40									
0222-89 Germany, 1989	Ortenauer	500 SC	0.38	500 (1500) <sup>2</sup>	0.075 (0.025) <sup>2</sup>	5 (3) <sup>1</sup>	77	fruit without stone	0	0.19
									7	0.27
									14	0.11
									21	<u>0.15</u>
28	0.12									
0384-89 Germany, 1989	Auerbacher	500 SC	0.38	500 (1500) <sup>2</sup>	0.075 (0.025) <sup>2</sup>	5 (3) <sup>1</sup>	76	fruit without stone	0	0.18
									7	0.13
									14	<u>0.19</u>
									21	0.11
28	0.08									
10301-80 S. France, 1980	Prunier d'Ente	25 WP	0.25	1000 (1500) <sup>2</sup>	0.03 (0.02) <sup>2</sup>	3	87	fruit without stone	9	<u>0.49</u>
									14	0.39
								whole fruit, calculated	9	0.45
									14	0.34
RA-2112/96 606855 S. France, 1996	Reine Claude	500 SC	0.3	1000 (1500) <sup>2</sup>	0.03 (0.02) <sup>2</sup>	3	77	fruit with stone	0	0.16
									3	0.11
									7	0.07
									10	<u>0.09</u>
14	0.05									
RA-2112/96 606863 S. France, 1996	Prune de' ente	500 SC	0.3	1000 (1500) <sup>2</sup>	0.03 (0.02) <sup>2</sup>	3	83	fruit with stone	0	0.41
									3	0.38
									7	0.26
									14	<u>0.34</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2112/96 606871 S. France, 1996	Quetsche	500 SC	0.3	1000 (1500) <sup>2</sup>	0.03 (0.02) <sup>2</sup>	3	81	fruit with stone	0	0.45
									3	0.33
									7	<u>0.36</u>
									14	0.28
RA-2112/96 606847 Portugal, 1996	Red Beauty	500 SC	0.3	1000 (1500) <sup>2</sup>	0.03 (0.02) <sup>2</sup>	3	81	fruit with stone	0	<0.02
									3	<0.02
									7	<0.02
									10	<0.02
14	<0.02									

<sup>1</sup>no. of treatments after flowering

<sup>2</sup>kg ai/hl calculated for 1500 l water/ha

Peaches and nectarines (Tables 29 and 30). The use of bitertanol is registered in southern Europe and South Africa.

Three trials on nectarines were conducted in Italy and two in southern France. The spray concentration was 0.019 kg ai/hl in 4 trials and 0.018 kg ai/hl in the fifth, corresponding to 0.25 or 0.26 kg ai/ha (water volume 1300-1400 l/ha). The nectarine trees were sprayed once in three trials and twice in the other two at an interval of 7 or 10 days. The final treatment was 7 days before harvest in all the trials.

In South Africa 2 trials were carried out with 4 applications at 0.012 or 0.025 kg ai/hl. The concentration of 0.012 kg ai/hl corresponded to 0.3 kg ai/ha (water volume 2500 l/ha). The spraying intervals were 18-24 days. In a third trial there were 2 applications at a concentration of 0.012 kg ai/hl, equivalent to 0.36 kg ai/ha (water 3000 l/ha). The spraying interval was 14 days.

In 6 residue trials on peaches in Spain and 1 in Portugal there were 3 applications: at flowering, at development of the fruit, and at maturity. The spray concentration was 0.038 or 0.030 kg ai/hl. This corresponded to 0.25-0.38 kg ai/ha for the first application (water volume 660-1000 l/ha), 0.24-0.51 kg ai/ha for the second application (water volume 800-1500 l/ha), and 0.3-0.71 kg ai/ha for the third (water volume 1000-1900 l/ha).

In South Africa 2 trials were with 3 treatments at either 0.0125 or 0.025 kg ai/hl sprayed to run-off. Assuming a water rate of 2000 l/ha this would correspond to 0.25 or 0.5 kg ai/ha. Four other trials were with 1 or 2 treatments at either 0.012 or 0.024 kg ai/hl, corresponding to 0.24 or 0.48 kg ai/ha (water volume 2000 l/ha).

Table 29. Residues of bitertanol from supervised trials on nectarines.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10360-85 Italy, 1985	Stark Red Gold	25 WP	0.26	1400	0.019	2	85	fruit without stone	7	<u>0.13</u>
									11	0.1
									18	0.13
10361-85 Italy, 1985	Fantasia	25 WP	0.26	1400	0.019	1	85	fruit without stone	7	<u>0.23</u>
									12	0.21
									18	0.23

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10362-85 Italy, 1985	Stark Red Gold	25 WP	0.26	1400	0.019	1	85	fruit without stone	7	<u>0.25</u>
									11	0.21
									18	0.21
10363-85 S. France, 1985	Fantasia	25 WP	0.25	1400	0.018	2	fruit diameter 60 mm	fruit without stone	0	0.31
									7	<u>0.20</u>
14	0.13									
10365-85 S. France, 1985	Fantasia	25 WP	0.25	1320	0.019	1	85	fruit without stone	0	0.1
									7	<u>0.12</u>
									14	<0.05
311/88419/ W212-A South Africa, 1982		300 EC	0.3	2500	0.012	4	-	fruit without stone	0	0.53
									3	0.47
									10	0.21
									14	0.18
									24	0.18
311/88419/ W212-B South Africa, 1982		300 EC	0.6	2500	0.025	4	-	fruit without stone	0	1.5
									3	0.68
									10	0.54
									14	0.51
									24	0.37
311/88933/ C181 South Africa, 1985		300 EC	0.36	2990	0.012	2	-	fruit without stone	0	1.9
									7	1.4
									14	0.60
									21	0.31
									28	0.20
									35	0.10
									42	0.16
									49	<u>0.17</u>
56	0.08									

Table 30. Residues of bitertanol from supervised trials on peaches.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2011/93 303305 Spain, 1993	Caterine	25 WP	0.37	992	0.038	1	85	fruit without stone	0	0.41
									3	0.67
									7	0.46
									10	0.42
									14	<u>0.43</u>
									whole fruit, calculated	10
14	0.41									
RA-2011/93 303380 Spain, 1993	Maycrest	25 WP	0.34	900	0.038	1	85	fruit without stone	0	1.2
									14	<u>0.74</u>
									whole fruit, calculated	14

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2083/94 403423 Spain, 1994	July Lady	25 WP	0.38	1000	0.038	1	82	fruit without stone	0	0.39
			0.45	1187	0.038	1			3	0.30
			0.61	1625	0.038	1			7	0.29
									10	<u>0.27</u>
									14	0.19
							3	0.28		
							7	0.27		
							10	0.26		
							14	0.18		
RA-2083/94 403431 Spain, 1994	Merril Gem Free	25 WP	0.25	666	0.038	1	84	fruit without stone	0	0.62
			0.38	1000	0.038	1			3	0.47
			0.47	1250	0.038	1			7	0.43
									10	<u>0.54</u>
									14	0.23
							10	0.49		
							14	0.21		
RA-2083/94 405167 Spain, 1994	Baby Gold 9	25 WP	0.29	762	0.038	1	81	fruit without stone	0	0.71
			0.51	1371	0.038	1			14	<u>0.26</u>
			0.72	1905	0.038	1				
							whole fruit, calculated	14	0.24	
RA-2111/96 606901 Spain, 1996	Mira-flores	500 SC	0.30	997	0.03	1	81-85	fruit with stone	0	0.10
			0.45	1491	0.03	1			3	0.10
			0.45	1510	0.03	1			7	0.10
									10	<u>0.05</u>
									14	0.04
RA-2111/96 606898 Portugal, 1996	Coronado	500 SC	0.25	814	0.03	1	87	fruit with stone	0	0.25
			0.24	800	0.03	1			3	0.32
			0.30	1000	0.03	1			7	0.19
									11	0.09
									14	<u>0.10</u>
311/88421/ W214-A South Africa, 1982	Wolte-made	300 EC	-	drip-off	0.0125	3	-	fruit with stone	0	0.55
									5	0.35
									11	0.25
									19	0.15
									26	<0.1
311/88421/ W214-B South Africa, 1982	Wolte-made	300 EC	-	drip-off	0.025	3	-	fruit with stone	0	1.8
									5	1.2
									19	0.5

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
311/88736/ B140-A South Africa, 1985	Kakamas	300 EC	0.24	2000	0.012	1	-	fruit without stone	0	0.62
									7	0.44
									14	0.24
									21	0.14
									28	0.11
									35	<u>0.12</u>
									42	0.07
49	0.06									
56	0.05									
311/88736/ B140-B South Africa, 1985	Kakamas	300 EC	0.24	2000	0.012	2	-	fruit without stone	0	1.3
									7	0.84
									14	0.31
									21	0.27
									28	0.29
									35	<u>0.12</u>
									42	0.06
49	0.06									
56	0.07									
311/88736/ B140-C South Africa, 1985	Kakamas	300 EC	0.48	2000	0.024	1	-	fruit without stone	0	2.0
									7	1.4
									14	0.69
									21	0.60
									28	0.51
									35	0.26
									42	0.23
49	0.16									
56	0.14									
311/88736/ B140-D South Africa, 1985	Kakamas	300 EC	0.48	2000	0.024	2	-	fruit without stone	0	1.8
									7	1.2
									14	1.0
									21	0.66
									28	0.37
									35	0.23
									42	0.31
49	0.17									
56	0.17									

Bananas (Table 31). There are recent registrations for the use of bitertanol on bananas throughout Central America, and in the Philippines, Taiwan, and Cameroon.

In Central America, residue trials were conducted in Costa Rica and Honduras with 9-16 applications, usually 12, at intervals of 8-15 days, usually 10. Application rates were 0.12-0.13 kg ai/ha (4 trials), 0.24-0.25 kg ai/ha (6 trials), and 0.29-0.3 kg ai/ha (6 trials). The treatments were high-volume (473 l/ha), low-volume (60-120 l/ha) or ultra-low-volume (19 l/ha). In order to cover all common use conditions, both bagged and unbagged fruit were included (as the bags may be torn during the growing season, possibly resulting in higher residues than would otherwise be expected). Both green and ripened fruit were analysed in 6 trials, and both washed and unwashed samples in 10 trials.

Six trials were carried out in the Philippines and Taiwan, four with bagged and two with unbagged fruit. The use patterns were  $26 \times 0.2$  kg ai/ha,  $10 \times 0.3$  kg ai/ha and  $12 \times 0.04$  kg ai/ha. In the Philippines the applications were by air, as recommended on the label (water volume 23-29 l/ha). In Taiwan the water volume was 40 l/ha.

In 2 trials in Cameroon bagged bananas were sprayed by air either 5 or 8 times with a 250 OF formulation (oil-miscible flowable concentrate or suspension) at 0.25 kg ai/ha, 15 l/ha. Samples were collected either 6 or 12 days after the last application.

Table 31. Residues of bitertanol from supervised trials on bananas.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage, bagged or unbagged	Sample	PHL, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10309-78 Costa Rica, 1978	Grand Naine	200 EC	0.25	100	0.25	16	-	pulp, peel, fruit <sup>1</sup>	4	<0.05
10350-80-A Costa Rica, 1980		300EC	0.12	60	0.2	10	before harvest, bagged	pulp, peel, fruit	8	<0.01
10350-80-B Costa Rica, 1980		300EC	0.12	60	0.2	10	before harvest, unbagged	pulp peel fruit	8	0.014 0.15 0.055
10330-80-A Costa Rica, 1980	Grand Naine	300EC	0.24	120	0.2	10	before harvest, bagged	pulp peel fruit	8	<0.01 0.039 0.015
10330-80-B Costa Rica, 1980	Grand Naine	300EC	0.24	120	0.2	10	before harvest, unbagged	pulp peel fruit	8	0.019 0.12 0.047
68896 Honduras, 1980	Cavendish	300EC	0.13	19	0.69	12	bagged	pulp w- <sup>2</sup> pulp w+ <sup>3</sup> peel w- peel w+ fruit w- fruit w+	0	0.01 0.02 0.02 0.03 0.01 0.02
68897 Honduras, 1980	Cavendish	300EC	0.13	19	0.69	12	unbagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	<u>0.04</u> 0.04 0.19 0.20 0.10 0.10
68898 Honduras, 1980	Cavendish	300EC	0.25	19	1.3	12	bagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	<0.01 <0.01 0.05 0.03 0.03 0.02

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
68899 Honduras, 1980	Cavendish	300EC	0.25	19	1.3	12	unbagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	<u>0.13</u> 0.11 0.64 0.41 0.32 0.23
68900 Honduras, 1980	Cavendish	25 WP	0.25	19	1.3	12	unbagged  bagged	pulp peel fruit pulp fruit	0	<u>0.03</u> 0.10 0.06 0.02 0.03
80469-A Costa Rica, 1981	Grand Nain	300EC	0.29	66	0.44	9	harvest stage, bagged	pulp gr. <sup>4</sup> , w- pulp ri. <sup>5</sup> , w- pulp gr., w+ pulp ri., w+  peel gr., w- peel ri., w- peel gr., w+ peel ri., w+  fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	3	<0.01 <0.01 0.01 0.02  <0.01 <0.01 0.05 0.05  <0.01 <0.01 0.03 0.03
80469-B Costa Rica, 1981	Grand Nain	300EC	0.29	66	0.44	9	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+  peel gr., w- peel ri., w- peel gr., w+ peel ri., w+  fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	3	<u>0.11</u> 0.06 0.09 0.11  0.53 0.25 0.41 0.45  0.24 0.13 0.22 0.23

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
80472 Honduras, 1981	Grand Nain	300EC	0.29	473	0.06	12	harvest stage, bagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+	0	0.01
										0.01
										0.02
										0.02
										0.04
										0.03
										0.04
										0.08
										0.02
										0.02
										0.03
										0.04
80473 Honduras, 1981	Grand Nain	300EC	0.29	473	0.06	12	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+	0	0.08
										0.08
										<u>0.17</u>
										0.14
										0.76
										0.32
										0.73
										0.51
										0.33
										0.17
										0.36
										0.28
80470 Honduras, 1981	Grand Nain	50 WP	0.3	473	0.06	12	harvest stage, bagged	pulp ri., w- pulp gr., w+ pulp ri., w+	0	0.01
										0.01
										<0.01
										0.12
										0.15
										0.03
										0.05
										0.06
										0.01



Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
80471 Honduras, 1981	Grand Nain	50 WP	0.3	473	0.06	12	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+	0	<u>0.03</u> <0.01 0.03 0.02
								peel gr., w- peel ri., w- peel gr., w+ peel ri., w+		0.10 0.03 0.09 0.05
								fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+		0.06 0.01 0.05 0.03
10320-80 Philippines, 1980	Giant Cavendish	200 EC	0.2	29	0.69	26	green, bagged	pulp, peel, fruit	0	<0.05
								pulp, peel, fruit	11	<0.05
10321-80 Philippines, 1980	Giant Cavendish	200 EC	0.2	23	0.87	26	green, bagged	pulp, peel, fruit	0	<0.05
								pulp, peel, fruit	11	<0.05
10344-81 Philippines, 1981	Dwarf Cavendish	300 EC	0.30	24	1.25	10	ripe for cutting, bagged	pulp peel fruit	2	<0.01 0.019 <0.01
10345-81 Philippines, 1981	Dwarf Cavendish	300 EC	0.30	24	1.25	10	ripe for cutting, unbagged	pulp peel fruit	2	0.015 0.14 0.06
10350-81-A Taiwan, 1981	native variety	300 EC	0.038	40	0.094	12	before harvest, bagged	pulp peel fruit	0	<0.01 0.09 <0.01
10350-81-B Taiwan, 1981	native variety	300 EC	0.038	40	0.094	12	before harvest unbagged	pulp peel fruit	0	0.14 2.1 0.51
10366-81-A Cameroon, 1981	Poyo	250 OF	0.25	15 + oil	1.7	5	bagged	pulp peel fruit	6	<0.01 0.01 <0.01
10366-81-B Cameroon, 1981	Poyo	250 OF	0.25	15 + oil	1.7	8	bagged	pulp, peel, fruit	12	<0.01 <0.01 <0.01

<sup>1</sup>fruit: whole fruit, residue calculated from peel and pulp

<sup>2</sup>w- : unwashed

<sup>3</sup>w+ : washed

<sup>4</sup>gr.: green

<sup>5</sup>ri. : ripened

Tomatoes (Table 32).The use of bitertanol on tomatoes grown in greenhouses is authorised in Belgium and The Netherlands.

There were 8 trials in the Netherlands and 2 in Belgium with three treatments at intervals of 4-6 days. Two of the trials were with cherry tomatoes.

Table 32. Residues of bitertanol from supervised trials on greenhouse tomatoes.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
0304-88 The Netherlands, 1988	Calipso	300 EC	0.9	3000	0.03	3	87-89	0	0.90
								1	0.96
								3	<u>0.96</u>
								5	0.90
								7	0.77
0305-88 The Netherlands, 1988	Nr. 704	300 EC	0.75	2500	0.03	3	87-89	0	1.1
								1	1.0
								3	<u>0.98</u>
								5	0.90
								7	0.87
0306-88 The Netherlands, 1988	Calipso	300 EC	0.6	2000	0.03	3	87-89	0	0.95
								1	1.2
								3	0.91
								5	<u>0.96</u>
								7	0.90
RA-2010/91 101796 The Netherlands, 1991	Evita (cherry)	300 EC	0.9	3000	0.03	3	A <sup>1</sup>	0	1.8
								1	2.3
								3	1.6
								5	<u>2.1</u>
								7	1.7
RA-2010/91 101818 The Netherlands, 1991	Viscon	300 EC	0.9	3000	0.03	3	A	0	0.61
								1	0.66
								3	0.52
								5	<u>0.56</u>
								7	0.51
RA-2010/91 104817 The Netherlands, 1991	Evita (cherry)	300 EC	0.9	3000	0.03	3	A	0	2.3
								1	2.8
								3	<u>2.4</u>
								5	2.1
								7	2.2
RA-2059/96 605557 Belgium, 1996	Macua	500 SC	0.6	2000	0.03	3	A	0	0.62
								3	<u>0.54</u>
RA-2059/96 605565 Belgium, 1996	Macua	500 SC	0.6	2000	0.03	3	A	0	0.52
								3	<u>0.48</u>
RA-2059/96 605573 The Netherlands, 1996	Aromate	500 SC	0.6	2200	0.027	3	A	0	0.61
								3	<u>0.39</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2059/96 605581 The Netherlands, 1996	Jamaica	500 SC	0.6	2000	0.03	3	A	0 3	0.45 <u>0.41</u>

<sup>1</sup>A: Several stages of fruit development on the same plant at the same time

Cucumbers (Table 33). At present the use of bitertanol on cucumbers grown in greenhouses is registered in Belgium, The Netherlands and Italy.

Eight greenhouse trials in The Netherlands were with 3 applications at intervals of 5-6 days and 2 in southern France were with 3 applications at intervals of 14 days.

The French trials approximated Italian GAP. The trials in The Netherlands complied with their critical national GAP.

Table 33. Residues of bitertanol from supervised greenhouse trials on cucumbers.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10304-80 S. France, 1980	Pendorax	25 WP	0.35	1875	0.02	3	87-89	17	<0.05
10304-80 S. France, 1980	Pendorax	25 WP	0.41	2200	0.02	3	85-87	17	<0.05
0561-88 The Netherlands, 1988	Sandra	300 EC	0.9	3000	0.03	3	87-89	0 1 2 3 5	0.25 0.22 0.21 <u>0.22</u> 0.18
0562-88 The Netherlands, 1988	Mustang	300 EC	0.9	3000	0.03	3	87-89	0 1 2 3 5	0.47 0.38 0.29 <u>0.21</u> 0.16
RA-2096/96 605603 The Netherlands, 1996	Escape	500 SC	0.6	2000	0.03	3	A <sup>1</sup>	0 3	0.36 <u>0.22</u>
RA-2096/96 606611 The Netherlands, 19956	Flamige	500 SC	0.6	2000	0.03	3	A	0 3	0.21 <u>0.10</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat- ments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2096/96 605638 The Netherlands, 1996	Venturea	500 SC	0.6	2000	0.03	3	A	0 3	0.19 <u>0.16</u>
RA-2096/96 605646 The Netherlands, 1996	Jessica	500 SC	0.53 0.55 0.62	1771 1823 2057	0.03 0.03 0.03	3	A	0 3	0.28 <u>0.17</u>
RA-2096/96 606654 The Netherlands, 1996	Ducan	500 SC	0.6	2000	0.03	3	A	0 1 3 5 7	0.34 0.24 <u>0.19</u> 0.12 0.06
RA-2096/96 606662 The Netherlands, 1996	Suprami	500 SC	0.86 0.77 0.86	2868 2689 2868	0.03 0.03 0.03	3	A	0 1 3 5 7	0.18 0.16 <u>0.11</u> 0.06 0.05

<sup>1</sup>A: Several stages of fruit development on the same plant at the same time

#### Seed treatments

Barley (Table 34). The use of bitertanol as a seed dressing on barley is authorised in France, The Netherlands and Sweden.

