Danish Ministry
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Control of Pesticides and Biocides 2010

Danish Technological Institute
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Contents

Control of Pesticides and Biocides 2010

Three different groups of products covered by the pesticide and biocide regulation were included in the 2010 analytical chemical authority control:

1. Wood preservatives
2. Rodenticides
3. Fungicides

All samples were examined for the content of one or more active ingredients and two selected fungicide products for the content of the degradation product desthio prothioconazole. 11 samples out of 25 tested products in this year's programme did not comply with the tolerance limits defined by the Danish Statutory Order on pesticides and biocides.

Sammenfatning

Den analytisk kemiske kontrol af pesticid- og biocidprodukter på det danske marked, der er udført i 2010 af de danske myndigheder, er beskrevet i denne rapport. Prøver fra udvalgte grupper af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. Grænsen for en accepteret afvigelse fra det dokumenterede indhold af aktivstof i forhold til det deklarerede indhold er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Tre forskellige grupper af produkter er inkluderet i den analytisk kemiske kontrol, der blev udført af myndighederne i 2010:

1. Træimprægneringsmidler indeholdende propiconazol, tebuconazol og IPBC
2. Rodenticider (rotte-/musegift) indeholdende bromadialone, difethialon og difenacoum
3. Fungicider indeholdende propiconazol, tebuconazol, prothioconazol og imazalil

Der blev undersøgt 25 bekæmpelsesmidler. Indholdet af aktivstof i 14 analyserede produkter var inden for den accepterede tolerance, der er fastsat i bekendtgørelsen om bekæmpelsesmidler.

Det målte indhold af IPBC i alle fire undersøgte træimprægneringsmidler ligger under de deklarerede indhold, hvorimod indholdet af både propiconazole og tebuconazole stemmer overens med det deklarerede indhold i alle fire produkter.

Ud af de fem undersøgte rodenticid-produkter baseret på bromadiolon indeholder tre af de undersøgte produkter mindre aktiv komponent end deklareret. Indholdet af difethialon stemmer, med undtagelse af et af produkterne, overens med det deklarerede indhold, hvorimod der i produkterne baseret på difenacoum er målt mindre indhold end deklareret. Det målte indhold i alle undersøgte fungicidprodukter stemmer overens med det deklarerede indhold.

Summary

The analytical chemical authority control of pesticide and biocide products on the Danish market in 2010 is described in this report. Samples of selected groups of pesticides and biocides have been collected from the market and analysed to verify whether the actual content of the respective active ingredients in the products comply with the labelled content. The tolerance of deviation from the labelled content of active ingredients is set by the Danish Statutory Order on pesticides and biocides.

Three different groups of products covered by the pesticide and biocide regulation were included in the 2010 analytical chemical authority control:

1. Wood preservatives containing propiconazole, tebuconazole and IPBC
2. Rodenticides containing bromadialone, difethialon and difenacoum
3. Fungicides containing propiconazole, tebuconazole, prothioconazole and imazalil

25 different pesticide products were analysed. The content of the active ingredient of 14 products comply with the labelled content.

The measured content of IPBC was under the declared content in all four examined wood preservatives, whereas the content of propiconazole and tebuconazole did comply with the declared content in all four products.

Three out of five tested rodenticides based on bromadiolone had content below the declared value of the active ingredient. All products but one containing difethialone comply with the declared content and all three examined rodenticides based on difenacoum had contents below the declared value.

All tested fungicides comply with the declared content of the controlled active ingredient.

1 Control campaigns in 2010

Control campaigns conducted in 2010 have covered active ingredients belonging to three different groups of pesticides and biocides: wood preservatives, rodenticides and fungicides.

All analytical chemical control has aimed at examining the content of active ingredients compared with the content declared on the product. Statutory Orders in Denmark specify the general tolerance of deviation from the declared content. These tolerances are given in Table 1.1.

Table 1.1 The tolerance of deviation from the declared content of active ingredients

Declared content [w/w-%]	Tolerance	
conc.›50	± 2.5%	Absolute
25 < conc. ≤ 50	± 5%	Relative
10 < conc. ≤ 25	± 6%	Relative
2.5 < conc. ≤ 10	± 10%	Relative
conc. ≤ 2.5	± 15%	Relative

Samples of the various pesticide and biocide formulations covered in the 2010 control campaigns have been collected by the Chemical Inspection Service at "Miljøstyrelsen, Pesticider og Genteknologi" during the period from July to October 2010 from either wholesale dealers/importers or at retailer outlets. One sample of each product has been collected.