Eight residue trials were conducted on spring barley in Germany, 3 with the 39.8 DS formulation, 3 with 298 LS, and 2 with 375 FS. Application rates were 57-75 g ai/100 kg seed. Forage was sampled 67-94 days after seed treatment and drilling, and straw and grain at harvest, 100-144 days after treatment.

Table 34. Residues of bitertanol from supervised trials on spring barley after seed treatment.

Report, Country Year	Variety	Form.	Application rate kg ai/100 kg seed	No. of treatments	Sample	PHI, days	Residues, mg/kg
10200-83 Germany 1983	Carina	39.8 DS <sup>1</sup>	0.075	1	forage grain straw	74 100 100	<0.05 <0.05 <0.05
10201-83 Germany 1983	Carina	39.8 DS <sup>1</sup>	0.075	1	forage grain straw	67 103 103	<0.05 <0.05 <0.05
10202-83 Germany 1983	Carina	39.8 DS <sup>1</sup>	0.075	1	forage grain straw	94 140 140	<0.05 <0.05 <0.05
10245-83 Germany 1983	Koral	375 FS <sup>2</sup>	0.057	1	forage grain straw	86 128 128	<0.05 <0.05 <0.05

Report, Country Year	Variety	Form.	Application rate kg ai/100 kg seed	No. of treatments	Sample	PHI, days	Residues, mg/kg
10246-83 Germany 1983	Koral	375 FS <sup>2</sup>	0.057	1	forage	86	<0.05
					grain	128	<0.05
					straw	128	<0.05
10202-84 Germany 1984	Carina	298 LS <sup>3</sup>	0.07	1	forage	89	<0.05
					grain	135	<0.05
					straw	135	<0.05
10203-84 Germany 1984	Aura	298 LS <sup>3</sup>	0.07	1	forage	84	<0.05
					grain	144	<0.05
					straw	144	<0.05
10204-84 Germany 1984	Carina	298 LS <sup>3</sup>	0.07	1	forage	80	<0.05
					grain	131	<0.05
					straw	131	<0.05

<sup>1</sup> 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole

<sup>2</sup> 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole

<sup>3</sup> 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

Oats (Table 35). Bitertanol seed dressings are registered in Austria, France, Germany, the UK, The Netherlands, Poland and Sweden.

In 7 residue trials in Germany, oat seeds were treated with a 39.8 DS, 375 FS, or 398 FS formulation at 56-75 g ai/t. Forage, straw and grain were collected in all trials, and also ears in 3 trials. Forage was sampled 63-101 days, ears 75-95 days and straw and grain 113-147 days after seed treatment and drilling.

Table 35. Residues of bitertanol from supervised trials on oats after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10366-82 Germany, 1982	Flämings- krone	39.8 DS <sup>1</sup>	0.075	forage	76	<0.1
				ears	86	<0.1
				grain	139	<0.05
				straw	139	<0.05
10367-82 Germany, 1982	Flämings- krone	39.8 DS <sup>1</sup>	0.075	forage	63	<0.1
					75	<0.1
				ears	75	<0.05
				grain	131	<0.05
straw	131	<0.05				
10368-82 Germany, 1982	Flämings- krone	39.8 DS <sup>1</sup>	0.075	forage	67	<0.1
					95	<0.1
				ears	95	<0.05
				grain	147	<0.05
straw	147	<0.05				
10241-83 Germany, 1983	Flämings Nova	375 FS <sup>2</sup>	0.057	forage	101	<0.05
				grain	136	<0.05
				straw	136	<0.05
10242-83 Germany, 1983	Flämings Nova	375 FS <sup>2</sup>	0.057	forage	75	<0.05
				grain	113	<0.05
				straw	113	<0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10212-83 Germany, 1983	Flämings Nova	398 FS <sup>3</sup>	0.055	forage	94	<0.05
				grain	140	<0.05
				straw	140	<0.05
10213-83 Germany, 1983	Flämings Nova	398 FS <sup>3</sup>	0.056	forage	97	<0.05
				grain	141	<0.05
				straw	141	<0.05

<sup>1</sup> 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole

<sup>2</sup> 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole

<sup>3</sup> 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole

**Rye** (Table 36). Seed dressings containing bitertanol are registered for use on rye in Austria, Denmark, France, Germany, the UK, The Netherlands, Poland and Sweden.

In 9 residue trials on winter rye in Germany the formulations were 39.8 DS, 375 FS, 398 FS, and 298 LS. The application rate was 56 or 57 g ai/t in 8 trials and 70 g ai/t in the 9th. Samples of forage were collected 218-269 days, and grain and straw 289-322 days after seed treatment and drilling. Samples of ears were also collected in 4 trials after 228-269 days.

Table 36. Residues of bitertanol from supervised trials on rye after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10363-82 Germany, 1981/82	Carokurz	39.8 DS <sup>1</sup>	0.056	forage	219	<0.1
				ears	228	<0.1
				grain	228	<0.05
				straw	297	<0.05
				straw	297	<0.05
10364-82 Germany, 1981/82	Carokurz	39.8 DS <sup>1</sup>	0.056	forage	220	<0.1
				ears	231	<0.1
				grain	231	<0.05
				straw	291	<0.05
				straw	291	<0.05
10365-82 Germany, 1981/82	Carokurz	39.8 DS <sup>1</sup>	0.056	forage	244	<0.1
				ears	269	<0.1
				grain	269	<0.05
				straw	322	<0.05
				straw	322	<0.05
10372-82 Germany, 1981/82	Kustro	398 FS <sup>2</sup>	0.056	forage	254	<0.1
				ears	254	<0.05
				grain	308	<0.05
				straw	308	<0.05
10210-83 Germany, 1982/83	Carokurz	398 FS <sup>2</sup>	0.056	forage	224	<0.05
				grain	295	<0.05
				straw	295	<0.05
10211-83 Germany, 1982/83	Carokurz	398 FS <sup>2</sup>	0.056	forage	220	<0.05
				grain	291	<0.05
				straw	291	<0.05
10240-83 Germany, 1982/83	Carokurz	375 FS <sup>3</sup>	0.057	forage	224	<0.05
				grain	295	<0.05
				straw	295	<0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10200-85 Germany, 1984/85	Carokurz	298 LS <sup>4</sup>	0.056	forage	220	<0.05
				grain	295	<0.05
				straw	295	<0.05
10202-85 Germany, 1984/85	Carokurz	298 LS <sup>4</sup>	0.070	forage	218	<0.05
				grain	289	<0.05
				straw	289	<0.05

<sup>1</sup> 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole

<sup>2</sup> 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole

<sup>3</sup> 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole

<sup>4</sup> 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

**Wheat** (Tables 37, 38). The use of bitertanol seed dressings is currently authorized in Austria, Belgium, Denmark, France, Germany, the UK, The Netherlands and Sweden.

There were 13 trials in Germany, 11 on spring wheat and 2 on winter wheat. The formulations were 39.8 DS, 199 FS, 375 FS, 398 FS, and 298 LS.

Table 37. Residues of bitertanol from supervised trials on spring wheat after seed treatment.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10341-80 Germany, 1980	Kolibri	39.8 DS <sup>1</sup>	0.075	forage	76	<0.1
				ears	90	<0.1
				grain	153	<0.1
				straw	90	<0.1
				straw	153	<0.1
10342-80 Germany, 1980	Kolibri	39.8 DS <sup>1</sup>	0.075	forage	76	<0.1
				ears	90	<0.1
				grain	154	<0.1
				straw	90	<0.1
				straw	154	<0.1
10343-80 Germany, 1980	Kolibri	39.8 DS <sup>1</sup>	0.075	forage	93	<0.1
				ears	121	<0.1
				grain	177	<0.1
				straw	121	<0.1
				straw	177	<0.1
10370-82 Germany, 1982	Kolibri	398 FS <sup>2</sup>	0.075	forage	62	<0.05
				forage	77	<0.05
				ears	77	<0.05
				grain	130	<0.05
				straw	130	<0.05
10371-82 Germany, 1982	Kolibri	398 FS <sup>2</sup>	0.076	forage	56	<0.05
				forage	73	<0.05
				ears	73	<0.05
				grain	134	<0.05
				straw	134	<0.05
10243-83 Germany, 1983	Max	375 FS <sup>3</sup>	0.076	forage	97	<0.05
				grain	143	<0.05
				straw	143	<0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10244-83 Germany, 1983	Max	375 FS <sup>3</sup>	0.076	forage	103	<0.05
				grain	147	<0.05
				straw	147	<0.05
10210-84 Germany, 1984	Kolibri	398 FS <sup>2</sup>	0.075	forage	104	<0.05
				grain	164	<0.05
				straw	164	<0.05
10211-84 Germany, 1984	Arkas	398 FS <sup>2</sup>	0.075	forage	80	<0.05
				grain	142	<0.05
				straw	142	<0.05
RA-2166/97 707643 Germany, 1997	Thasos	199 FS <sup>4</sup>	0.075	forage	50	<0.05
				grain	138	<0.05
				straw	138	<0.05
RA-2166/97 707651 Germany, 1997	Thasos	199 FS <sup>4</sup>	0.075	forage	42	<0.05
				grain	132	<0.05
				straw	132	<0.05

<sup>1</sup> 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole

<sup>2</sup> 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole

<sup>3</sup> 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole

<sup>4</sup> 199 FS : 187.5 g/l bitertanol + 11 g/l fuberidazole

Table 38. Residues of bitertanol from supervised trials on winter wheat after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10201-85 Germany, 1984/85	Kanzler	298 LS <sup>1</sup>	0.07	forage	246	<0.05
				grain	323	<0.05
				straw	323	<0.05
10203-85 Germany, 1984/85	Caribo	298 LS <sup>1</sup>	0.07	forage	221	<0.05
				grain	285	<0.05
				straw	285	<0.05

<sup>1</sup> 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

### Livestock feeding studies

Leimkuehler et al., 1984a (Tables 39, 40). Three groups of 3 dairy cows were dosed with bitertanol by bolus capsule for 28 days at levels equivalent to 25, 75 or 250 ppm in the feed on a dry weight basis, or 0.63, 1.88 and 6.25 mg per kg body weight per day based on the initial body weights. Three animals maintained as controls were dosed with vehicle only. At the end of the test period, all the treated animals and one control were slaughtered and their tissues and milk analysed for total extractable residues of bitertanol and its metabolites as 1,2,4-triazole (Leimkuehler et al., 1983).

No dose-related differences between the treated and control animals were evident in food consumption, body weight changes or milk production.

The mean residues in the tissues of the 250 ppm group were liver 2.8 mg/kg, kidneys 0.76 mg/kg, fat 0.84 mg/kg, and muscle 0.32 mg/kg. The residues were correspondingly lower at the lower feeding levels. At 25 ppm the residues averaged 0.63 mg/kg in the liver and were just above the limit of



determination (0.01 mg/kg) in the fat, muscle and kidneys. The residues in the milk reached a plateau after 3-4 weeks in the intermediate-dose group but not in the high-dose group, and were at or below the limit of determination in the 25 ppm group.

Table 39. Residues in tissues of cows dosed with bitertanol for 28 days (Leimkuehler *et al.*, 1984a).

Animal no.	Dietary level, ppm	Total residues, mg/kg				Report no.
		Fat	Muscle	Kidneys	Liver	
203	Control	<0.01	<0.01	<0.01	0.01	86316, 86317, Doc.-No. 84-653
205	25	<0.01	<0.01	0.03	0.66	
206	25	0.01	0.02	0.03	0.78	
209	25	0.06	0.06	0.05	0.44	
207	75	0.18	0.08	0.30	1.3	
210	75	0.16	0.08	0.31	0.87	
212	75	0.16	0.09	0.36	1.9	
201	250	1.3	0.32	0.69	1.9	
208	250	0.89	0.44	1.1	2.7	
211	250	0.36	0.19	0.52	3.7	

Table 40. Residues in milk of cows dosed with bitertanol for 28 days (Leimkuehler *et al.*, 1984a).

Animal no.	Dietary level, ppm	Total residues, mg/kg					Report no.
		Day 0	Day 7	Day 14	Day 21	Day 28	
202	Control	n.a. <sup>1</sup>	n.a.	n.a.	n.a.	<0.01 <sup>2</sup>	86316, 86317
203	Control						
204	Control						
205	25	n.a.	n.a.	n.a.	n.a.	<0.01	Doc.-No. 84-653
206	25	n.a.	n.a.	n.a.	n.a.	<0.01	
209	25					0.01	
207	75					0.07	
210	75	<0.01 <sup>2</sup>	0.09	0.10	0.13	0.03	
212	75					0.02	
201	250					0.25	
208	250	<0.01 <sup>2</sup>	0.11	0.19	0.17	0.21	
211	250					0.26	

<sup>1</sup>n.a.: not analysed as residues in later samples were at or below the limit of determination

<sup>2</sup> composite samples

Leimkuehler *et al.*, 1984b (Tables 41, 42). Four groups of 10 laying hens were fed daily rations containing bitertanol at levels of 1, 3, 10 or 100 ppm for 28 days, with ten birds as controls. Ten additional hens were fed the 100 ppm diet for 28 days, then five were maintained on untreated rations for an additional 14 days and three for 28 days before slaughter to determine the rate of decrease of residues.

No sample from the 10 ppm birds were analysed because an interruption in their drinking water supply led to decreased egg production and feed consumption. No significant pesticide-related effects on feed consumption body weight, or egg production occurred.

The tissues and eggs were analysed for total extractable bitertanol and metabolite residues. The samples were extracted with various solvents and acid-hydrolysed to liberate 1,2,4-triazole which was converted to triazolypinacolone for determination by gas chromatography (Leimkuehler *et al.*, 1983).

Composite samples of tissues and eggs from the 3 ppm and 100 ppm treatment groups were analysed. Eggs were analysed at 7, 14, 21 and 28 days. The residues in tissues from the 100 ppm group were liver 1.03 mg/kg, gizzard 0.23 mg/kg, heart 0.10 mg/kg, muscle 0.07 mg/kg, and fat 0.07 mg/kg.

Liver, gizzard and muscle from the 3 ppm group contained quantifiable residues, highest in the liver at 0.21 mg/kg. The residues in the livers from the 1 ppm feeding level were less than 0.01 mg/kg. Residues in eggs were quantifiable only in the 100 ppm feeding group, reaching 0.11 mg/kg at 28 days. Residues in all samples of eggs, and tissues except liver, were below 0.01 mg/kg 28 days after the birds had been returned to untreated feed. Liver contained 0.04 mg/kg.

Repeat analyses confirmed the original results.

Table 41. Residues in tissues of hens fed on feed containing bitertanol (Leimkuehler *et al.*, 1984b).

Sample	Total residues, mg/kg						Report no.
	28 days <sup>1</sup>				14 days depuration <sup>2</sup>	28 days depuration <sup>2</sup>	
	Control	1 ppm	3 ppm	100 ppm	100 ppm	100 ppm	
Liver	<0.01	<0.01	0.21	1.03	0.05	0.04	86312, 8613, Doc.-No. 84-656
Gizzard	<0.01	n.a. <sup>3</sup>	0.07	0.23	0.02	<0.01	
Muscle	<0.01	n.a.	0.01	0.07	0.07	<0.01	
Fat	<0.01	n.a.	<0.01	0.07	<0.01	<0.01	
Heart	<0.01	n.a.	<0.01	0.10	0.04	<0.01	

<sup>1</sup> composite samples from 10 birds

<sup>2</sup> composite samples from 5 birds at 14 days and 3 at 28 days after removal from fortified feed

<sup>3</sup> n.a.: not analysed because residues were low at higher feeding levels

Table 42. Residues in eggs of hens fed on feed containing bitertanol (Leimkuehler *et al.*, 1984b).

Day	Total residues, mg/kg					Report no.
	Control	1 ppm	3 ppm	100 ppm	100 ppm depuration <sup>3</sup>	
7	n.a. <sup>1</sup>	n.a. <sup>2</sup>	<0.01	0.07	<0.01	86312, 8613, Doc.-No. 84-656
14	n.a. <sup>1</sup>	n.a. <sup>2</sup>	<0.01	0.05	<0.01	
21	n.a. <sup>1</sup>	n.a. <sup>2</sup>	<0.01	0.05	<0.01	
28	<0.01	n.a. <sup>2</sup>	<0.01	0.11	<0.01	

<sup>1</sup>n.a.: not analysed

<sup>2</sup>n.a.: eggs of 1 mg/kg group were not analysed because all residues from 3 mg/kg group were <0.01 mg/kg

<sup>3</sup> analysed 7, 14, 21 and 28 days after removal from fortified feed

## FATE OF RESIDUES IN STORAGE AND PROCESSING

### In storage

No information. Bitertanol is not used on stored products.

### In processing

The residues of bitertanol on raw agricultural commodities imply a need for processing studies on fruiting vegetables, pome fruit, and stone fruit. Studies on tomatoes, apples, cherries, peaches and plums were reported.

Tomatoes (Table 43). Washed tomatoes, preserved fruit, juice and dried paste were prepared from tomatoes treated 3 times with bitertanol at 0.9 kg ai/ha (0.03 kg ai/hl) in The Netherlands. The residue after a PHI of 3 days was 0.52 mg/kg.

The processing simulated industrial practice. Washed tomatoes were cut into pieces. The preparation of preserves involved the addition of a pickling liquor (NaCl solution), pasteurization and maceration (Figure 7). To prepare juice and paste, washed tomatoes were blanched in water, the

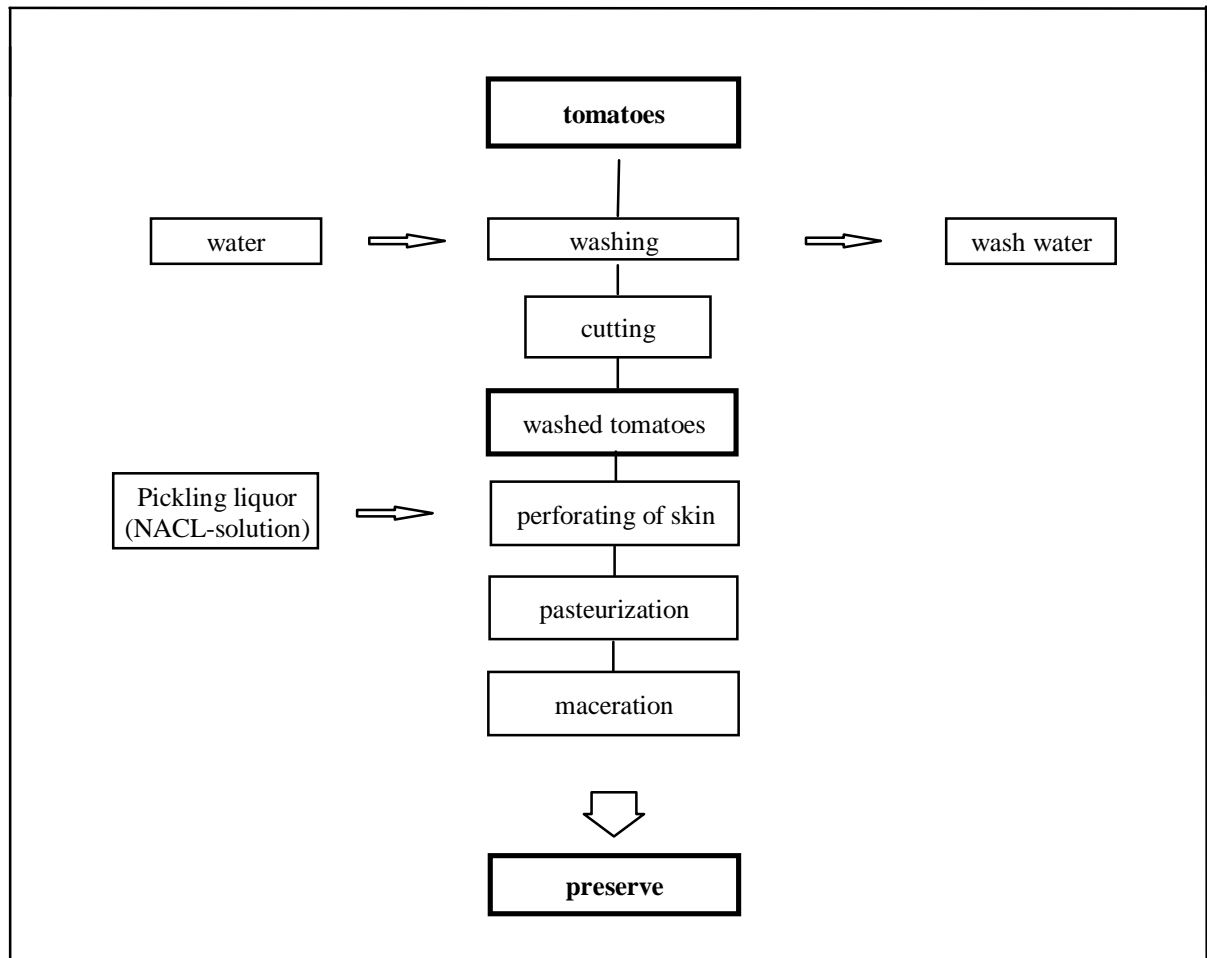
tomato pulp was passed through a strainer and the raw juice separated into two parts for juice and paste. NaCl was added to produce juice which was then pasteurized in an autoclave. To obtain paste the raw juice was concentrated, dried to about 40% dry weight, and finally also pasteurized (Figure 8).

Washing reduced the residues from 0.52 to 0.42 mg/kg. Processing decreased the residues in preserves and juice to 0.19 and 0.07 mg/kg respectively, but concentrated them in paste to 1.1 mg/kg giving a processing factor of 2.1.

Table 43. Bitertanol residues in tomatoes and processed products.

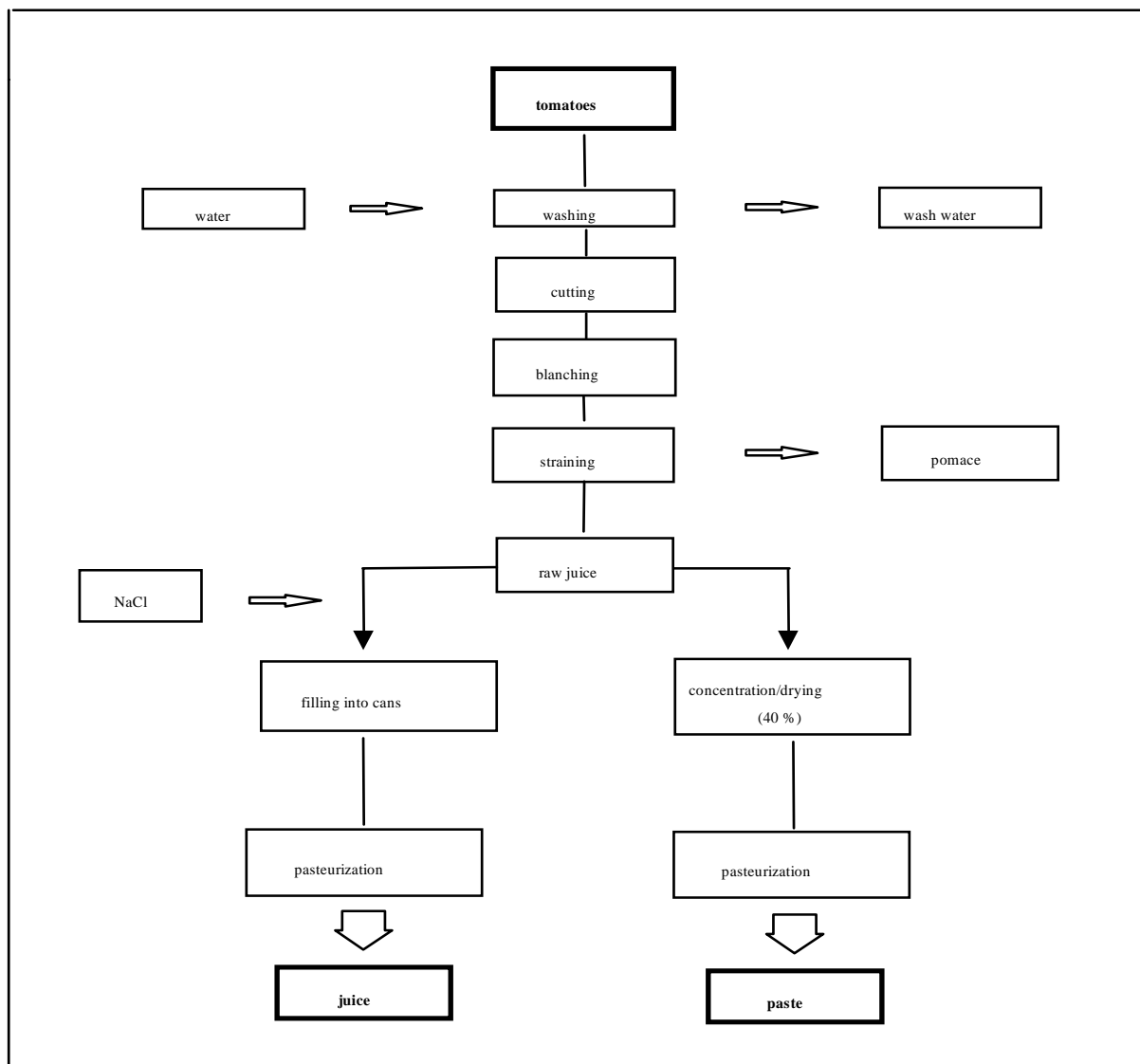
Country	Sample	PHI, days	Residues, mg/kg	Processing factor	Report no., Study no.
Netherlands	fruit	3	0.52	-	<i>RA-2010/91</i> 0181-91
	fruit, washed		0.42	0.81	
	preserves		0.19	0.365	
	juice		0.07	0.135	
	paste		1.1	2.1	

Figure 7. Preparation of preserved tomatoes.



bold framed items analysed

Figure 8. Preparation of tomato juice and paste.



Bold framed items analysed

Apples (Tables 44-46). Apples from 4 German residue trials which had been treated 8 times at 0.28 kg ai/ha were sampled at a PHI of 14 days. Bitertanol residues in the raw commodity ranged from 0.08 to 1.0 mg/kg.

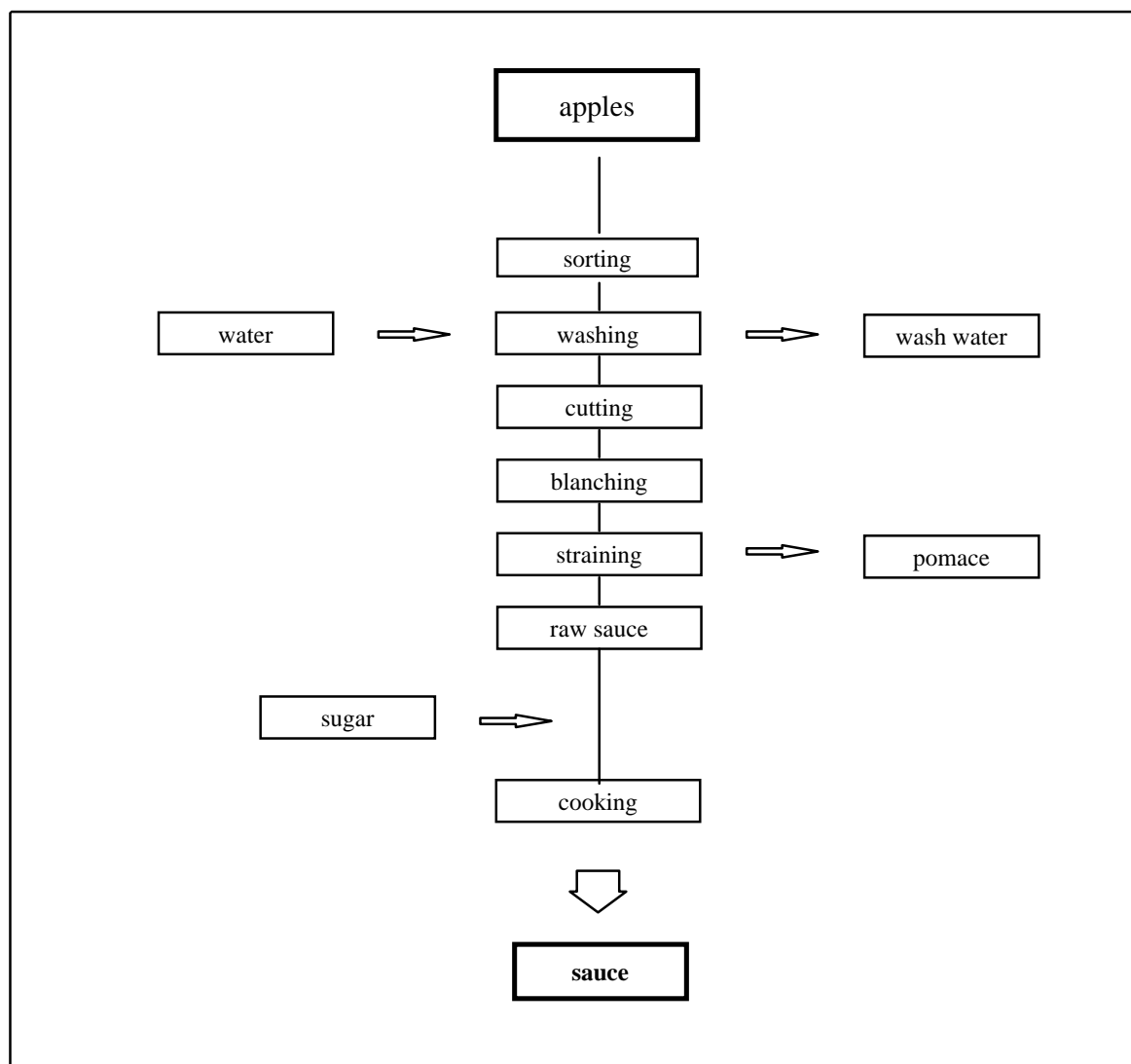
Apple sauce was made according to household procedures and juice by simulated industrial techniques. Apple sauce was prepared by discarding damaged fruit, then washing and cutting the remaining apples, blanching, straining through a sieve and cooking (Figure 9). To prepare apple juice washed apples were pressed to give raw juice, which was then centrifuged and finally pasteurized in an autoclave (Figure 10).

In all 4 studies the residues in apple sauce and juice were either not detectable or below the LOD of 0.02 mg/kg.

Table 44. Bitertanol residues in processed fractions of apples (Germany,1984).

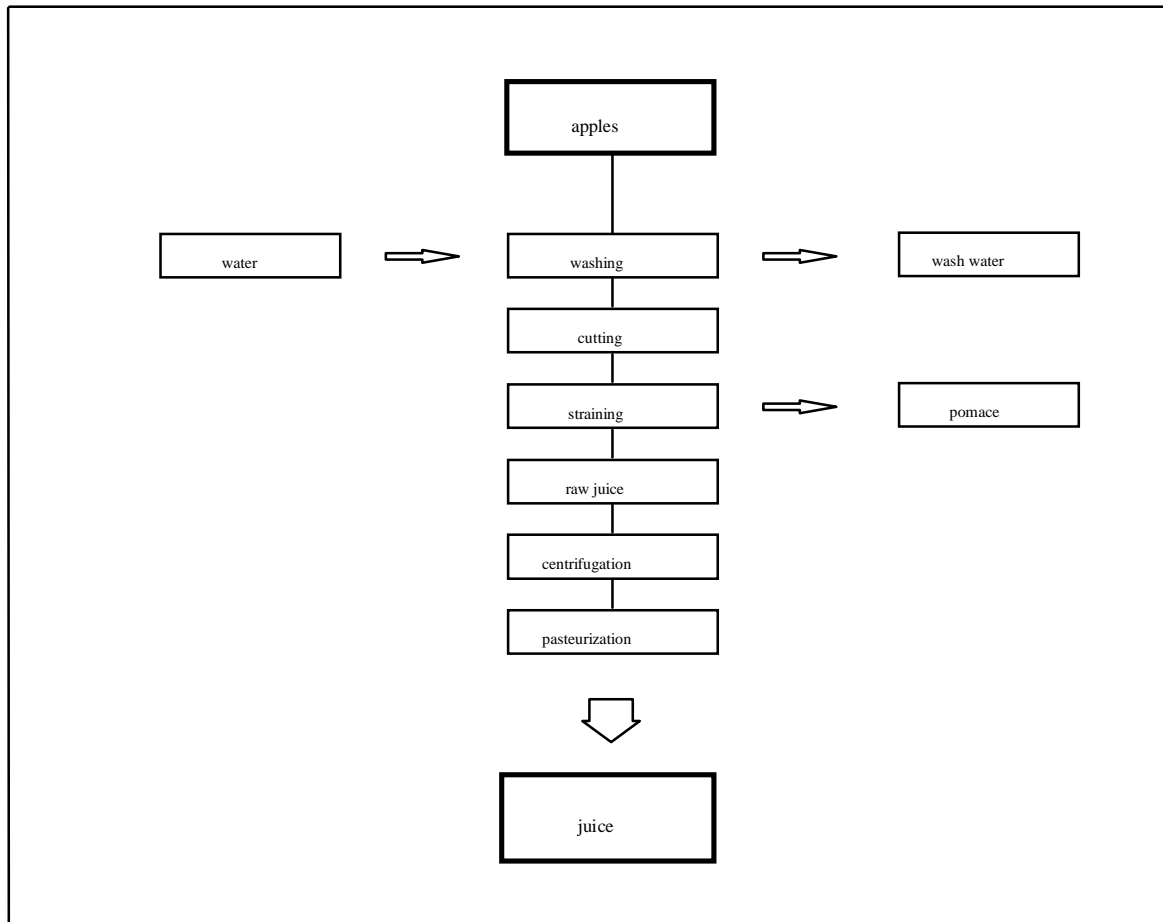
Sample	PHI,days	Residues,mg/kg	Study No.
fruit	14	0.55	10300-84
sauce		<0.02	
juice		<0.02	
fruit	14	0.08	10301-84
sauce		<0.02	
juice		<0.02	
fruit	14	0.23	10302-84
sauce		<0.02	
juice		<0.02	
fruit	14	1.0	10303-84
sauce		<0.02	
juice		<0.02	

Figure 9: Processing of apples to sauce.



bold framed products = residue samples

Figure 10. Preparation of apple juice.



Sandie and Thornton, 1984. As pomace is used for animal feed a study was carried out to determine whether residues were concentrated in it. Ripe apples were sprayed to run-off with bitertanol in the laboratory three times at 0.2 kg ai/hl during of 1 day. This procedure was substituted for spraying in the field because the metabolism study by Puhl and Hurley (1981a) showed that there is very little penetration of bitertanol into the pulp of apples and very little metabolism.

The apples were processed under simulated commercial conditions. Unwashed apples (17 kg) were chopped and pressings into 8 “cheeses” in a small-scale commercial hydraulic apple press. Juice from the eight pressings was pooled and mixed well to suspend the solids. The wet pomace was dried in a forced-draught oven at 77°C for 6.5 hours. The yields and residues of all fractions are shown in Table 45.

Table 45. Bitertanol residues in apples and processed products.

Sample	Residues, mg/kg	Processing factor	Yield, kg	Report no.
Whole fruit, control (chopped)	<0.01		16	86466
Whole fruit, treated (chopped)	8.2		14	
Juice, control	<0.01		7.8	
Juice, treated	0.84	0.1	8.3	
Wet pomace, control	<0.05		6.7	
Wet pomace, treated	21	2.6	5.2	
Dry pomace, control	<0.05		1.9	
Dry pomace, treated	61	7.4	1.6	

Mobay Chemical Corporation, 1985. Apple trees were sprayed with 15 x 1.1 kg ai/ha in Kansas City, Missouri (USA). The processing procedure was similar to that of Sandie and Thornton (1984) except that the pomace was not dried. The results are shown in Table 46.

Table 46. Bitertanol residues in apples and processed products.

Sample	Residues, mg/kg	Processing factor	Report no.
Whole fruit, control	<0.01		87036
Whole fruit, treated	0.49		
Juice, control	<0.01		
Juice, treated	0.09	0.18	
Wet pomace, control	<0.01		
Wet pomace, treated	1.37	2.8	

Cherries (Table 47). Sour cherries were processed into preserved fruit and juice, and jam (2 trials) or pomace (1 trial) in Germany. The trees were treated five times at either 0.38 or 0.56 kg ai/ha. The samples used for processing were collected at a PHI of 21 days and contained residues of 0.36-0.52 mg/kg.

Jam was made by household methods, and preserved fruit and juice by simulated industrial procedures (Figures 11 and 12). The first steps in both processes were discarding damaged fruit, washing, and stoning. Jam was cooked by adding sugar and gelling agent to the chopped fruit and slowly bringing to the boil. Preserves were produced by adding sugar solution to stoned cherries and pasteurizing the canned mixture in an autoclave. Juice was prepared by pressing in a high-pressure press and pasteurizing the juice. The preparation of juice also yielded pomace.

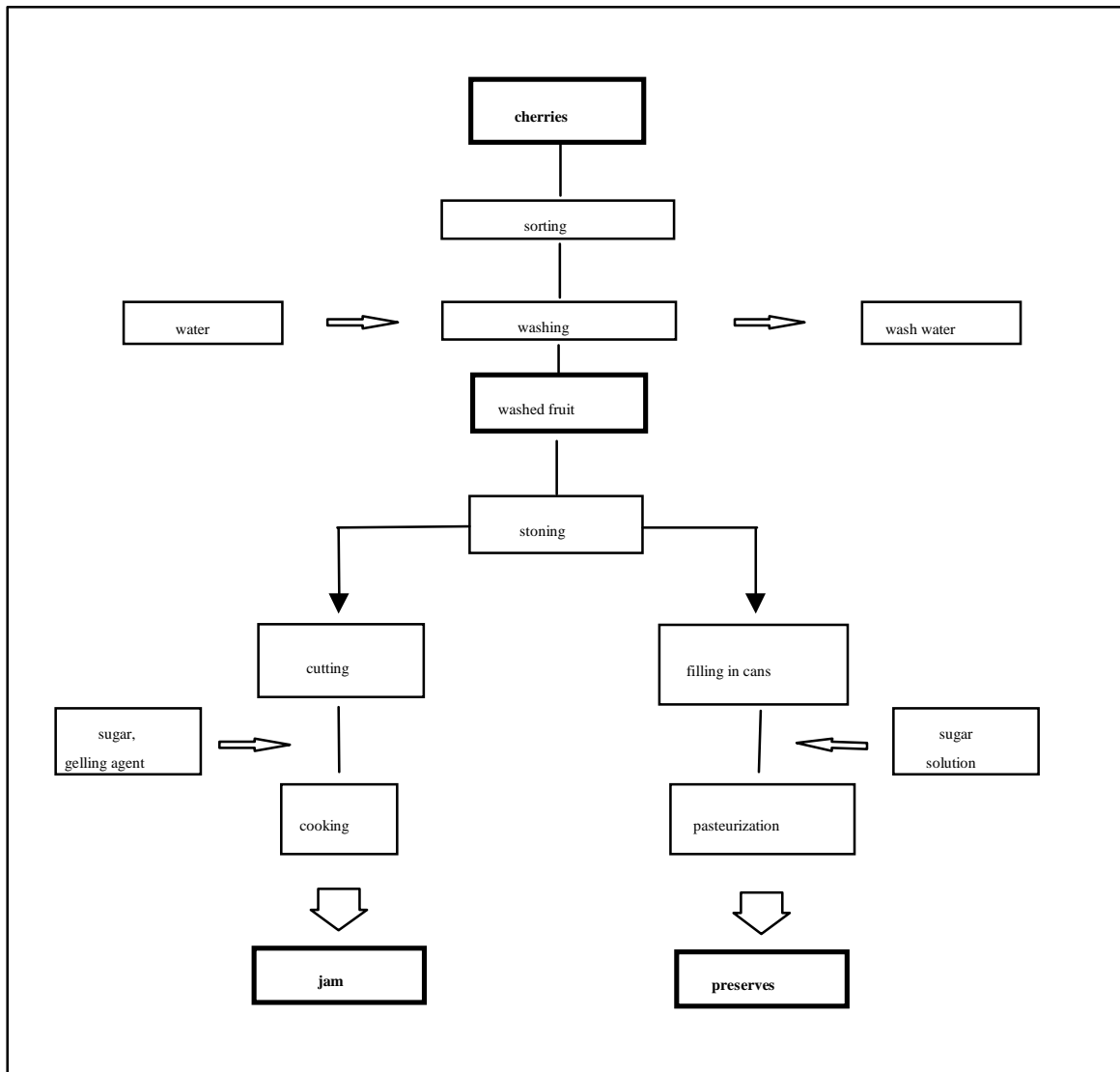
Bitertanol residues in washed and preserved cherries were somewhat lower than in the raw agricultural commodity, were markedly reduced in jam and juice, and hardly changed in pomace.

Table 47. Bitertanol residues in cherries and processed products (Germany, 1986-89).