The samples were stored at Danish Technological Institute in the original packaging until the analysis was initiated. The samples were stored at ambient temperature protected from light until the analysis was started.

1.1 Biocides

1.1.1 Wood preservatives

1.1.1.1 Introduction

Four wood preservatives containing propiconazole, tebuconazole and IPBC as active ingredients were selected for the control campaign for 2010. All products were examined for the content of one or more active ingredients.

Propiconazole

Propiconazole (Figure 1.1) belongs to the group of triazole fungicides. It is used in Denmark for wood preservatives. Propiconazole inhibits steroid demethylation. It is a systemic foliar fungicide with protective and curative action. Fungicide formulations containing propiconazole were also selected for authority control in 2006.

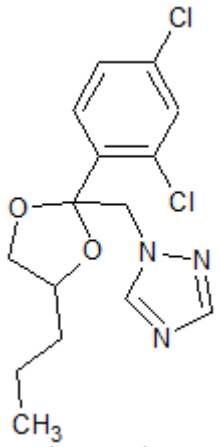

Figure 1.1 Molecule structure of propiconazole, cas. no. 60207-90-1

Tebuconazole

Tebuconazole (Figure 1.2) is a fungicide, which also belongs to the group of triazole fungicides. It is used in Denmark for wood preservatives.
Tebuconazole is a broad spectrum systemic fungicide with protective and curative action, inhibiting steroid demethylation. Fungicide formulations containing tebuconazole was also selected for authority control in 2008, 2002 and 1998.

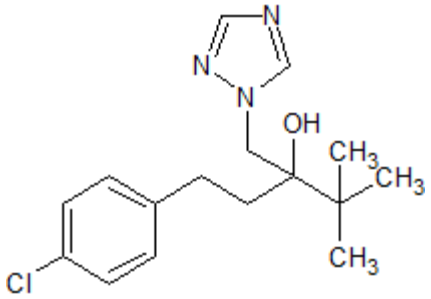

Figure 1.2 Molecule structure of Tebuconazole, cas. no. 107534-96-3

IPBC

IPBC (3-Iodo-2-propynyl-butylcarbamate) (Figure 1.3) is a fungicide that belongs to the group of carbamates. IPBC is commonly used as a mildewcide in water-based architectural coating films and for wood preservatives. The principal mode of action is thought to be through the iodine moiety. Oxidation of the sulfhydryl group of the amino acid cysteine results in loss of the ability to connect protein chains by disulfide (-S-S-) bridges, an important factor in the synthesis of proteins.
Fungicide formulation containing IPBC has not previously been selected for authority control.

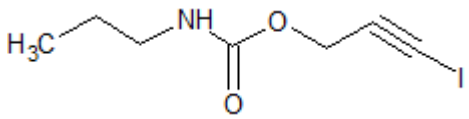

Figure 1.3 Molecule structure of IPBC, cas. no. 55406-53-6

1.1.1.2 Samples

The selected wood preservatives are chosen based on how long time has passed since the active substances were last analysed or if there have been problematic issues in the past with products containing a given active substance.

The four selected wood preservatives containing propiconazole, tebuconazole and IPBC were analysed for active ingredients in the period from October 2010 to January 2011.

The analysis of the controlled products was performed as eight measurements distributed on two days.

1.1.1.3 Results and Discussion

The content of tebuconazole was determined by a modified GC-MS method according to CIPAC-method no. 494. Prior to the analysis, a validation of the applied analytical method was conducted.

The content of propiconazole was determined by a modified GC-MS method according to CIPAC-method no. 408. Prior to the analysis, a validation of the applied analytical method was conducted.

The content of IPBC was determined by reversed phase high performance liquid chromatography combined with UV-detection, HPLC-UV. As no officially accepted method exists, the applied analytical method was validated prior to the execution of the measurement of the investigated products.
The results from the performed measurements and the corresponding tolerance intervals are listed in Table 1.2.