Sample	PHI, days	Residues, mg/kg	Processing factor	Study no.
Fruit	21	0.48	-	10312-86
Fruit, washed		0.44	0.92	
Preserve		0.33	0.68	
Jam		0.26	0.54	
Juice		0.18	0.375	
Fruit	21	0.52	-	10314-87
Fruit, washed		0.39	0.75	
Preserve		0.26	0.5	
Juice		0.06	0.115	
Pomace		0.56	1.1	
Fruit	21	0.36	-	0210-89
Preserve		0.21	0.58	
Jam		0.13	0.36	
Juice		0.01	0.028	

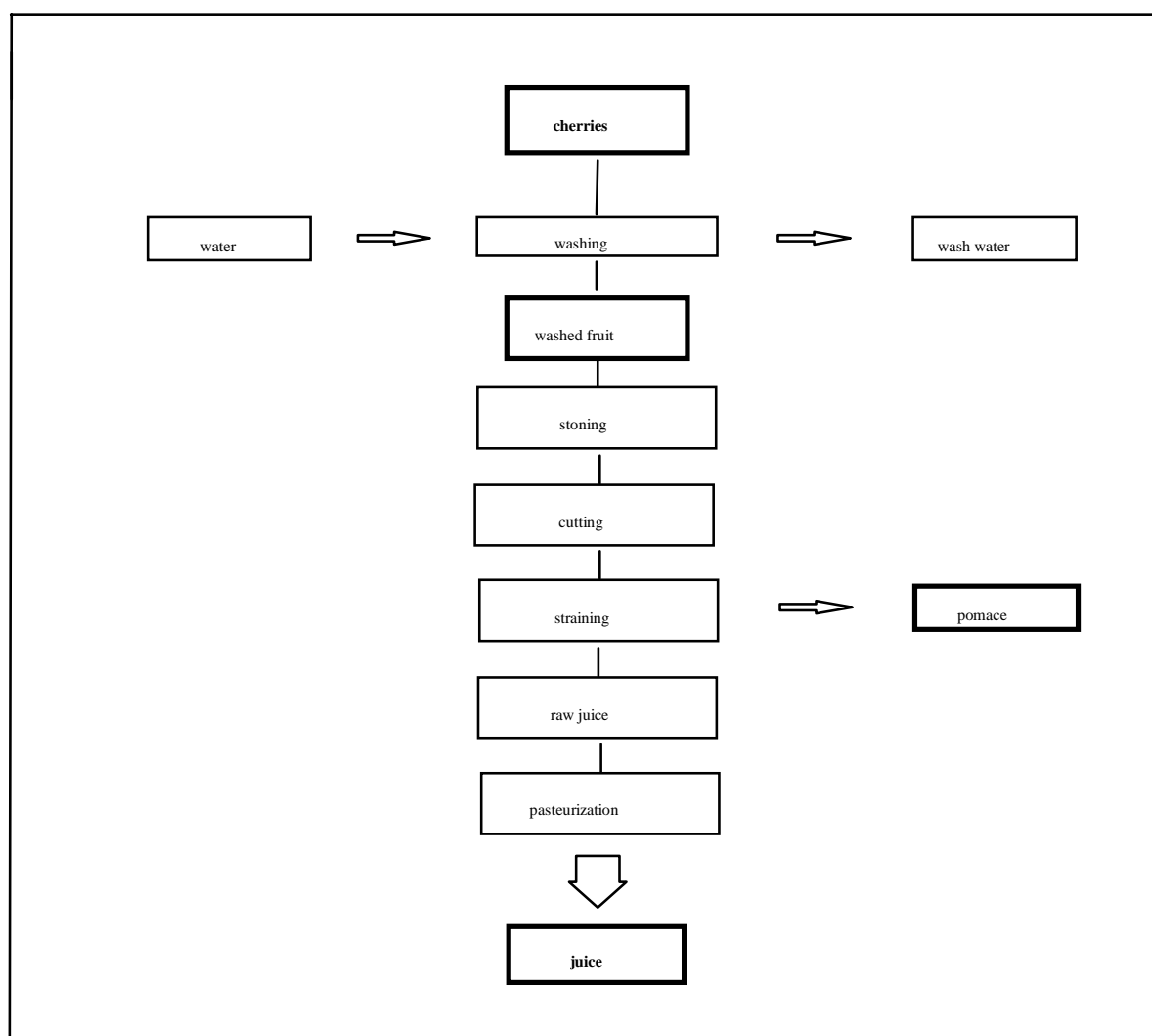


Figure 11. Processing of cherries to jam and preserved fruit.



Bold framed items analysed

Figure 12. Processing of cherries to juice and pomace.



Bold framed items analysed

Peaches (Table 48). Samples from 2 Spanish residue trials with 3 treatments at 0.25-0.61 kg ai/ha (0.038 kg ai/hl) and a PHI of 14 days, containing residues of 0.19 and 0.23 mg/kg, were processed into jam, preserved peaches and juice (Figures 13 and 14). Jam was prepared by domestic methods, and preserves and juice by simulated industrial procedures on a laboratory scale. In both cases, peaches were washed, peeled (except for juice preparation) stoned and cut into pieces. Jam was made by mashing the fruit pieces, adding sugar and gelling agent, and cooking the mixture. Preserves were produced by transferring fruit halves together with a hot sugar solution into cans and pasteurizing them in an autoclave, and peach juice by pressing the fruit pieces in a high-pressure press and pasteurizing the centrifuged raw juice.

No residues above the LOD of 0.02 mg/kg were found in jam or preserves. The residue in the juice was 0.03 mg/kg in both studies. There was thus a considerable decrease of residues in the processed commodities.

The higher residues in washed than in unwashed fruit were not considered to indicate a true increase. A more likely explanation is that the unwashed and washed peaches were from different portions of the field sample.

Table 48. Bitertanol residues in peaches and processed fractions (Spain, 1994).

Sample	PHI, days	Residues, mg/kg	Processing factor	Report no. Study no.
fruit	14	0.19	-	RA-2083/94 0342-94
Fruit, washed		0.3	not calculated <sup>1</sup>	
jam		<0.02		
preserve		<0.02		
juice		0.03		
fruit	14	0.23	-	RA-2083/94 0343-94
Fruit, washed		0.36	not calculated <sup>1</sup>	
jam		<0.02		
preserve		<0.02		
juice		0.03		

<sup>1</sup> not calculated because of aberrant relation between residues in washed and unwashed peaches (see text)

Figure 13. Processing of peaches to jam and preserved fruit.

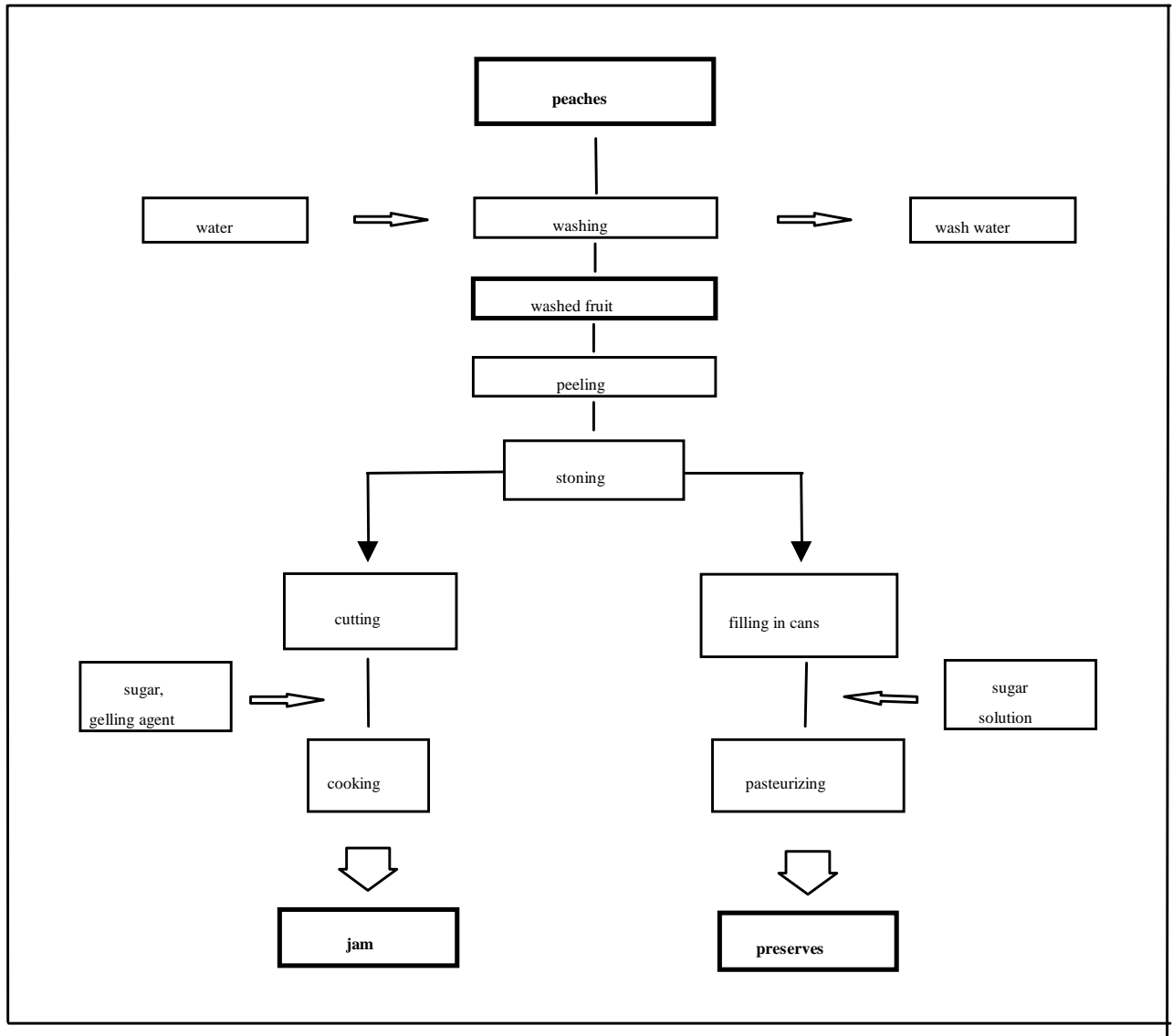
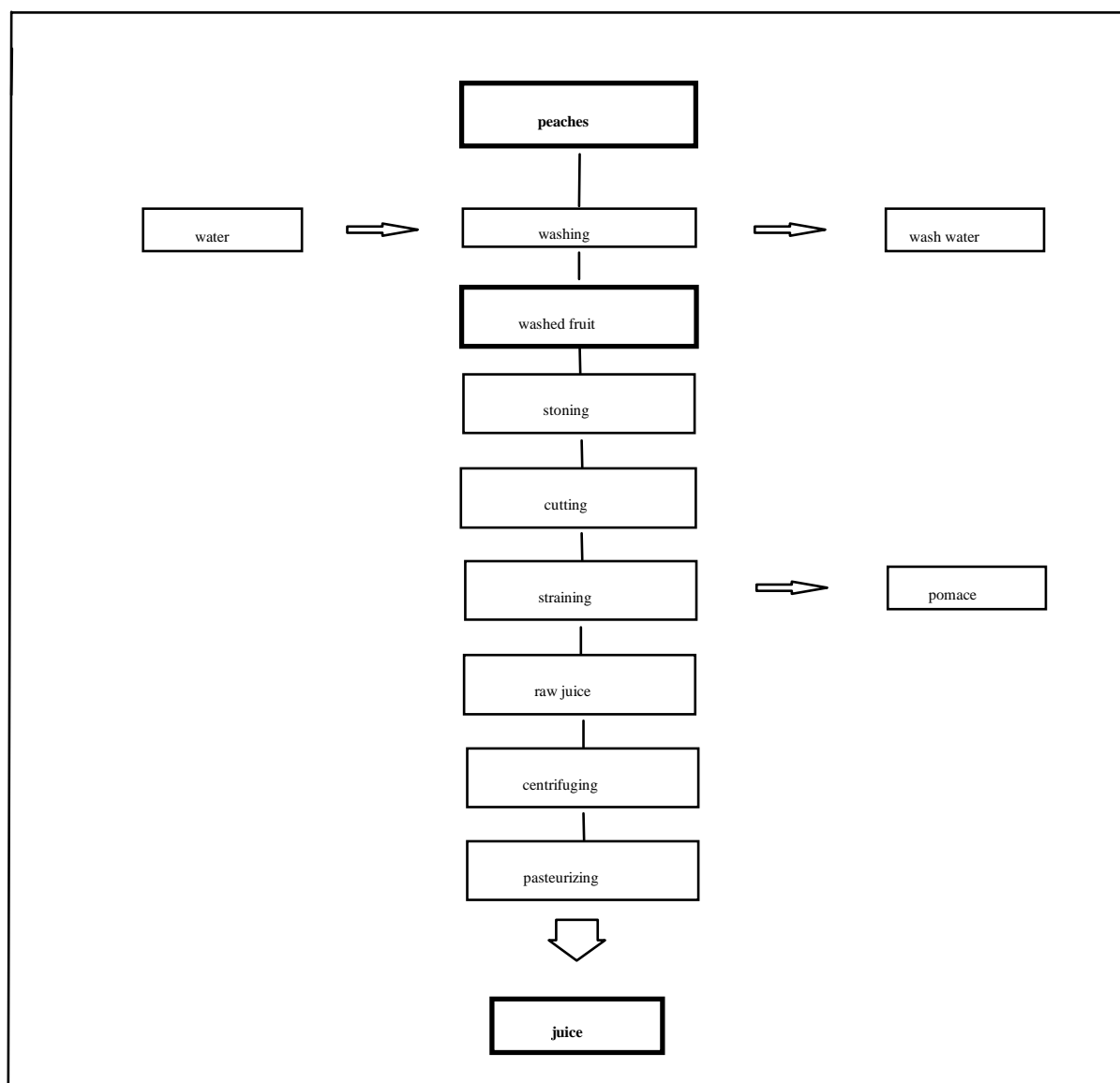


Figure 14. Processing of peaches to juice.



Plums (Table 49). A processing study was included in 2 residues trials on plums in Germany. The plum trees were treated 5 times with bitertanol at 0.38 kg ai/ha (0.025 kg ai/hl). At a PHI of 21 days the residues were 0.21 and 0.22 mg/kg.

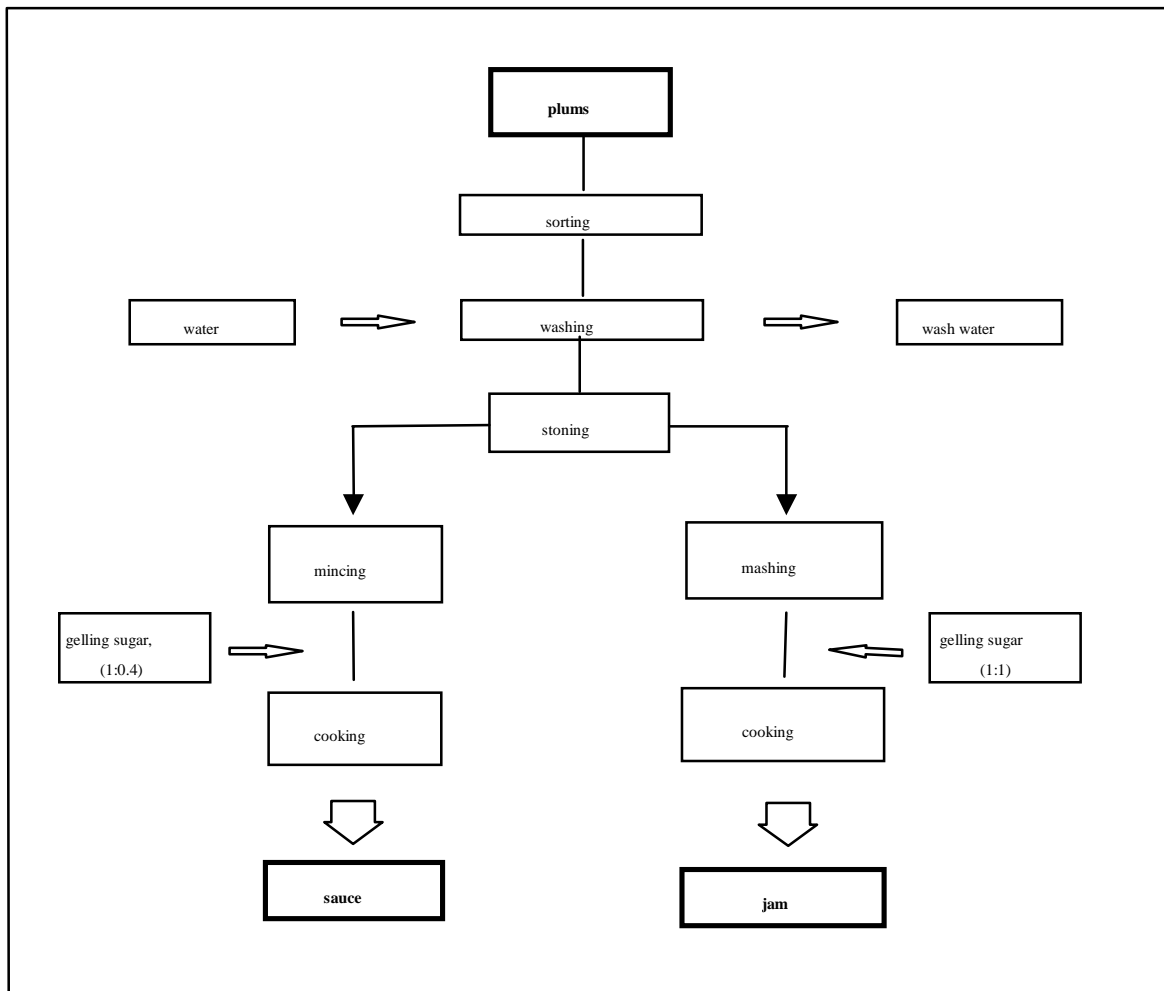
Plum sauce was made in 1 trial and jam in both trials by household methods (Figure 15). Damaged plums were discarded and the others were washed and stoned. Plum sauce was prepared by putting the plums through a mincer, adding gelling sugar (1:0.4), and cooking. Jam was produced by mashing the plums, adding gelling sugar (1:1), and cooking the mixture.

The bitertanol residue in plum sauce was about the same as in the raw plums, and the residues in the jam were about half those in the raw commodity.

Table 49. Bitertanol residues in plums and processed fractions (Germany, 1988).

Sample	PHI, days	Residues, mg/kg	Processing factor	Study no.
Fruit	21	0.22	-	0230-88
Jam		0.14	0.64	
Fruit	21	0.21	-	0232-88
Sauce		0.22	1	
Jam		0.12	0.57	

Figure 15. Preparation of plum sauce and jam.



### Residues in the edible portion of food commodities

Apart from the processing studies the only information was on banana pulp, recorded in the section on supervised trials (Table 31).

### RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information on bitertanol residues in food in commerce in The Netherlands 1994-1996 (Table 50) and 1997 (Table 51) was submitted (Olthof, 1999b).

Table 50. Residues of bitertanol in food in commerce, The Netherlands 1994-1996.

Product	Samples analysed	Samples without residues <sup>1</sup>	Samples with residues below MRL	Samples with residues above MRL	Residues above MRL, mg/kg	MRL, mg/kg
Apples	1654	1653	1	-	-	1
Pears	447	445	2	-	-	1
Peaches	283	282	-	1	0.08	0.05*
Cucumbers	1089	1087	2	-	-	1
Peppers, sweet	1655	1635	20	-	-	1
Tomatoes	1242	1213	29	-	-	1
Celery	300	298	1	1	1.4	0.05*
Other arable products	759	758	-	1	0.91	0.05*

<sup>1</sup>LOD = 0.05 mg/kg

Table 51. Residues of bitertanol in food in commerce, The Netherlands 1997.

Product	Samples analysed	Samples without residues <sup>1</sup>	Samples with residues below MRL	Samples with residues above MRL	Residues above MRL, mg/kg	MRL, mg/kg
Pears	90	89	1	-	-	1
Peaches	39	37	-	2	0.39, 0.55	0.05*
Nectarines	65	64	-	1	0.31	0.05*
Currants (black, red and white)	142	141	-	1	0.07	0.05*
Peppers, sweet	605	602	3	-	-	1
Courgettes	79	78	1	-	-	1
Beans (with pods)	262	261	-	1	0.25	0.05*

<sup>1</sup>LOD = 0.05 mg/kg

## NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country/Commodity	MRL, mg/kg	Notes
<b>Argentina</b>		
Apple	1	
Banana	0.5	
Peanut	0.2	
<b>Australia</b>		
Apple	1	
Beans, except Broad bean and Soya bean	0.3	
Bean, Broad (green pods and/or immature seeds)	0.3	
Cereals, forage	0.1	
Cereals, grain	0.05	Level at or about the LOD
Eggs	0.01	Level at or about the LOD
Meat, Mammalian	0.2	
Edible offal, Mammalian	1	
Meat, fat	1	
Milks, fat	2	
Peanut	0.2	Level at or about the LOD
Peanut fodder	100	
Peanut forage	100	
Poultry meat	0.2	
Poultry, Edible offal of	1	
Pulses	0.3	
<b>Austria</b>		

Country/Commodity	MRL, mg/kg	Notes
Beet, Sugar	0.2	
Cereals	0.1	
Other plant commodities	0.05	
Pome fruit	1	
<b>Belgium</b>		
Cherry, sweet	0.3	
Cucumber	0.3	
Gherkin	0.3	
Other plant commodities	0	Below the LOD (0.05 mg/kg)
Pome fruit	0.3	
Strawberry	0.3	
Tomato	1	
<b>Brazil</b>		
Apple	1	
Bean	0.1	
Peanut	0.2	
<b>Denmark</b>		
Apple	2	
Cherry	2	
Pear	2	
<b>Finland</b>		
Apple	1	
<b>France</b>		
Apricot	1	
Beet, Sugar	0.05	T
Beet, Sugar, leaf	0.05	T
Peach	1	
Plum	1	
Pome fruit	1	
<b>Germany</b>		
Banana	0.5	
Bean, pods and/or immature seeds	0.5	
Cereals	0.1	
Cucumber	0.5	
Other plant commodities	0.05	
Pome fruit	2	
Stone fruit	2	
<b>India</b>		
Tea	5	
<b>Israel</b>		
Almond	1	
Apple	1	
Loquat	2	
Pear	1	
Plum	2	
<b>Italy</b>		
Almond	1	
Bean, without pod	0.5	
Beet, Sugar	0.5	
Cucumber	0.5	
Leek	0.5	
Pome fruit	1	
Stone fruit	1	
Wheat	0.02	
Zucchini	0.5	
<b>Japan</b>		
Apple	0.6	
Apricot	2	
Apricot, Japanese	2	
Banana	0.5	
Barley	0.05	
Bean, Adzuki	0.2	

Country/Commodity	MRL, mg/kg	Notes
Bean, Broad	0.2	
Bean, Kidney (pods and/or immature seeds)	0.3	
Beet, Sugar	0.5	
Buckwheat, Common	0.05	
Cherry	3	
Cucumber	0.5	
Loquat	0.6	
Maize/Corn	0.05	
Melon	1	
Other cereals	0.1	
Other pulses	0.2	
Pea, Garden	0.2	
Peach	1	
Peanut	0.1	
Pear	0.6	
Pear, Oriental	0.6	
Plum	1	
Quince	0.6	
Rye	0.1	
Soya	0.2	
Strawberry	1	
Wheat	0.1	
<b>Luxembourg</b>		
Cherry, Sour	0.3	
Cucumber	0.3	
Gherkin	0.3	
Other plant commodities	0.05	LOD
Pome fruit	0.3	
<b>Malaysia</b>		
Apple	1	
Banana	0.5	
Peanut	0.2	
Pear	1	
<b>Mexico</b>		
Bean	0.05	
Cotton	1	
<b>Netherlands</b>		
Blackberry	0.05	Level at or about the LOD
Cereals	0.05	Level at or about the LOD
Cherry	1	
Fruiting vegetables	1	
Other plant commodities	0	Below the LOD (0.05 mg/kg)
Pome fruit	0.1	
<b>New Zealand</b>		
Pome fruit	1	
<b>Poland</b>		
Banana	0.5	
Pome fruits	1	
Stone fruits	2	
Fruits except as otherwise listed	0.2	
Cereal grains	0.1	
<b>South Africa</b>		
Apple	1	
Apple	0.05	E
Apricot	0.5	
Apricot	0.05	E
Bean	0.1	
Nectarine	0.5	
Nectarine	0.05	E
Peach	0.5	
Peach	0.05	E
Peanut, shelled	0.05	



Country/Commodity	MRL, mg/kg	Notes
Pear	1	
Pear	0.05	E
Plum	0.5	
Plum	0.05	E
<b>South Korea</b>		
Apple	0.6	
Apricot	1	
Apricot, Japanese	2	
Banana	0.5	
Barley	0.05	
Bean, Adzuki	0.2	
Bean, Broad	0.2	
Bean, Kidney	0.2	
Bean, Mung	0.2	
Buckwheat, Common	0.1	
Cherry	2	
Cucumber	0.5	
Maize/Corn	0.05	
Millet, French	0.1	
Oats	0.1	
Other pulses	0.2	
Pea	0.2	
Peach	1	
Peanut	0.1	
Pear	0.6	
Plum	1	
Quince	0.6	
Rye	0.1	
Sorghum, grain	0.1	
Soya	0.2	
Strawberry	1	
Wheat	0.1	
<b>Spain</b>		
Beet, Sugar	0.05	
Berries and small fruit	0.05	
Cacao	0.05	
Cereals	0.05	
Citrus fruit	0.05	
Coffee	0.05	
Cola	0.05	
Forage crops and straw	0.05	
Fruit and vegetables, dried	0.05	
Hops	0.05	
Nuts	0.05	
Oil plants, seed	0.05	
Pome fruit	1	
Potato	0.05	
Pulses	0.05	
Spices	0.05	
Stone fruit	1	
Sugar cane	0.05	
Tea	0.05	
Tobacco	0.05	
Tropical. and subtropical fruits	0.05	
Vegetables	0.05	
<b>Switzerland</b>		
Cereals	0.05	
Pome fruit	0.6	
Stone fruit	0.6	
<b>Taiwan</b>		
Banana	1	
Peanut	0.1	

Country/Commodity	MRL, mg/kg	Notes
Pome fruit	0.5	
<b>UK</b>		
Apple	1	
Apricot	1	
Banana	0.5	
Nectarine	1	
Other pome fruit	1	
Peach	1	
Pear	1	
Plum	1	
Quince	1	
<b>Uruguay</b>		
Apple	2	
<b>USA</b>		
Banana, whole fruit	0.2	I
<b>Venezuela</b>		
Banana	0.1	
Bean	0.1	
Bean, Broad	0.1	
Cacao	0.1	
Peach	0.1	
Peanut	0.2	
Plantain	0.1	
Soya	0.1	
Strawberry	0.1	
Vegetables	0.1	

T: temporary tolerance

I: import tolerance

E: export tolerance

LOD: limit of determination

## APPRAISAL

Bitertanol, 1-(biphenyl-4-yloxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol (2 diastereoisomers), is an effective fungicide used as a foliar spray on fruits and vegetables and as a seed treatment for cereals for certain diseases. The compound was originally evaluated for residues in 1984 when TMRLs were recommended for a number of commodities. The fungicide was evaluated under the CCPR Periodic Review Programme in 1998 for toxicology and by the present Meeting for residues.

The Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP, supervised trials on crops, animal feeding studies and the effects of processing on residues.

### Metabolism and environmental fate

In animal metabolism studies, the compound was uniformly-labelled with <sup>14</sup>C in the phenyl ring remote from the oxygen. The absorption, distribution, metabolism and excretion of [<sup>14</sup>C]bitertanol has been studied in rats, cows and hens.

Bitertanol is rapidly absorbed from the intestinal lumen, and is readily distributed within the body. The excretion of the parent compound and its biotransformation products is fast (in rats almost complete within 72 h) and occurs mainly in the faeces (about 90%) by biliary excretion, owing to the lipophilic nature of the compound.

The main metabolic reactions are hydroxylation of the phenyl ring in the *para* position and oxidation of the *tert*-butyl moiety to form bitertanol alcohol and the corresponding carboxylic acid. There is no significant difference between the metabolism in rats, cows and poultry. Unchanged bitertanol and its *para*-hydroxylated metabolite in free and conjugated form were the main residues in the edible tissues and eggs of poultry (75-92% and 81-83% of the total  $^{14}\text{C}$  respectively), and in the edible tissues and milk of the dairy cow (23-51% and 84% of the total  $^{14}\text{C}$  respectively).

Plant metabolism studies were carried out with biphenyl- and triazole-labelled bitertanol on apples, peanuts, cotton (foliar spray treatment) and wheat (seed treatment).

Bitertanol was metabolised slowly in the investigated crop species after foliar spray application (half-lives 141 days in peanuts, 150 days in apples). Unchanged bitertanol was the main residue in apple fruits (83% of the biphenyl label, 96% of the triazole label), peanut shoots (86% of the total  $^{14}\text{C}$ ) and cotton plants (79% of the total  $^{14}\text{C}$ ). Oxidation of the hydroxyl group yields the keto analogue (BUE 1662) and oxidative cleavage of the biphenyl moiety yields bitertanol benzoic acid (BUE 2684). The compound is also conjugated at the free hydroxyl group to form a malonyl glucoside.

After seed treatment of wheat at a commercial application rate, the metabolites detected at harvest in the grain from the triazole label were derivatives of 1,2,4-triazole: triazolylalanine (50–66% of the total  $^{14}\text{C}$ , 0.12–0.16 mg/kg) and triazolylacetic acid (22–34% of the total  $^{14}\text{C}$ , 0.04–0.07 mg/kg). The parent compound was not detectable.

The degradation of bitertanol does not lead to environmentally significant levels of degradation products in soil or water.

The degradation of bitertanol in soil was comparable in all the studies. It was quickly degraded (half-life <1 to 9 days). At the end of the test period the degradation curve flattened, so the DT-90 value was 15 to 102 days depending on the soil type. The main degradation product was  $\text{CO}_2$  (50-64% of the applied  $^{14}\text{C}$ ). Owing to the rapid degradation only small amounts of intermediate products were detected. Bitertanol benzoic acid (BUE 2684) represented less than 0.3% of the applied  $^{14}\text{C}$ ; no other degradation products were identified. The unidentified compounds in the extracts represented  $\leq 4.2\%$  of the applied  $^{14}\text{C}$ . Unextractable residues, which were bound to the stable humin fraction, increased within the first 22 days up to 30-50% of the applied  $^{14}\text{C}$ , then decreased while mineralisation continued.

Aged bitertanol residues exhibit only a very low mobility in soil. In BBA standard soil 2.1 which showed the highest mobility the TRR in the leachate at 22°C and after 30 days of ageing was 0.5–1% of the applied radioactivity after 48 h rainfall, indicating that the leaching potential is negligible, which would be expected from the strong adsorption to the soil matrix. Photolysis on soil surfaces plays a minor role in the environmental destruction of the compound.

Bitertanol is stable to hydrolysis in aqueous solutions but it can easily be degraded by light owing to the chromophoric biphenyl moiety. However the photolytic effect might be of little significance under environmental conditions since only little light of the relevant wavelengths (<290 nm) penetrates water.

In water/sediment systems a high proportion of the applied radioactivity was transported into the sediment, reaching a maximum of 69-91% after 25 days. This decreased to 38-44% of the applied  $^{14}\text{C}$  at the end of the test period of 120 days. Only 2-3% of the applied  $^{14}\text{C}$  was identified as the parent compound in the surface water after 53 days. In the sediment extracts 24-59% of the applied  $^{14}\text{C}$  was identified as bitertanol at 53 days, decreasing to 3-4% at 120 days. The mineralization rate is high and intermediate products are found only in trace amounts.

Residues in rotational crops were determined in kale, mustard, sugar beet, and wheat planted in the soil 31, 118 and 364 days after treatment (DAT) of the target crop of peanuts with biphenyl-labelled bitertanol eight times at 0.56 kg ai/ha as a foliar spray. Total radioactive residues in harvested samples ranged from 0.1 mg/kg (118 DAT) to 0.02 mg/kg (364 DAT) in leafy vegetables (kale, mustard), from 0.38 mg/kg (118 DAT) to 0.01 mg/kg (364 DAT) in sugar beet roots, and from 0.23 (31 DAT) to 0.01 mg/kg (364 DAT) in wheat ears.

No information was reported on the fate of the 1,2,4-triazole moiety in succeeding crops.

### Methods of residue analysis

Residue analytical methods for bitertanol *per se* in plant and animal products are based on extraction with acetone/water, clean-up by liquid-liquid partition with dichloromethane, and purification of the organic phase by gel permeation chromatography. Bitertanol is determined by gas chromatography using a nitrogen-selective thermionic detector. This method has been modified in the clean-up procedures (e.g. by the use of Chem-Elut). Validation for plant and animal commodities showed recoveries of about 70-110%. The typical limits of determination in plant materials and animal products are 0.01- 0.05 mg/kg.

The analytical method provided by The Netherlands is based on a similar extraction. There is no clean-up for plant materials but animal products are cleaned up by gel permeation chromatography (GPC), HPLC or liquid-liquid partitioning (LLP). Determination is carried out by gas chromatography with an ion trap detector or nitrogen-phosphorus detector (NPD). The LOD was reported as 0.05 mg/kg for non-fatty and fatty foods and recoveries were generally between 90 and 100%.

A method was developed to quantify bitertanol and its metabolites ("total bitertanol") in bovine and poultry tissues, milk and eggs. Extraction was with various solvents (acetone, methanol, hexane), depending on the sample, and the extracts were acid-hydrolysed to release 1,2,4-triazole. The 1,2,4-triazole was derivatized to form triazolylpinacolone which was determined by gas chromatography using a thermionic nitrogen detector. Several clean-up steps were required including partitioning, ion exchange chromatography and high performance liquid chromatography. Recoveries were determined at 0.05 mg/kg and 0.1 mg/kg from all samples and additionally at 0.5 mg/kg and 2 mg/kg from bovine liver. The recoveries were between 60 and 120%.

For the enforcement determination of bitertanol in ground and drinking water a thin-layer separation with UV detection, based on automated multiple development (AMD), was developed. Recoveries were between 85 and 116%, and the LOD was 0.05 µg/l.

Information was submitted on the stability of bitertanol residues in various stored analytical samples. The Meeting concluded that the compound was stable for the duration of the studies (at least 3.5 years in apples, 2 years in cherries and peaches, 1 year in green and dry beans and 2 years in bovine tissues).

### Definition of the residue

On the evidence of studies with foliar spray treatments of apples, cotton and peanuts, the residue of concern was bitertanol *per se*.

After seed treatment of wheat at a commercial application rate, the metabolites detected at harvest in the grain from the triazole label were conjugates of 1,2,4-triazole: triazolylalanine (50–66% of the total <sup>14</sup>C) and triazolylacetic acid (22–34% of the total <sup>14</sup>C). Neither the parent nor free 1,2,4-triazole were detectable.

As 1,2,4-triazolylalanine can arise as a plant metabolite of several pesticides that contain a 1,2,4-triazole moiety, being formed by the conjugation of the latter with serine, it was evaluated by

the 1989 JMPR for toxicology and residues. A biotransformation study on rats showed that 1,2,4-triazolylalanine is rapidly absorbed and excreted, mainly as the unchanged compound in the urine. The 1989 Meeting concluded that residues of 1,2,4-triazolylalanine arising from the use of triazole fungicides do not present a toxicological hazard.

The animal metabolism studies on rats, a cow and laying hens indicate that the parent compound bitertanol and the metabolite *p*-hydroxybitertanol (free and conjugated) are the main residue components in animal tissues, milk and eggs.

As bitertanol has no acidic or basic properties in aqueous solution, the partition coefficient will not be influenced by the pH. The octanol-water partition coefficients ( $\log P_{OW} = 4.04$  diastereomer A, 4.15 diastereomer B) indicate that bitertanol is fat-soluble.

The Meeting concluded that the following residue definitions are appropriate.

For compliance with MRLs. For plant and animal products: bitertanol.

For estimations of dietary intake. For plant products: bitertanol. For animal products: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

### **Residues resulting from supervised trials**

Information was reported to the Meeting on registered uses of bitertanol and on supervised residue trials on apples, cherries, plums, nectarines, peaches, bananas, tomatoes, cucumbers, barley, oats, rye, wheat, cereal fodder and forage. Most trials were carried out in Europe. It was assumed that for the conduct of residue trials the European climatic conditions and weather influences could be divided into two regions.

Northern and central Europe: Sweden, Norway, Denmark, the UK, Ireland, northern and central France, Belgium, The Netherlands, Germany, Poland.

Southern Europe and the Mediterranean: Spain, Portugal, southern France, Italy, Greece.

Pome fruits. Trials on apples were reported from France, Germany, Italy, Spain and South Africa and on pears from Germany. French and Greek GAP for the use of bitertanol on pome fruit call for a spray concentration of 0.025 kg ai/hl with a PHI of 14 days for preventive and curative treatments. The labels recommend 2 applications with an interval of 1 week for curative treatments followed by preventive sprayings every 10-14 days. The labels also require an increase in concentration of the pesticide if the spray volume is reduced.

Twelve German trials on apples were carried out according to French and Greek GAP (8-12 x 0.025 kg ai/hl, PHI 14 days). These trials, which can also be used to represent the residue situation in Northern France, gave residues in rank order of 0.08, 0.09, 0.13, 0.13, 0.23, 0.25, 0.55, 0.62, 0.7, 0.86, 1.0 and 1.8 mg/kg.

In the 7 Southern European apple trials (1 in Spain according to Spanish GAP; 2 in Spain, 3 in Italy and 1 in France according to French GAP) the residues after 5 applications were 0.08, 0.09, 0.18, 0.23, 0.24, 0.34 and 0.36 mg/kg.

Current GAP for South Africa includes 1 or 2 treatments at 0.008 kg ai/hl with a PHI of 14 days, but the 9 apple trials reported were at higher rates (6-7 x 0.013–0.025 kg ai/hl). The residues were from 0.25 to 0.71 mg/kg.

In summary, the bitertanol residues in apples from trials according to French, Spanish and Italian GAP in rank order (median underlined) were 0.08, 0.08, 0.09, 0.09, 0.13, 0.13, 0.18, 0.23, 0.23, 0.24, 0.25, 0.34, 0.36, 0.55, 0.62, 0.7, 0.86, 1.0 and 1.8 mg/kg.

Twelve German trials on pears were carried out according to the German registered application rate (0.0125 kg ai/hl), but the number of treatments was 12 instead of the 5 specified on the label. The residues at the GAP PHI of 14 days in rank order were 0.22, 0.23, 0.25, 0.33, 0.63, 0.65, 0.91, 0.92, 0.92, 0.93, 0.97 and 1.1 mg/kg. The Meeting noted that higher residues could occur in pears than in apples from the same application rate.

The Meeting agreed to recommend maintaining the CXL of 2 mg/kg for pome fruits. An STMR of 0.24 mg/kg was estimated for pome fruits on the basis of the residues found in apples.

### Stone fruits

The residues from trials carried out before 1996 were mainly reported for fruit without stones, but from trials in 1996 as fruit including stones. The Meeting was informed that the stone represents about 10% of the whole fruit weight and agreed to combine the data on fruit with and without stones.

Cherries. Residue trials were conducted in Germany and France. The trials in Germany were evaluated against German GAP (3 x 0.038 kg ai/hl, PHI 21 days), and the trials in southern France against Greek GAP (0.025-0.038 kg ai/hl, PHI 10 days). The samples from the southern French trials were analysed including the stones, but the residues from Germany were reported for fruit without stones, although the residue in the whole fruit was calculated in 2 trials, where the fruit pulp represented 82–92% (mean 87.6%) of the whole fruit weight.

Of the 14 German trials on sour cherries, 6 trials with 3–4 treatments after flowering with 0.038 kg ai/hl ( $\pm$  34%) and a PHI of 21 days complied with GAP. The remaining 8 trials were with 5 treatments after flowering or no sample was taken at the recommended PHI. The results showed residues in fruits without stones of 0.19, 0.36, 0.52, 0.68, 0.83 and 0.85 mg/kg.

In 6 French trials sweet cherries were treated twice at 0.03 kg ai/hl. Four of the trials were carried out in southern France and evaluated against Greek GAP. The residues in fruit with stones were 0.08, 0.15, 0.17 and 0.37 mg/kg. The 2 other trials in northern France could not be evaluated against Greek GAP and did not comply with German GAP.

The bitertanol residues in all the evaluated German and French trials in rank order (median underlined) in fruit **without**/with stone were 0.08, 0.15, 0.17, **0.19**/0.17, 0.36/0.32, 0.37, **0.52**, **0.68**, **0.83** and **0.85** mg/kg. The Meeting estimated an STMR of 0.365 mg/kg and a maximum residue level for bitertanol in cherries of 1 mg/kg to replace the CXL (2 mg/kg).

Plums. Residue trials were carried out in Germany (12), southern France (4) and Portugal (1).

In the German trials, the residues were reported for fruit without stones, but with calculation of the residue in the whole fruit in 4 trials. In the samples at the GAP PHI, the fruit pulp represented 93–95% (mean 94%) of the whole fruit weight. The results of the French trials were also reported for fruit without stones but with calculation of fruit including stone in one trial.