Table 1.2 Documented content of wood preservatives in the analysed samples

TI sample no.	Active Ingredient	Content in w/w-%		
		Label claim	Analysis	Tolerance
35590-1	Propiconazole	0.59	0.559 ± 0.0084	0,50 – 0.68
	Tebuconazole	0.2	0.190 ± 0.0027	0.17 – 0.23
	IPBC	0.2	0.016 ± 0.00094	0.17 – 0.23
35590-2	Propiconazole	0.9	0.946 ± 0.0087	0.77 – 1.04
	IPBC	0.3	0.242 ± 0.0099	0.26 – 0.35
35590-3	Propiconazole	0.9	0.907 ± 0.0100	0.77 – 1.04
	IPBC	0.3	0.243 ± 0.00049	0.26 – 0.35
35590-4	Propiconazole	0.25	0.213 ± 0.0081	0.21 – 0.29
	IPBC	0.75	0.620 ± 0.015	0.64 – 0.86

The measured content of IPBC was under the declared content in all four examined wood preservatives, whereas the content of propiconazole and tebuconazole did comply with the declared content in all 4 products.

1.1.2 Rodenticides

1.1.2.1 Introduction

11 different products containing bromadiolone, difenacoum and difethialon as active ingredients were selected for the control campaign for 2010. All products were examined for the content of one active ingredient.

Bromadiolone

Bromadiolone (Figure 1.4) is vitamin K antagonist. The main site of its action is the liver, where several of the blood coagulation precursors under vitamin K- dependent post translation processing take place before they are converted into the respective procoagulant zymogens. The point of action appears to be the inhibition of K1 epoxide reductase. Rodenticide formulations containing bromadiolone was also selected for authority control in 2005.

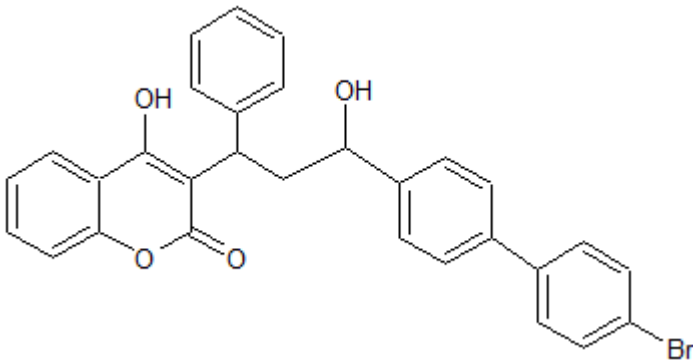

Figure 1.4 Molecule structure of bromadiolone, cas. no. 28772-56-7

Difenacoum

Difenacoum (Figure 1.5) is a multi-feed rodenticide, which is used for control of mice and rats in Denmark. Difenacoum is an indirect anticoagulant. It inhibits the vitamin K-dependent steps in synthesis of clotting factors II, IX and X. Rodenticide formulations containing difenacoum was also selected for authority control in 2002.

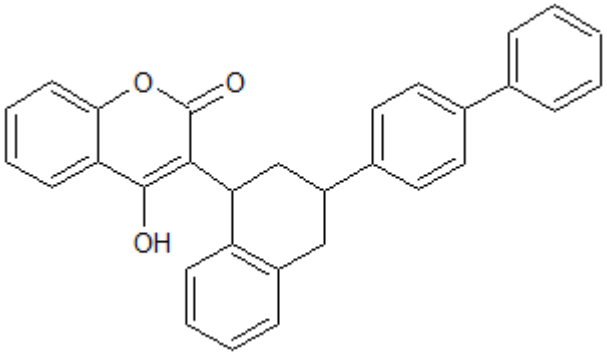

Figure 1.5 Molecule structure of defenacoum, cas. no. 56073-07

Difethialone

Difethialone (Figure 1.6) is also a multi-feed rodenticide, which is used for control of mice and rats in Denmark. Difethialone is an indirect anticoagulant. It inhibits the vitamin K-dependent steps in synthesis of clotting factors II, IX and X. Rodenticide formulations containing difethialone were also selected for authority control in 1994.

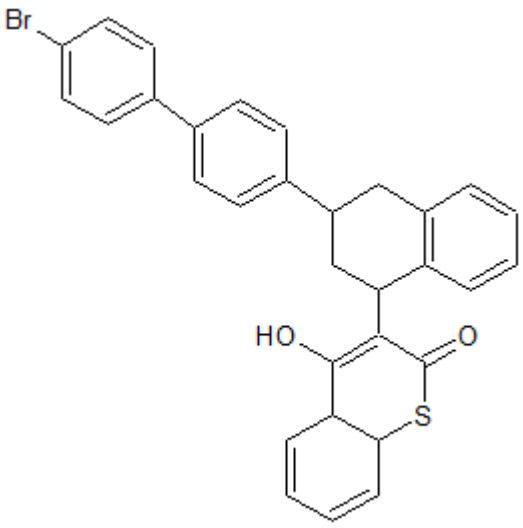

Figure 1.6 Molecule structure of difethialone, cas. no. 104653-34-1

1.1.2.2 Samples

The selected rodenticides are chosen based on how long time has passed since the active substances were last analysed or if there have been problematic issues in the past with products containing a given active substance. The samples containing bromadiolone, difenacoum and difethialone were analysed for active ingredients in the period from January 2011 to March 2011.