The German trials were evaluated against French GAP (0.02–0.03 kg ai/hl, PHI 14 days, number of preventive, curative and eradicated treatments not specified). Based on a water rate of 1000 and 1500 l/ha, the spray concentration was 0.025 and 0.38 kg ai/hl. The number of treatments after flowering was 3 in 6 trials, 4 in 1 trial and 5 in 5 trials. The residues in rank order in fruit **without**/with stone were **0.04**, **0.15**, **0.16**, **0.19**, **0.21**, **0.33**, **0.58**/0.55, **0.59**, **0.89**/0.85, **0.94**, **1.4**/1.3 and **1.8**/1.7 mg/kg.

Portuguese GAP (2 x 0.02 kg ai/hl, PHI 7 days) was used to evaluate 4 trials in southern France. Fruits **without**/with stones showed residues of **0.09**, **0.34**, **0.36** and **0.49**/0.45 mg/kg.

All results evaluated gave residues in rank order of **0.04, 0.09, 0.15, 0.16, 0.19, 0.21, 0.33, 0.34, 0.36, 0.49/0.45, 0.58/0.55, 0.59, 0.89/0.85, 0.94, 1.4/1.3** and **1.8/1.7** mg/kg.

On the basis of the German and French residue data the Meeting estimated an STMR of 0.35 mg/kg and agreed to recommend maintaining the CXL of 2 mg/kg.

Peaches and nectarines. GAP is the same for nectarines and peaches in southern Europe and South Africa.

Residue trials on nectarines were carried out in Italy (3), southern France (2) and South Africa (3). The Italian and southern French trials with 1-2 x 0.018-0.019 kg ai/hl, PHI 7 days, complied with Portuguese GAP (1-2 x 0.017-0.02 kg ai/hl, PHI 7 days). The residues in fruits without stones were 0.12, 0.13, 0.20, 0.23 and 0.25 mg/kg.

Two of the 3 South African trials on nectarines could not be evaluated because the application rate was twice the rate prescribed by GAP or samples were not taken at the PHI of 35 days. In the third trial conducted according to GAP, the residue in the fruit without stone was 0.1 mg/kg at day 35, but 0.17 mg/kg at day 49.

On peaches, 6 trials were conducted in Spain, 1 in Portugal and 6 in South Africa. The Portuguese and Spanish trials with 3 x 0.03-0.038 kg ai/hl were according to Spanish GAP (1-3 x 0.025-0.038 kg ai/hl, PHI 15 days) and most of them also complied with Greek GAP (0.025-0.038 kg ai/hl, PHI 10 days). The residues in fruit **without/with** stones were **0.05, 0.10, 0.26/0.24, 0.27/0.26, 0.43/0.41, 0.54/0.49, and 0.74/0.71** mg/kg.

Four of the 6 South African trials on peaches could not be evaluated because the application rate was twice the rate prescribed by GAP or samples were not taken at the PHI of 35 days. In both the 2 trials according to GAP, the residues were 0.12 mg/kg at day 35 in fruit without stones.

Because GAP for nectarines and peaches is the same, a maximum residue level and STMR were estimated from the combined data. All the residues in nectarines and peaches **without/with** stone in rank order were **0.05, 0.10, 0.12, 0.12, 0.12, 0.13, 0.17, 0.20, 0.23, 0.25, 0.26/0.24, 0.27/0.26, 0.43/0.41, 0.54/0.49** and **0.74/0.71** mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg (the same as the CXL) and an STMR of 0.20 mg/kg for peaches and nectarines.

Apricots. As no residue data were provided, the Meeting agreed to propose the withdrawal of the CXL of 1 mg/kg.

Bananas. Bitertanol is registered in Belize, Costa Rica, the Dominican Republic, Guatemala, Nicaragua and Panama with application at 0.15 kg ai/ha and 0.5-1.4 kg ai/hl. Further uses are in Honduras (0.15 kg ai/ha, 0.02-0.2 kg ai/hl), Cameroon (0.15 kg ai/ha, 1.5-3 kg ai/hl), Philippines (0.15-0.2 kg ai/ha, 0.5-0.65 kg ai/hl) and Taiwan (0.12 kg ai/ha, 0.4 kg ai/hl). The PHI is either 0 days or not specified. Residue trials were carried out in Costa Rica, Honduras, the Philippines, Taiwan and Cameroon.

Five trials in Costa Rica at 10–16 x 0.12-0.24 kg ai/ha, 0.2-0.25 kg ai/hl could not be evaluated because the interval between the final application and harvest was 4 and 8 days whereas GAP permits a 0-day PHI. The residues in 2 further trials with treatments of 9 x 0.44 kg ai/hl, PHI 3 days (88% of the lowest recommended concentration rate) in the whole fruit/pulp were 0.24/0.11 mg/kg unbagged and 0.03/0.02 mg/kg bagged.

Five trials in Honduras with 12 x 0.69–1.3 kg ai/hl were evaluated as they complied with the GAP of the other Central American countries. On day 0, the residues in the whole fruit/pulp were

0.1/0.04, 0.32/0.13 and 0.06/0.03 mg/kg in unbagged bananas, and 0.02/0.02, 0.03/<0.01 and 0.03/0.02 mg/kg in bagged. Four further trials in Honduras (12 x 0.06 kg ai/hl, PHI 0 days) were according to Honduras GAP (0.02-0.2 kg ai/hl). The residues in the whole fruit/pulp in unbagged bananas were 0.06/0.03 and 0.36/0.17 mg/kg and in bagged bananas 0.06/0.01 and 0.04/0.02 mg/kg.

Four trials were carried out in the Philippines: 2 were at exaggerated rates (10 x 1.25 kg ai/hl) and the others (26 x 0.69–0.87 kg ai/hl) approximated GAP. As the residues were determined in bagged bananas, they were <0.05 mg/kg in fruit, pulp and peel.

The 2 trials in Taiwan (12 x 0.094 kg ai/hl) could not be evaluated because they did not comply with GAP.

The 2 trials in Cameroon could not be evaluated because the intervals between the final applications and harvest were 6 and 12 days whereas Cameroon GAP does not specify a PHI, implying that 0 days is permitted.

In summary, the residues in unbagged whole bananas in trials in accordance with GAP were Costa Rica 0.24 mg/kg, Honduras 0.06, 0.06, 0.1, 0.32 and 0.36 mg/kg. The respective values for bagged bananas were Costa Rica 0.03 mg/kg, Honduras 0.02, 0.03, 0.03, 0.04, 0.06 mg/kg, and the Philippines <0.05 mg/kg (2). An STMR was estimated from the residues in the pulp of unbagged bananas: 0.03, 0.03, 0.04, 0.11, 0.13 and 0.17 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg, the same as the current CXL, and an STMR of 0.075 mg/kg.

Tomatoes. Ten trials were carried out in The Netherlands according to GAP with 3 x 0.03 kg ai/hl in a greenhouse. At the GAP PHI of 3 days the residues in normal sized tomatoes ranged from 0.39 to 0.98 mg/kg. In cherry tomatoes, the residues were twice as high: 2.1 and 2.4 mg/kg. All the residues in normal and cherry tomatoes in rank order were 0.39, 0.41, 0.48, 0.54, 0.56, 0.96, 0.96, 0.98, 2.1 and 2.4 mg/kg.

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.76 mg/kg for tomatoes.

Cucumbers. Greenhouse trials were carried out in southern France (2) and The Netherlands (8).

The French trials (3 x 0.02 kg ai/hl, PHI 17 days) were not according to GAP.

The residues in the 8 trials carried out in The Netherlands according to GAP (3 x 0.03 kg ai/hl) in rank order were 0.1, 0.11, 0.16, 0.17, 0.19, 0.21, 0.22 and 0.22 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg (the same as the existing CXL) and an STMR of 0.18 mg/kg for cucumbers.

Common beans, bean forage, peanuts, peanut forage. As no data on GAP or residue trials were provided, the Meeting agreed to recommend the withdrawal of the CXLs of 0.5 mg/kg for common bean, 10 mg/kg for bean forage, 0.1\* mg/kg for peanut and 20 mg/kg for peanut forage (green).

#### Seed treatments

Barley. The highest application rates are in Sweden (0.07 kg ai/100 kg seed) and The Netherlands (0.056 kg ai/100 kg seed). Eight supervised trials were conducted in Germany, 6 with 0.07-0.075 kg ai/100 kg seed according to Swedish GAP and 2 with 0.057 kg ai/100 kg seed according to GAP in The Netherlands. The residues were below the LOD of 0.05 mg/kg in grain harvested 100 to 144 days after treatment in all the samples.



Oats. The highest application rates are in Sweden (the same as barley) and Austria (0.038-0.075 kg ai/100 kg seed). In Germany, The Netherlands and the UK the rate is 0.056 kg ai/100 kg seed. Seven supervised trials were conducted in Germany, 3 at 0.075 kg ai/100 kg seed according to Swedish GAP and 4 at 0.055-0.057 kg ai/100 kg seed according to GAP in Germany, The Netherlands and the UK. The residues were below the LOD of 0.05 mg/kg in all samples harvested 113 to 147 days after treatment.

Rye. The highest application rates are in Austria (0.038-0.075 kg ai/100 kg seed), Germany, The Netherlands, Sweden and the UK (all 0.056 kg ai/100 kg seed). In nine trials in Germany, 8 were with 0.056 kg ai/100 kg seed and 1 with 0.07 kg ai/100 kg seed. The residues were below the LOD of 0.05 mg/kg in all grain samples harvested 289 to 322 days after treatment.

Wheat. The highest application rates are in Germany (0.075 kg ai/100 kg seed), Poland (0.07 kg ai/100 kg), Sweden (0.056-0.07 kg ai/100 kg), The Netherlands (0.056 kg ai/100 kg) and the UK (0.038-0.056 kg ai/100 kg). In Germany 11 supervised trials were carried out on spring wheat and 2 on winter wheat at 0.07-0.076 kg ai/100 kg. The residues were below the LOD of 0.05 mg/kg in all the grain samples.

Triticale. Uses are registered in Denmark, Poland and the UK and are identical with those for wheat and/or rye in those countries. The Meeting agreed to extrapolate the results from wheat and rye to triticale.

The Meeting estimated a maximum residue level of 0.05\* mg/kg for bitertanol in barley, oats, rye, triticale and wheat as being a practical limit of determination, and recommended the withdrawal of the existing CXLs for oats, rye and wheat (0.1\* mg/kg). As the residues were below the LOD in all samples, and this was consistent with the results of a metabolism study with [<sup>14</sup>C]bitertanol where no parent compound was detected in the grain at harvest, an STMR of 0 mg/kg was estimated.

Straw and fodder of cereal grains. Supervised trials according to GAP in several European (0.056-0.075 kg ai/100 kg seed) were carried out on barley (8), oats (7), rye (9) and wheat (13). The residues in all straw and forage samples were below the LOD of 0.05 mg/kg.

The Meeting agreed to recommend the withdrawal of the current CXLs for straw and fodder (dry) of oats, rye and wheat of 0.1\* mg/kg. A maximum residue level of 0.05\* mg/kg was estimated for the straw and fodder (dry) of barley, oats, rye, triticale and wheat as a practical limit of determination. As no detectable residue is to be expected in cereal straw after seed treatment, an STMR of 0 was estimated.

Oat and rye forage. Cereals such as oats and rye are grown to a limited extent as forage crops. The immature crop is fed to livestock animals as succulent forage or as silage.

Seven supervised trials on oats and 9 on rye with seed treatments of 0.055-0.075kg ai/100 kg seed were reported. Green oats and rye were harvested at 63-101 and 218-254 days after application respectively. The residues were not detected in any of the green plants.

The Meeting recommended replacement of the current CXLs for oat and rye forage (green) of 0.1\* mg/kg by 0.05\* mg/kg (dry weight basis) as a practical limit of determination. According to the results of the metabolism study, the possibility of residues of bitertanol in cereal forage after seed treatment cannot be excluded, and an STMR of 0.05 mg/kg was estimated.

### Animal feeding studies

Groups of 3 cows were dosed by capsule for 28 days with bitertanol at levels corresponding to 25, 75 and 250 ppm in the feed or 0.63, 1.88 and 6.25 mg/kg bw per day. Milk samples were collected from all cows on days 0, 7, 14, 21 and 28. At the end of the test period, the animals were slaughtered and their tissues and milk analysed for total extractable bitertanol and metabolite residues. The results are summarized in the following table.

Dose mg/kg bw/day	Total bitertanol residues, mg/kg									
	Milk high	mean	Liver high	mean	Kidney high	mean	Muscle high	mean	Fat high	mean
0.63	0.01	<0.01	0.78	0.63	0.05	0.037	0.06	0.03	0.06	0.027
1.88	0.07	0.04	1.9	1.4	0.36	0.32	0.09	0.08	0.18	0.17
6.25	0.26	0.24	3.7	2.8	1.1	0.77	0.44	0.32	1.3	0.85

In a metabolism study on a dairy cow dosed for 5 days with 0.2 mg/kg bw/day the milk contained only 0.008 mg/kg bitertanol equivalents (0.2% of the applied <sup>14</sup>C) but the residues had not reached a plateau. In the tissues the total <sup>14</sup>C residues were liver 0.82, kidney 0.11, muscle 0.01 and fat 0.03 mg/kg bitertanol equivalents.

As the residue of bitertanol in the milk reached a plateau slowly (3-4 weeks after treatment at the earliest), the STMRs of the feed items should be used to estimate the dietary burden. The highest exposure to bitertanol residues may arise from the consumption of wet apple pomace with an STMR level of 0.648 mg/kg. With the theoretical assumption that the daily maximum feed consumption of beef cattle (body weight 550 kg) would be 20 kg on a dry matter basis, including 40% of wet pomace (containing 40% dry matter), the intake may be calculated as follows.

0.648 mg/kg wet weight is equivalent to 1.62 mg/kg on a dry matter basis.

As apple pomace forms 40% of the diet it will contribute  $1.62 \times 0.4 = 0.648$  ppm in the total feed on a dry matter basis.

On this basis beef cattle may be exposed to 0.0236 mg bitertanol/kg bw/day.

The lowest dose rate in the feeding study represents approximately 27 times the estimated dietary burden (0.63/0.0236). The Meeting noted the high ratio and concluded that an extrapolation downwards to the real intake would result in residues below the 0.05 mg/kg reported as a practical limit of determination in the official method of analysis of The Netherlands.

The Meeting estimated 0.05\* mg/kg as a maximum residue level for milk, edible offal and meat (fat) and 0.05 mg/kg as an STMR for milk, edible offal and meat. As the metabolism is similar in rats and cows, these levels are estimated for cattle, goats, sheep and pigs.

A metabolism study in hens showed that approximately 98% of the dose was recovered in the excreta. Eggs contained <0.2% of the total dose.

Laying hens (10 birds/group) were fed daily rations containing bitertanol at total residue levels of 1, 3 and 100 ppm for 28 days. Additional hens were fed the 100 ppm diet for 28 days and then maintained on untreated rations for an additional 14 days (five birds) or 28 days (three birds) before slaughter to determine the rate of decline of residues in the tissues and eggs. The tissues and eggs were analysed for total extractable bitertanol and metabolite residues.

Tissues from the 3 ppm and 100 ppm treatment groups were pooled in each group and analysed. Eggs from those groups were analysed at 7, 14, 21 and 28 days. The residues found in the 100 ppm group were liver 1.03 mg/kg, gizzard 0.23 mg/kg, heart 0.10 mg/kg, muscle 0.07 mg/kg and fat 0.07 mg/kg. Liver, gizzard and muscle samples from the 3 ppm group contained quantifiable residues, the liver having the highest level (0.21 mg/kg), followed by gizzard (0.07 mg/kg) and muscle (0.01 mg/kg). The residues in the livers at the lowest feeding level (1 ppm) were below 0.01 mg/kg, and other tissues were not

analysed as the residues from the higher dose rates were so low. The residues in eggs were only quantifiable in the 100 ppm feeding group; day 28 eggs from that group contained 0.11 mg/kg bitertanol. All tissue and egg residue levels in the residue decline group were below 0.01 mg/kg 28 days after the birds had been returned to untreated feed except in the liver, which contained 0.04 mg/kg).

The exposure to bitertanol residues would arise from cereal grains, with a maximum residue level of 0.05\* mg/kg (STMR 0 mg/kg).

With the theoretical assumption that the daily maximum feed consumption of a chicken (bw 1.9 kg) is 0.12 kg dry matter consisting of 100% cereal grains (e.g. wheat or oats with 89% dry matter) the intake may be calculated as follows.

A maximum residue of 0.05 mg/kg wet weight is equivalent to 0.056 mg/kg on a dry weight basis.

As cereal grain forms 100% of the diet, the bitertanol residue in the total feed (dry matter basis) is equivalent to 0.056 ppm, and hence to an intake of 0.0035 mg/kg bw/day.

In view of the results of the metabolism and feeding studies, no residues are to be expected in edible tissues or eggs. The Meeting estimated an STMR of 0 and a maximum residue level of 0.01\* mg/kg for eggs, poultry meat, and edible offal of poultry as a practical limit of determination.

### Processing

Studies have been carried out to determine the effect of processing on residues of bitertanol in apples, cherries, peaches, plums and tomatoes.

Apples containing 0.08, 0.23, 0.55 and 1 mg/kg bitertanol were processed to juice and sauce, which did not contain residues above the LOD of 0.02 mg/kg.

In 2 further trials, the residues in raw apples were 0.49 and 8.2 mg/kg, in juice 0.09 and 0.84 mg/kg and in wet pomace 1.37 and 21 mg/kg. The wet pomace in the second trial (8.2 mg/kg in unprocessed apples) was processed to dry pomace, which contained a residue of 61 mg/kg (processing factor 7.4).

The Meeting agreed to calculate the STMR levels on the basis of the trials which included the determination of bitertanol in the pomace, which is a potential feeding-stuff. From the STMR of 0.24 mg/kg for apples and mean processing factors of 0.14 for juice and 2.7 for wet pomace as well as the factor of 7.4 for dry pomace, the Meeting estimated STMRs of 0.0336 mg/kg for apple juice and sauce, 0.648 for wet apple pomace and 1.78 mg/kg for dry apple pomace.

The processing data on stone fruit indicate that residues of bitertanol do not concentrate in any processed commodity which may be used as food. Three trials were carried out on cherries and 2 each on peaches and plums. The peach trials could not be evaluated as the residues in washed and unwashed fruit were inconsistent and it was not clear which fruit was further processed.

Cherries were processed into juice, preserve and jam, and plums into sauce and jam. The procedures for jam production were nearly identical for cherries and plums. The processing factors for cherry juice were 0.028, 0.115 and 0.375 (mean 0.17), for cherry jam 0.36 and 0.54 (mean 0.45), for cherry preserve 0.5, 0.58 and 0.68 (mean 0.59), and for plum jam 0.57 and 0.64 (mean 0.605).

On the basis of the mean processing factors and the STMRs of 0.365 mg/kg for cherries and 0.34 mg/kg for plums, the Meeting estimated the following STMRs. Cherries: 0.062 mg/kg juice, 0.16 mg/kg jam, 0.22 mg/kg preserve. Plum jam 0.21 mg/kg.

One processing study on tomatoes was reported. The residues of bitertanol were lower in juice and preserves (processing factors 0.135 and 0.365), but higher in paste (processing factor 2.1). The Meeting estimated STMRs of 0.1, 0.28 and 1.6 mg/kg for tomato juice, preserve and paste respectively, based on the STMR for tomato of 0.76 mg/kg.

## RECOMMENDATIONS

The Meeting estimated the maximum residue and STMR levels shown below. The maximum residue levels are recommended for use as MRLs.

### Definition of the residue

For compliance with MRLs for plant and animal commodities: bitertanol.

For dietary intake for plant commodities: bitertanol.

For dietary intake for animal commodities: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

The compound is fat-soluble.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
JF 0226	Apple juice			0.034
AB 0226	Apple pomace, dry			1.78
	Apple pomace, wet			0.648
	Apple sauce			0.035
FS 0240	Apricot	W	1	
FI 0327	Banana	0.5	0.5	0.075
GC 0640	Barley	0.05*	-	0
AS 0640	Barley straw and fodder, d`ry	0.05*	-	0
AL1030	Bean forage (green)	W	10	
FS 0013	Cherries	1	2	0.365
	Cherry jam			0.16
	Cherry juice			0.062
	Cherry preserve			0.22
VP 0526	Common bean (pods and/or immature seeds)	W	0.5	
VC 0424	Cucumber	0.5	0.5	0.18
MO 0105	Edible offal (Mammalian)	0.05*		0.05
PE 0112	Eggs	0.01*		0
MM 0095	Meat (from mammals other than marine mammals)	0.05* (fat)		0.05
ML 0106	Milks	0.05*		0.05
FS 0245	Nectarine	1	1	0.20
AF 0647	Oat forage (green)	0.05* (dry wt.)	0.1*	0.05
AS 0647	Oat straw and fodder, dry	0.05*	0.1*	0
GC 0647	Oats	0.05*	0.1*	0
FS 0247	Peach	1	1	0.20
SO 0697	Peanut	W	0.1*	
AL 1270	Peanut forage (green)	W	20	
FS 0014	Plums (including Prunes)	2	2	0.34
	Plum jam			0.21
FP 0009	Pome fruits	2	2	0.24
PM 0110	Poultry meat	0.01*		0
PO 0111	Poultry, Edible offal of	0.01*		0
GC 0650	Rye	0.05*	0.1*	0
AF 0650	Rye forage (green)	0.05* (dry wt.)	0.1*	0.05
AS 0650	Rye straw and fodder, dry	0.05*	0.1*	0

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
VO 0448	Tomato	3	-	0.76
JF 0448	Tomato juice			0.1
	Tomato paste			1.6
	Tomato preserve			0.28
GC 0653	Triticale	0.05*	-	0
	Triticale straw and fodder, dry	0.05*	-	0
GC 0654	Wheat	0.05*	0.1*	0
AS 0654	Wheat straw and fodder, dry	0.05*	0.1*	0

W: withdrawal recommended

## DIETARY RISK ASSESMENT

### Chronic intake

International Estimated Daily Intakes (IEDIs) of bitertanol were estimated from the STMRs of 23 commodities.

International Estimated Daily Intakes for the five GEMS/Food regional diets, based on estimated STMRs, were in the range of 2% to 10% of the ADI. The Meeting concluded that the intake of residues of bitertanol resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

### Acute intake

The 1998 JMPR concluded that it was unnecessary to establish an acute RfD because bitertanol has been classified by WHO as unlikely to present an acute hazard in normal use and has not shown any specific adverse effects (teratogenicity, neurotoxicity) after single doses 100 times the lowest relevant NOAEL in long- and short-term studies that were used to establish the ADI. The Meeting therefore concluded that the short-term dietary intake of bitertanol residues is unlikely to present a risk to consumers.

## REFERENCES

Allmendinger, H. 1998. Modification of method 00462 for the determination of residues of tebuconazole and triadimenol in wheat, barley, oat (grain, green material, straw) and tobacco (green and dry leaves) and for the determination of bitertanol and fuberidazole in wheat (grain, green material, straw) by LC/MS/MS. Unpublished report no. MR-935/97, amendment M002 to method no. 00462, Bayer AG.

Bachmann, J. 1994a,b. See Brennecke, R. 1988a.

Bachmann, J., 1995. Determination of residues of Baycor 25 WP in/on peach under actual use conditions in Spain. Unpublished report no. RA-2011/93 (incl. 303305 = 30330-93, 303380 = 0338-93).

Bayer AG. 1978a. Residue trials with Baycor 25 WP in apples in Germany. Unpublished report no. 10300-78, 10301-78, 10303-78.

Bayer AG. 1978b. Residue trial with Baycor 200 EC in bananas in Costa Riabout Unpublished report no. 10309/78.

Bayer AG. 1979. Residue trial with Baycor 25 WP in apples in Germany. Unpublished report no. 10305-79.

Bayer AG. 1980a. Residue trial with Baycor 25 WP in apples in Germany. Unpublished report no. 10313-80.

Bayer AG. 1980b. Residue trial with Baycor 25 WP in plums in France. Unpublished report no. 10301-80.

Bayer AG. 1980c. Residue trials with Baycor 25 WP in cucumbers under plastic or in the greenhouse in France. Unpublished report no. 10304-80, 10305-80.

Bayer AG. 1980d. Residue trials with Sibutol 39.8 DS in summer wheat in Germany. Unpublished report no. 10341-80, 10342-80, 10343-80.

- Bayer AG. 1980e. Residue trials with Baycor 200 EC in bananas in the Philippines. Unpublished report no. 10320-80, 10321-80.
- Bayer AG. 1980f. Residue trials with Baycor 300 EC in bananas in Costa Riabout Unpublished report no. 10330-80 (incl. 10330-80-A, 10330-80-B).
- Bayer AG. 1980g. Residue trials with Baycor 300 EC in bananas in Costa Riabout Unpublished report no. 10350-80 (incl. 10350-80-A, 10350-80-B).
- Bayer AG. 1981a. Residue trials with Baycor 300 EC in plums in Germany. Unpublished report no. 10328-81, 10329-81, 10330-81, 10356-81.
- Bayer AG. 1981b. Residue trials with Baycor 300 EC in bananas in the Philippines. Unpublished report no. 10344-81, 10345-81.
- Bayer AG. 1981c. Residue trials with Baycor 300 EC in bananas in Taiwan. Unpublished report no. 10350-81 (incl. 10350-81-A, 10350-81-B).
- Bayer AG. 1981d. Residue trials with Baycor 250 OF in bananas in Cameroon. Unpublished report no. 10366-81 (incl. 10366-81A, 10366-81-B).
- Bayer AG. 1982a. Residue trials with Baycor 25 WP in cherries in Germany. Unpublished report no. 10300-82, 10301-82, 10302-82, 10303-82.
- Bayer AG. 1982b. Residue trials with Sibutol 39.8 DS in oats in Germany. Unpublished report no. 10366-82, 10367-82, 10368-82.
- Bayer AG. 1982c. Residue trials with Sibutol 398 FS in summer wheat in Germany. Unpublished report no. 10370-82, 10371-82.
- Bayer AG. 1982d. Residue trials with Sibutol 39.8 DS in winter rye in Germany. Unpublished report no. 10363-82, 10364-82, 10365-82.
- Bayer AG. 1982e. Residue trial with Sibutol 398 FS in winter rye in Germany. Unpublished report no. 10372-82.
- Bayer AG. 1983a. Residue trials with Sibutol 39.8 DS in summer barley in Germany. Unpublished report no. 10200-83, 10201-83, 10202-83.
- Bayer AG. 1983b. Residue trials with Sibutol 398 FS in oats in Germany. Unpublished report no. 10212-83, 10213-83.
- Bayer AG. 1983c. Residue trials with Sibutol 375 FS in oats in Germany. Unpublished report no. 10241-83, 10242-83.
- Bayer AG. 1983d. Residue trials with Sibutol 398 FS in winter rye in Germany. Unpublished report no. 10210-83, 10211-83.
- Bayer AG. 1983e. Residue trial with Sibutol 375 FS in winter rye in Germany. Unpublished report no. 10240.
- Bayer AG. 1983f. Residue trials with Sibutol 375 FS in summer wheat in Germany. Unpublished report no. 10243-83, 10244-83.
- Bayer AG. 1983g. Residue trials with Sibutol 375 FS in summer barley in Germany. Unpublished report no. 10245-83, 10246-83.
- Bayer AG. 1983h. Residue trial with Baycor 25 WP in apples in Germany. Unpublished report no. 10304-83.
- Bayer AG. 1984a. Residue trials with Baycor 25 WP in apples in Germany. Unpublished report no. 10300-84, 10301-84, 10302-84, 10303-84, 10304-84, 10305-84.
- Bayer AG. 1984b. Residue trials with Sibutol 298 LS in summer barley in Germany. Unpublished report no. 10202-84, 10203-84, 10204-84.
- Bayer AG. 1984c. Residue trials with Sibutol 398 FS in summer wheat in Germany. Unpublished report no. 10210-84, 10211-84.
- Bayer AG. 1985a. Residue trials with Baycor 25 WP in nectarines in Italy. Unpublished report no. 10360-85, 10361-85, 10362-85.
- Bayer AG. 1985b. Residue trials with Baycor 25 WP in nectarines in France. Unpublished report no. 10363-85, 10365-85.
- Bayer AG. 1985c. Residue trials with Sibutol 298 LS in winter rye in Germany. Unpublished report no. 10200-85, 10202-85.
- Bayer AG. 1985d. Residue trials with Sibutol 398 LS in winter wheat in Germany. Unpublished report no. 10201-85, 10203-85.
- Bayer AG. 1986. Residue trials with Baycor 500 SC in cherries in Germany. Unpublished report no. 10312-86, 10313-86, 10315-86.
- Bayer AG. 1987. Residue trials with Baycor 500 SC in cherries in Germany. Unpublished report no. 10311-87, 10313-87, 10314-87.
- Bayer AG. 1988a. Residue trials with Baycor 500 SC in plums in Germany. Unpublished report no. 0230-88, 0232-88, 0233-88, 0234-88.
- Bayer AG. 1988b. Residue trials with Baycor 300 EC in cucumbers in the greenhouse in the Netherlands. Unpublished report no. 0561-88, 0562-88.
- Bayer AG. 1988c. Residue trials with Baycor 300 EC in tomatoes in the greenhouse in the Netherlands. Unpublished report no. 0304-88, 0305-88, 0306-88.
- Bayer AG. 1989a. Residue trials with Baycor 500 SC in cherries in Germany. Unpublished report no. 0206-89, 0207-89, 0209-89, 0210-89.
- Bayer AG. 1989b. Residue trials with Baycor 500 SC in plums in Germany. Unpublished report no. 0220-89, 0221-89, 0222-89, 0384-89.

- Bayer AG. 1998. Specification AR 04 904 206, version 02 of May 19, 1998. Unpublished.
- Becker, R.D. 1980. See Thornton, J.S. 1977.
- Brennecke, R. 1981a,b. See Specht and Tillkes. 1980b.
- Brennecke, R. 1982a. Decomposition and metabolism of [biphenyl-UL-<sup>14</sup>C]bitertanol (BAYCOR) in soil. Unpublished report no. RA 1272/82, Bayer AG.
- Brennecke, R. 1982b-e. See Specht and Tillkes. 1980b.
- Brennecke, R. 1983a. Leaching characteristics of aged [biphenyl-UL-<sup>14</sup>C]bitertanol soil residues. Unpublished report no. RA 981/83, Bayer AG.
- Brennecke, R. 1983b-d. See Specht and Tillkes. 1980b.
- Brennecke, R. 1985. Method for gas-chromatographic determination of residues of the fungicide Baycor in plant material, soil and water. Pflanzenschutz-Nachrichten Bayer **38**, pages 33-54, Method no.: 000031, formerly F 223.
- a) supplemented: Möllhoff, 1986, March 10, 1986 E003  
b) supplemented: Brennecke, R. 1995, August 14, 1995 E006
- Brennecke, R. 1986. Accountability study on [<sup>14</sup>C]Bitertanol after application to spring wheat seed: Plant uptake and distribution and metabolism in plant and soil. Unpublished report no. RA 75/86, Bayer AG.
- Brennecke, R. 1987. Bitertanol, DFG analytical method 613. Bayer method no.: 00053, formerly F 285. Deutsche Forschungsgesellschaft, VCH Verlagsgesellschaft, 9th edition, 1987.
- Brennecke, R. 1988a. A method for the determination of residues of the fungicide Baycor in plant material and beverages by high-pressure liquid chromatography with fluorescence detection. Pflanzenschutz-Nachrichten Bayer, **41** pages 113-136, Method no.00003, formerly F 281.
- a) modified: Brennecke, R. 1988b, RA-1280, December 21, 1988 M002  
b) modified: Bachmann, J. 1994a, RA-435/93, January 13, 1994 M004  
c) modified: Bachmann, J. 1994b, January 17, 1994 M006  
e) supplemented: Nüßlein, F. 1995, MR-421/95, June 1, 1995 M006/E003  
f) supplemented: Köhler, J. 1989, October 18, 1989 E001  
g) supplemented: Krebber, R. 1991, November 25, 1991 E002
- Brennecke, R. 1988b. See Brennecke, R. 1988a.
- Brennecke, R. 1995. See Brennecke, R. 1985.
- Brennecke, R. and Vogeler, K. 1987. Fungicides, Water. DFG analytical multiresidue method W 5, Bayer method no.: 00054, formerly F 286. Deutsche Forschungsgesellschaft, VCH Verlagsgesellschaft, 9th edition, 1987.
- Burger, K. 1988. Multiple method for ultratrace determination: pesticide active ingredients in ground and drinking water analysed by TLC/AMD (Automated Multiple Development), Bayer Pflanzenschutz-Nachrichten **41**, pages 175-228, Method no. 000116, formerly H 231.
- Burhenne, J. 1996. ID: 1310004-9 Unpublished report no. FM 759, Bayer AG.
- Discher, A.D. 1982. See Thornton, J.S. 1977.
- EC. 1998: Guidelines for the generating of data concerning residues, EU-Doc. 1607/VI/97, Appendix D: Comparability, extrapolation, group tolerances and data requirements. Doc.7525/VI/95-rev.3
- Fent, G. 1997. Degradation and metabolism of [phenyl-UL-<sup>14</sup>C]Bitertanol on four different soils. Staatliche Lehr- und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau (SLFA), Neustadt, Germany; Project ID: BAY20. Unpublished report no. M 9557 Bayer AG.
- Fritz, R. 1990. Metabolism of bitertanol under aerobic conditions in the aquatic model ecosystem. Unpublished report no. PF 3366, Bayer AG.
- Heinemann O. and Allmendinger, H. 1998. Determination of residues of Sibusol 199 FS in/on spring wheat following seed treatment in the field in Germany. Unpublished report no. RA-2166/97 (incl. 707643 = 0764-97, 707651 = 0765-97), Bayer AG.
- Hellpointner, E. 1991. Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of bitertanol in water. Unpublished report no. PF 3544, Bayer AG.
- Herrmann, U. 1981a. Vapour Pressure Determination of Bitertanol (Diastereomer A). Unpublished report no. PC620, Bayer AG.
- Herrmann, U. 1981b. Vapour Pressure Determination of Bitertanol (Diastereomer B). Unpublished report no. PC621, Bayer AG.
- Klein, O. 1988a. [Phenyl-U-<sup>14</sup>C] Bitertanol: absorption, excretion, tissue-distribution and biokinetic profile of the total radioactivity in the rat following single oral and intraduodenal dosage. Unpublished report no. PF 3076, Bayer AG.
- Klein, O. 1988b. [Phenyl-U-<sup>14</sup>C] Bitertanol: distribution of the parent compound in the excreta and in some organs at different times following oral administration to rats. Unpublished report no. PF 3096, Bayer AG.
- Klein, O. 1991. [Phenyl-U-<sup>14</sup>C] Bitertanol: distribution of the metabolites in some organs at different times following oral administration to rats. Unpublished report no. PF 3501, Bayer AG.
- Klusacek, H. 1986. Thermal stability of the agrochemical active ingredient bitertanol. Unpublished report no. PC627, Bayer AG.

- Köhler, J. 1989. See Brennecke, R. 1988a.
- Köhler, J. 1993. Determination of storage stability of bitertanol in fortified samples during frozen storage. Unpublished report no. RA-212/93, Bayer AG.
- Krebber, R. 1991. See Brennecke, R. 1988a.
- Krebber, R. 1992. Determination of residues of Baycor 300 EC in/on cherry tomato and tomato under actual use conditions in the Netherlands. Unpublished report no. RA-2010/91 (101796 = 0179-91, 101818 = 0181-91, 104817 = 0481-91), Bayer AG.
- Krohn, J. 1989. Melting Points of Bitertanol (KWG 0599) Diastereomers A and B. Unpublished report no. PC 618, Bayer AG.
- Krohn, J. 1992. Calculation of the Henry law constant of bitertanol. Unpublished report no. PC622, Bayer AG.
- Krohn, J. 1996. Solubilities and partition coefficient of bitertanol. Unpublished report no. 14 660 0892, Bayer AG.
- Leimkuehler, W.M. 1983. The stability of Baycor residues in bovine tissue held in frozen storage. Unpublished report no. MR 84126, Mobay Chemical Corporation.
- Leimkuehler, W.M., Cain, K.S., Whitefield, S.L. and Clay, V.E. 1983. Determination of Baycor residues in bovine and poultry tissues, milk and eggs. Unpublished report no. 86315, method no. F 218, October 21, 1983, Mobay Corporation.
- Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984a. The effect of feeding Baycor™ to dairy cows. Unpublished report no. MR 86317. Mobay Chemical Corporation.
- Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984b. The effect of feeding Baycor™ to chickens. Unpublished report no. MR 86312. Mobay Chemical Corporation.
- Mobay Chemical Corporation. 1980a. Residue trials with Baycor 300 EC in bananas in Honduras. Unpublished report no. 68896, 68897, 68898, 68899.
- Mobay Chemical Corporation. 1980b. Residue trial with Baycor 25 WP in bananas in Honduras. Unpublished report no. 68900.
- Mobay Chemical Corporation. 1982a. Residue trials with Baycor 300 EC in bananas in Costa Riabout Unpublished report no. 80469 (incl. 80469-A, 80469-B).
- Mobay Chemical Corporation. 1982b. Residue trials with Baycor 50 WP in bananas in Honduras. Unpublished report no. 80470, 80471.
- Mobay Chemical Corporation. 1982c. Residue trials with Baycor 300 EC in bananas in Honduras. Unpublished report no. 80472, 80473.
- Mobay Chemical Corporation. 1983a. Effect of frozen storage at 0 to -10°F on residues of bitertanol in dry beans. Unpublished report no. 84252.
- Mobay Chemical Corporation. 1983b. Effect of frozen storage at 0 to -10°F on residues of bitertanol in peaches. Unpublished report no. 84222. MR 86313.
- Mobay Chemical Corporation. 1984a. Effect of frozen storage at 0 to -10°F on residues of bitertanol in green beans. Unpublished report no. 84571.
- Mobay Chemical Corporation. 1984b. Effect of frozen storage at 0 to -10°F on residues of bitertanol in apples. Unpublished report no. 84264.
- Mobay Chemical Corporation. 1984c. Raw data from the analysis of bovine tissues and milk for residues of Baycor™. Unpublished report no. MR 86316.
- Mobay Chemical Corporation. 1984d. Raw data from the analysis of chicken tissues and eggs for residues of Baycor™. Unpublished report no. 86313.
- Mobay Chemical Corporation. 1984e. Technical information of Baycor™. Unpublished report no. PC 628.
- Mobay Chemical Corporation. 1985. Processing study with Baycor 50WP on apples in the USA. Unpublished report no. 87036.
- Möllhoff. 1986. See Brennecke, R. 1985.
- Nichols, S.S. and Thornton, J.S. 1979. The Behavior of BAYCOR™ in Sterile Aqueous Solutions. Unpublished report no. MR 68273, Bayer AG.
- Nüßlein, F. 1995. See Brennecke, R. 1988a.
- Nüßlein, F. 1996. Determination of residues of Baycor 25 WP in/on apple under actual use conditions in Italy and Spain. Unpublished report no. RA-2010/93 (incl. 303267 = 0326-93, 303283 = 0328-93, 303291 = 0329-93), Bayer AG.
- Nüßlein, F. 1997. Determination of residues of Baycor 500 SC on peach in Portugal and Spain. Unpublished report no. RA-2111/96 (incl. 606898 = 0689-96, 606901 = 0690-96), Bayer AG.
- Nüßlein, F. 1998a. Determination of residues of Baycor (500 SC) in/on cherry in the field in France. Unpublished report no. RA-2113/96 (incl. 606804 = 0680-96, 606812 = 0681-96, 606820 = 0682-96, 606839 = 0683-96, 607460 = 0746-96, 607479 = 0747-96), Bayer AG.
- Nüßlein, F. 1998b. Determination of residues of Baycor (500 SC) in/on plum in the field in Portugal and France. Unpublished report no. RA-2112/96 (incl. 606847 = 0684-96, 606855 = 0685-96, 606863 = 0686-96, 606871 = 0686-96), Bayer AG.
- Nüßlein, F. 1998c. Determination of residues of Baycor (500 SC) on cucumber in the greenhouse in Netherlands. Unpublished report no. RA-2096/96 (incl. 605603 =



0560-96, 605611 = 0561-96, 605638 = 0563-96, 605646 = 0564-96, 605654 = 0565-96, 605662 = 0566-96), Bayer AG.

Nüßlein, F. 1998d. Determination of residues of Baycor (500 SC) on tomato in the greenhouse in Belgium and Netherlands. Unpublished report no. RA-2059/96 (incl. 605557 = 0555-96, 605565 = 0556-96, 605573 = 0557-96, 605581 = 0558-96), Bayer AG.

Nüßlein, F. 1998e. Determination of residues of Baycor 500 SC on apple in the field in Spain, Italy and France. Unpublished report no. RA-2104/96 (incl. 606944 = 0694-96, 606960 = 0696-96, 606979 = 0697-96, 606987 = 0698-96, 606995 = 0699-96), Bayer AG.

Nüßlein, F. and Walz-Tylla, B. 1996. Determination of residues of Baycor 25 WP on peach in Spain and in diverse processing products. Unpublished report no. RA-2083/94 (incl. 403423 = 0342-94, 403431 = 0343-94, 405167 = 0516-94), Bayer AG.

Obrist, J.J. and Puhl, R.J. 1986. The metabolism and excretion of BAYCOR-phenyl-UL-<sup>14</sup>C by chickens. Unpublished report no. 82614, Mobay Chemical Corporation.