The analysis of the controlled products was performed as eight measurements distributed on two days.

1.1.2.3 Results and Discussion

The content of bromadiolone was determined by reversed phase high performance liquid chromatography combined with UV-detection, HPLC-UV according to CIPAC method no. 371.

The content of difethialone was determined by reversed phase high performance liquid chromatography combined with UV-detection, HPLC-UV. As no officially accepted method exists, the applied analytical method was validated prior to the execution of the measurements of the investigated products.

The content of difenacoum was determined by reversed phase high performance liquid chromatography combined with UV-detection, HPLC-UV. As no officially accepted method exists, the applied analytical method was validated prior to the execution of the measurements of the investigated products.

The results from the performed measurements and the corresponding tolerance intervals are listed in Table 1.3.

Table 1.3 Documented content of Rodenticides in the analysed samples

TI sample no.	Active Ingredient	Content in w/w-%		
		Label claim	Analysis	Tolerance
35590-6	Bromadiolone	0.01	0.00442 ± 0.00061	0.0085 - 0.0115
35590-7	Bromadiolone	0.01	0.00325 ± 0.00025	0.0085 - 0.0115
35590-8	Bromadiolone	0.25	0.249 ± 0.013	0.22 - 0.29
35590-9	Bromadiolone	0.01	0.00886 ± 0.0071	0.0085 - 0.0115
35590-10	Bromadiolone	0.01	0.00617 ± 0.00086	0.0085 - 0.0115
35590-11	Difethialone	0.0025	0.00225 ± 0.00014	0.0021-0.0029
35590-12	Difethialone	0.0025	0.00219 ± 0.00030	0.0021-0.0029
35590-13	Difethialone	0.0025	0.00180 ± 0.00015	0.0021-0.0029
35590-14	Difenacoum	0.01	0.00288 ± 0.00032	0.0085 - 0.012
35590-16	Difenacoum	0.005	0.00309 ± 0.000071	0.0043 - 0.0058
35590-17	Difenacoum	0.005	0.00258 ± 0.00026	0.0043 - 0.0058

Three out of five tested products based on bromadiolone did not comply with the declared content of the active ingredient. All products but one containing difethialone comply with the declared content and all three examined rodenticides based on difenacoum did not comply with the applied tolerances.

1.2 Pesticides

1.2.1 Fungicides

1.2.1.1 Introduction

10 products containing propiconazole, tebuconazole, prothioconazole and imazalil as active ingredients were selected for the control campaign for 2010. All products were examined for the content of one or more active ingredients and two selected products for the content of the degradation product desthio prothioconazole.

Propiconazole

Propiconazole (Figure 1.7) belongs to the group of triazole fungicides. It is used in Denmark for treatment of fungal diseases in cereals, grass seed, beets and lawns, and off-label to red and black currant, gooseberry and strawberry and in nurseries. Propiconazole inhibits steroid demethylation. It is a systemic foliar fungicide with protective and curative action. Fungicide formulations containing propiconazole were also selected for authority control in 2006.

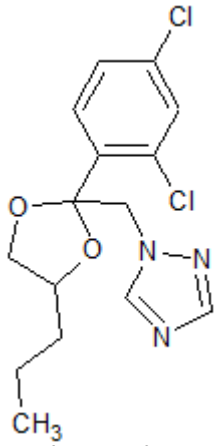

Figure 1.7 Molecule structure of propiconazole, cas. no. 60207-90-1

Tebuconazole

Tebuconazole (Figure 1.8) is a fungicide, which also belongs to the group of triazole fungicides. It is used in Denmark for treatment of fungal diseases in cereals, grass seed, rape, ornamentals, and off-label on golf courses and minor crops as leek, spring onion and chives. Tebuconazole is a broad spectrum systemic fungicide with protective and curative action, inhibiting steroid demethylation. Fungicide formulations containing tebuconazole was also selected for authority control in 2008, 2002 and 1998.