Obrist, J.J. and Thornton, J.S. 1979. Soil thin-layer mobility of BAYCOR<sup>TM</sup>, @BAYTAN, @DYRENE and PEROPAL<sup>TM</sup>. Unpublished report no. 68272, Mobay Chemical Corporation.

Obrist, J.J., Puhl, R.J. and Thornton, J.S. 1981. Excretion and tissue levels of <sup>14</sup>C following oral administration of BAYCOR-[phenyl-UL-<sup>14</sup>C] to a dairy cow. Unpublished report no. 69400, Mobay Chemical Corporation.

Obrist, J.J., Puhl, R.J. and Thornton, J.S. 1983. The metabolism and excretion of BAYCOR-[phenyl-UL-<sup>14</sup>C] following oral administration to a dairy cow. Unpublished report no. 84062, Mobay Chemical Corporation.

Olthof, P.D.A. 1999a. Information of The Netherlands to be considered by the 1999 JMPR for bitertanol, May 18, 1999: Multi-residue Methods, part I, Multi-residue Method 1, Pesticides amenable to gas chromatography, p 1-9 and 17-22 and the Annex A-p.1, Annex B-p.1, Annex C-p.1 and Annex D-p.1, "Analytical Methods for Pesticide Residues in Foodstuffs" 6<sup>th</sup> edition /1996). Ministry of Health, Welfare and Sport, The Hague, The Netherlands. SDU Publishers, The Hague, NL, ISBN 90 12 06712 5.

Olthof, P.D.A. 1999b. Information of The Netherlands to be considered by the 1999 JMPR for bitertanol, May 18, 1999: Information on residues in food in commerce or at consumption. Ministry of Health, Welfare and Sport, The Hague, The Netherlands.

Pither, K.M. and Stevenson, T.L. 1987a. Metabolism of Baycor in apple fruit. Unpublished report no. 94373, Mobay Chemical Corporation.

Pither, K.M. and Stevenson, T.S. 1987b. Metabolism of Baycor-triazole-<sup>14</sup>C in cotton. Unpublished report no. 94382, Mobay Chemical Corporation.

Puhl, R.J. and Hurley, J.B. 1979a. Soil adsorption and desorption of BAYCOR. Unpublished report no. 68003, Mobay Chemical Corporation.

Puhl, R.J. and Hurley, J.B. 1979b. The metabolism and degradation of BAYCOR-[biphenyl-UL-<sup>14</sup>C] on soil. Unpublished report no. 67998, Mobay Chemical Corporation.

Puhl, R.J. and Hurley, J.B. 1981a. The metabolism of Baycor-biphenyl-UL <sup>14</sup>C in apple fruit. Unpublished report no. 68305, Mobay Chemical Corporation.

Puhl, R.J. and Hurley, J.B. 1981b. Metabolism of Baycor-biphenyl-UL-<sup>14</sup>C in peanut plants. Unpublished report no. 68310, Mobay Chemical Corporation.

Puhl, R.J., Hurley, J.B. and Close, C.L. 1982. Total radioactive residues in rotational crops following a target crop of peanuts treated with Baycor-<sup>14</sup>C. Unpublished report no. 80059, Mobay Chemical Corporation.

Puhl, R.J. and Hurley, J.B. 1983. The Absorption, excretion, and metabolism of BAYCOR-[phenyl-UL-<sup>14</sup>C] by rats. Unpublished report no. 85832, Mobay Chemical Corporation.

Puhl, R.J., Obrist, J.J. and Pither, K.M. 1979. The excretion of BAYCOR-[phenyl-UL-<sup>14</sup>C] following administration of a single oral dose to rats. Unpublished report no. 68307, Mobay Chemical Corporation.

Sandie, F.E. and Coffman, M. 1985. An enforcement method for the determination of Baycor residues in bovine and poultry tissues, milk and eggs. Unpublished report no. 100217, method no. V079, April 09, 1985, Mobay Chemical Corporation.

Sandie, F.E. and Thornton, J.S. 1984. The effect of processing on residues of Baycor in apples. Unpublished report no. 86466, March 29, 1984, Mobay Chemical Corporation.

Sietsema, W.K. 1982. Photodegradation of BAYCOR on a soil surface. Unpublished report no. 82572, Mobay Chemical Corporation.

Sietsema, W.K. 1983. Photodegradation of BAYCOR<sup>TM</sup> in Water. Unpublished report no. MR 86103, Bayer AG.

South African Bureau of Standards, 1982a. Biloxazol residues in apples (Baycor 25 WP). Unpublished report no. 311/88195/V144.

South African Bureau of Standards, 1982b. Biloxazol residues in apples (Baycor 25 WP). Unpublished report no. 311/88161/V16 (incl. 88161/V16-A, 88161/V16-B).

South African Bureau of Standards, 1983a. Bitertanol residues in nectarines. Unpublished report no. 311/88419/W212 (incl. 88419/W212-A, 88419/W212-B).

South African Bureau of Standards, 1983b. Bitertanol residues in peaches. Unpublished report no. 311/88421/W214 (incl. 88421/W214-A, 88421/W214-B).

South African Bureau of Standards, 1983c. Bitertanol residues in apples (Baycor 25 WP). Unpublished report no. 311/88352/W26 (incl. 88352/W26-A, 88352/W26-B, 88352/W26-C).

South African Bureau of Standards, 1983d. Bitertanol residues in apples (Baycor 25 WP). Unpublished report no. 311/88355/W29 (incl. 88355/W29-A, 88355/W29-B, 88355/W29-C).

South African Bureau of Standards, 1985. Bitertanol residues in peaches. Unpublished report no. 311/88736/B140 (incl. 88736/B140-A, 88736/B140-B, 88736/B140-C, 88736/B140-D).

South African Bureau of Standards, 1986. Bitertanol residues in nectarines. Unpublished report no. 311/88933/C181.

Specht, W. and Thier, H.-P. 1989. Organochlorine, Organophosphorous, Nitrogen-Containing and Other Pesticides. DFG analytical multiresidue method S 19, Bayer method no. 00086, formerly F 184. Deutsche Forschungsgesellschaft, VCH Verlagsgesellschaft, 9th and 10th edition, 1989.

Specht, W. and Tillkes, M. 1980a. Gas-chromatographic determination of pesticide residues after clean-up by gel-permeation chromatography and mini-silica gel-column chromatography. Fresenius Z. Anal. Chem. 301, pages 300–307. Bayer method no. 00179, formerly F 163.

Specht, W. and Tillkes, M. 1980b. Method for gas-chromatographic determination of crop protectant residues after cleanup by gel permeation chromatography and silica gel mini-column chromatography. Pflanzenschutz-Nachrichten Bayer 33, pages 61-85, Method no. 00029, formerly F 136.

a) modified: Specht, W. and Tillkes, M. 1982, RA-1303, December 06, 1982 M003

b) supplemented: Brennecke, R. 1983b, April 11, 1983 M003/E013

c) modified: Specht, W. and Tillkes, M. 1981a, RA-383, May 27, 1981 M004

d) modified: Specht, W. and Tillkes, M. 1981b, RA-752, September 15, 1981 M006

e) modified: Brennecke, R. 1981a, RA-1117, December 18, 1981 M009

f) supplemented: Brennecke, R. 1983c, October 24, 1983 E001

g) supplemented: Brennecke, R. 1981b, July 07, 1981 E002

h) supplemented: Brennecke, R. 1982b, July 17, 1982 E003

i) supplemented: Brennecke, R. 1982c, November 23, 1982 E005

j) supplemented: Brennecke, R. 1982d, July 01, 1982 E006

k) supplemented: Brennecke, R. 1983d, August 11, 1983 E007

l) supplemented: Brennecke, R. 1982e, November 12, 1982 E008

Specht, W. and Tillkes, M. 1981a,b; 1982. See Specht, W. and Tillkes, M., 1980b.

Stupp, H.-P. 1996. Dissociation constant of KWG 0599. Unpublished report no. 15-550-2030, Bayer AG

Takase, I. and Yoshimoto, Y. 1980. Residues of KWG 0599 in upland soils under laboratory and field conditions. Unpublished report no. NR 1134, Nihon Tokushu Noyaku Seizo K.K.

Thielert, W. and Kuck, K.H. 1992. Uptake and distribution of [phenyl-UL-<sup>14</sup>C] bitertanol in plant and soil after cereal seed treatment. Unpublished report no. M 7596, Bayer AG.

Thornton, J.S. 1977. A gas chromatographic method for Bayleton and its metabolite in apples

Unpublished report no. 54166, Method no. F107, December 30, 1977, Mobay Chemical Corporation.

a) supplemented: Becker, R.D. 1980, 68895, August 20, 1980

b) supplemented: Discher, A.D. 1982, 80395, January 15, 1982

Wilmes, R. 1980. Preliminary studies on stability to light-active ingredient KWG 0599 (bitertanol). Unpublished report no. FM 320, Bayer AG.

Wilmes, R. 1981. Abiotic degradation of bitertanol (KWG 0599). Unpublished report no. FM 336, Bayer AG

#### CROSS-INDEX OF REPORT NUMBERS, STUDY NUMBERS AND REFERENCES

REPORTS AND STUDIES ARE LISTED IN ALPHANUMERICAL ORDER, AND EACH IS LINKED TO A REFERENCE.

BAYER AG REPORTS ARE LISTED SEPARATELY.

10300 -78 BAYER AG. 1978A

10301 -78 Bayer AG. 1978a

10303 -78 Bayer AG. 1978a

10309 -78 Bayer AG. 1978b

10305 -79 Bayer AG. 1979

10313 -80 Bayer AG. 1980a

10301 -80 Bayer AG. 1980b

10304 -80 Bayer AG. 1980c

10305 -80 Bayer AG. 1980c

10320 -80 Bayer AG. 1980e

10321 -80 Bayer AG. 1980e

10330 -80 Bayer AG. 1980f

10330 -80-A Bayer AG. 1980f

10330 -80-B Bayer AG. 1980f

10341 -80 Bayer AG. 1980d

10342 -80 Bayer AG. 1980d

10343 -80 Bayer AG. 1980d

10350 -80 Bayer AG. 1980g

10350 -80-A Bayer AG. 1980g

10350 -80-B Bayer AG. 1980g

10329 -81 Bayer AG. 1981a

10344 -81 Bayer AG. 1981b

10345 -81 Bayer AG. 1981b

10350 -81 Bayer AG. 1981c

10328 -81 Bayer AG. 1981a

10330 -81 Bayer AG. 1981a

10350 -81-A Bayer AG. 1981c

10350 -81-B Bayer AG. 1981c

- 10356 -81 Bayer AG. 1981a  
10366 -81 Bayer AG. 1981d  
10366 -81A Bayer AG. 1981d  
10366 -81B Bayer AG. 1981d  
10300 -82 Bayer AG. 1982a  
10303 -82 Bayer AG. 1982a  
10301 -82 Bayer AG. 1982a  
10302 -82 Bayer AG. 1982a  
10366 -82 Bayer AG. 1982b  
10367 -82 Bayer AG. 1982b  
10368 -82 Bayer AG. 1982b  
10370 -82 Bayer AG. 1982c  
10371 -82 Bayer AG. 1982c  
10363 -82 Bayer AG. 1982d  
10364 -82 Bayer AG. 1982d  
10365 -82 Bayer AG. 1982d  
10372 -82 Bayer AG. 1982e  
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10201 -83 Bayer AG. 1983a  
10202 -83 Bayer AG. 1983a  
10210 -83 Bayer AG. 1983d  
10211 -83 Bayer AG. 1983d  
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10213 -83 Bayer AG. 1983b  
10241 -83 Bayer AG. 1983c  
10242 -83 Bayer AG. 1983c  
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10244 -83 Bayer AG. 1983f  
10245 -83 Bayer AG. 1983g  
10246 -83 Bayer AG. 1983g  
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10202 -84 Bayer AG. 1984b  
10211 -84 Bayer AG. 1984c  
10300 -84 Bayer AG. 1984a  
10301 -84 Bayer AG. 1984a  
10302 -84 Bayer AG. 1984a  
10303 -84 Bayer AG. 1984a  
10304 -84 Bayer AG. 1984a  
10305 -84 Bayer AG. 1984a  
10203 -84 Bayer AG. 1984b  
10204 -84 Bayer AG. 1984b  
10210 -84 Bayer AG. 1984c  
10200 -85 Bayer AG. 1985c  
10202 -85 Bayer AG. 1985c  
10201 -85 Bayer AG. 1985d  
10203 -85 Bayer AG. 1985d  
10360 -85 Bayer AG. 1985a  
10361 -85 Bayer AG. 1985a  
10362 -85 Bayer AG. 1985a  
10363 -85 Bayer AG. 1985b  
10365 -85 Bayer AG. 1985b  
10312 -86 Bayer AG. 1986  
10313 -86 Bayer AG. 1986  
10315 -86 Bayer AG. 1986  
10311 -87 Bayer AG. 1987  
10313 -87 Bayer AG. 1987  
10314 -87 Bayer AG. 1987  
0230 -88 Bayer AG. 1988a  
0232 -88 Bayer AG. 1988a  
0233 -88 Bayer AG. 1988a  
0234 -88 Bayer AG. 1988a  
0304 -88 Bayer AG. 1988c  
0305 -88 Bayer AG. 1988c  
0306 -88 Bayer AG. 1988c  
0561 -88 Bayer AG. 1988b  
0562 -88 Bayer AG. 1988b  
0207 -89 Bayer AG. 1989a  
0209 -89 Bayer AG. 1989a  
0210 -89 Bayer AG. 1989a  
0220 -89 Bayer AG. 1989b  
0221 -89 Bayer AG. 1989b  
0222 -89 Bayer AG. 1989b  
0206 -89 Bayer AG. 1989a  
0384 -89 Bayer AG. 1989b  
0680-96 Nüßlein, F. 1998a  
0681-96 Nüßlein, F. 1998a  
0682-96 Nüßlein, F. 1998a  
0683-96 Nüßlein, F. 1998a  
0746-96 Nüßlein, F. 1998a  
0747-96 Nüßlein, F. 1998a  
100217 Sandie, F.E. and Coffman, M. 1985  
101796 Krebber, 1992  
101818 Krebber, 1992  
104817 Krebber, 1992  
10240 Bayer AG. 1983e  
303267 Nüßlein, F. 1996  
303283 Nüßlein, F. 1996  
303291 Nüßlein, F. 1996  
311/88161/V16 S. African Bureau of Standards, 1982b  
311/88195/V144 S. African Bureau of Standards, 1982a  
311/88352/W26 S. African Bureau of Standards, 1983c  
311/88355/W29 S. African Bureau of Standards, 1983d  
311/88419/W212 S. African Bureau of Standards, 1983a  
311/88421/W214 S. African Bureau of Standards, 1983b  
311/88736/B140 S. African Bureau of Standards, 1985  
311/88933/C181 S. African Bureau of Standards, 1986  
403423 Nüßlein, F. and Walz-Tylla, B. 1996  
403431 Nüßlein, F. and Walz-Tylla, B. 1996  
405167 Nüßlein, F. and Walz-Tylla, B. 1996  
54166 Thornton, J.S. 1977  
605557 Nüßlein, F. 1998d  
605565 Nüßlein, F. 1998d  
605573 Nüßlein, F. 1998d  
605581 Nüßlein, F. 1998d  
605603 Nüßlein, F. 1998c  
605611 Nüßlein, F. 1998c  
605638 Nüßlein, F. 1998c  
605646 Nüßlein, F. 1998c  
605654 Nüßlein, F. 1998c  
605662 Nüßlein, F. 1998c  
606847 Nüßlein, F. 1998b  
606855 Nüßlein, F. 1998b  
606863 Nüßlein, F. 1998b  
606871 Nüßlein, F. 1998b  
606898 Nüßlein, F. 1997  
606901 Nüßlein, F. 1997  
606944 Nüßlein, F. 1998e  
606960 Nüßlein, F. 1998e  
606979 Nüßlein, F. 1998e  
606987 Nüßlein, F. 1998e  
606995 Nüßlein, F. 1998e  
67998 Puhl, R.J. and Hurley, J.B. 1979b  
68003 Puhl, R.J. and Hurley, J.B. 1979a  
68272 Obrist, J.J. and Thornton, J.S. 1979  
68305 Puhl, R.J. and Hurley, J.B. 1981a  
68307 Puhl, R.J., Obrist, J.J. and Pither, K.M. 1979  
68310 Puhl, R.J. and Hurley, J.B. 1981b  
68897 Mobay Chemical Corporation 1980a  
68898 Mobay Chemical Corporation 1980a  
68899 Mobay Chemical Corporation 1980a  
68900 Mobay Chemical Corporation 1980b  
69400 Obrist, J.J., Puhl, R.J. and Thornton, J.S. 1981  
80059 Puhl, R.J., Hurley, J.B. and Close, C.L. 1982  
80469 Mobay Chemical Corporation 1982a

- 80469-A Mobay Chemical Corporation 1982a  
80469-B Mobay Chemical Corporation 1982a  
80470 Mobay Chemical Corporation 1982b  
80471 Mobay Chemical Corporation 1982b  
80472 Mobay Chemical Corporation 1982c  
80473 Mobay Chemical Corporation 1982c  
84252 Mobay Chemical Corporation 1983a  
82572 Sietsema, W.K. 1982  
82614 Obrist, J.J. and Puhl, R.J. 1986  
84062 Obrist, J.J., Puhl, R.J. and Thornton, J.S. 1983  
84222 Mobay Chemical Corporation 1983b  
84571 Mobay Chemical Corporation, 1984a  
84264 Mobay Chemical Corporation, 1984b  
85832 Puhl, R.J. and Hurley, J.B. 1983  
86315 Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1983  
86466 Sandie, F.E. and Thornton, J.S., 1984  
87036 Mobay Chemical Corporation 1985  
88161/V16-A S. African Bureau of Standards, 1982b  
88161/V16-B S. African Bureau of Standards, 1982b  
88352/W26-A S. African Bureau of Standards, 1983c  
88352/W26-B S. African Bureau of Standards, 1983c  
88352/W26-C S. African Bureau of Standards, 1983c  
88355/W29-A S. African Bureau of Standards, 1983d  
88355/W29-B S. African Bureau of Standards, 1983d  
88355/W29-C S. African Bureau of Standards, 1983d  
88419/W212-A S. African Bureau of Standards, 1983a  
88419/W212-B S. African Bureau of Standards, 1983a  
88421/W214-A S. African Bureau of Standards, 1983b  
88421/W214-B S. African Bureau of Standards, 1983b  
88736/B140-A S. African Bureau of Standards, 1985  
88736/B140-B S. African Bureau of Standards, 1985  
88736/B140-C S. African Bureau of Standards, 1985  
88736/B140-D S. African Bureau of Standards, 1985  
FM 320 Wilmes, R. 1980  
FM 336 Wilmes, R. 1981  
FM 759 Burhenne, J. 1996  
M 7596 Thielert, W. and Kuck, K.H. 1992  
M 9557 Fent, G. 1997  
MR 68273 Nichols, S.S. and Thornton, J.S. 1979  
MR 84126 Leimkuehler, W.M. 1983  
MR 86103 Sietsema, W.K. 1983  
MR 86131 Mobay Chemical Corporation 1984d  
MR 86312 Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984b  
MR 86316 Mobay Chemical Corporation 1984c  
MR 86317 Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984a  
MR 935/97 Allmendinger, H. 1998  
NR 1134 Takase, I. and Yoshimoto, Y. 1980  
PF 3076 Klein, O. 1988a.  
PF 3096 Klein, O. 1988b.  
PF 3366 Fritz, R. 1990  
PF 3501 Klein, O. 1991  
PF 3544 Hellpointner, E. 1991  
PC 618 Krohn, J. 1989  
PC 622 Krohn, J. 1992  
PC 620 Herrmann, U. 1981a  
PC 621 Herrmann, U. 1981b  
PC 627 Klusacek, H. 1986  
PC 628 Mobay Chemical Corporation 1984e  
RA 75/86 Brennecke, R. 1986  
RA 2112/96 Nüßlein, F. 1998b  
RA 1272/82 Brennecke, R. 1982a  
RA 981/83 Brennecke, R. 1983a  
RA 2104/96 Nüßlein, F. 1998e  
RA 2010/91 Krebber, 1992  
RA 2010/93 Nüßlein, F. 1996  
RA 2011/93 Bachmann, 1995  
RA 2059/96 Nüßlein, F. 1998d  
RA 2083/94 Nüßlein, F. and Walz-Tylla, B. 1996  
RA 2096/96 Nüßlein, F. 1998c  
RA 2111/96 Nüßlein, F. 1997  
RA 2113/96 Nüßlein, F. 1998a  
RA 212/93 Köhler, J. 1993  
RA 2166/97 Heinemann O. and Allmendinger, H. 1998