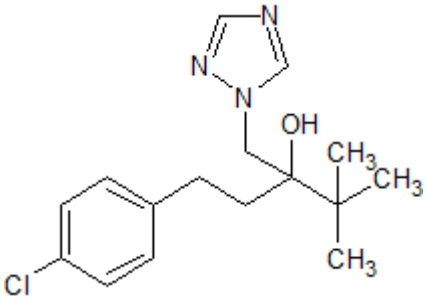

Figure 1.8 Molecule structure of Tebuconazole, cas. no. 107534-96-3

Prothioconazole

Prothioconazole (Figure 1.9) is a fungicide, which belongs to the group of triazole fungicides. It is used in Denmark only for the treatment of fungal diseases in cereals. Prothioconazole is a broad spectrum systemic fungicide with protective and curative action, inhibiting steroid demethylation. Fungicide formulations containing prothioconazole were also selected for authority control in 2008.

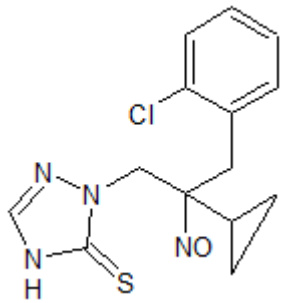

Figure 1.9 Molecule structure of prothioconazole, cas. no. 178928-70-6

Imazalil

Imazalil (Figure 1.10) is an azole type of fungicide that in Denmark is used as seed dressing, and to control fungal diseases on tomatoes, cucumber, seed potatoes and in greenhouses on roses and ornamentals. Fungicide formulations containing imazalil were also selected for authority control in 1998.

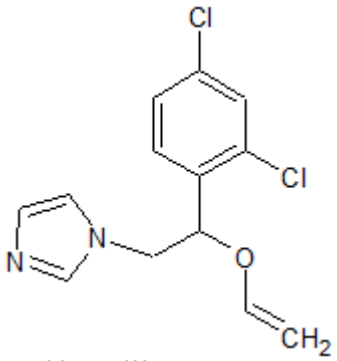

Figure 1.10 Molekyle structure of imazalil, cas. no. 35554-44-0 35554-44-0

1.2.1.2 Samples

The selected fungicides are chosen based on how long time has passed since the active substances were last analysed or if there have been problematic issues in the past with products containing a given active substance.

The samples containing propiconazole and tebuconazole were analysed for active ingredients in the period from October 2010 to January 2011. The single sample containing imazalil was analysed in February 2011. The samples containing prothioconazole were analysed in March 2011.

The analysis of the controlled products was performed as eight measurements distributed on two days.

1.2.1.3 Results and Discussion

The content of tebuconazole was determined by a modified GC-MS method according to CIPAC-method no. 494. Prior to the analysis, a validation of the applied analytical method was conducted.

The content of propiconazole was determined by a modified GC-MS method according to CIPAC-method no. 408. Prior to the analysis, a validation of the applied analytical method was conducted.

The content of imazalil was determined by GC-FID according to CIPAC-method no. 335.

The content of prothioconazole and the corresponding degradation product dethio prothioconazole was determined by reversed phase high performance liquid chromatography combined with DAD-detection, HPLC-DAD. As no officially accepted method exists, the applied analytical method was validated prior to the execution of the measurements of the investigated products.

The products marked 35590-18 and 35590-19 have declared contents of fenpropidine and cyprodinil, respectively. These two active ingredients were not covered by the control programme for 2010.

The results from the performed measurements and the corresponding tolerance intervals are listed in Table 1.4.

Table 1.4 Documented content of fungicides in the analysed samples

TI sample no.	Active Ingredient	Content in w/w-%		
		Label claim	Analysis	Tolerance
35590-5	Propiconazol	25	25.1 ± 2.3	23.5 – 26.5
35590-18	Propiconazol	13	13.2 ± 0.88	12.2 - 13.8
35590-19	Propiconazol	6	5.72 ± 0.22	5.4 - 6.6
35590-20	Prothioconazole	25.9	25.1 ± 0.48	24.6 - 27.2
35590-21	Tebuconazole	25.9	24,3 ± 1.0	24.6 – 27.2
35590-22	Tebuconazole	4.7	4.23 ± 0.27	4.2 – 5.2
35590-23	Tebuconazole	0.015	0.0136 ± 0.00030	0.013 – 0.017
35590-24	Tebuconazole	19.8	18.5 ± 0.59	18.6 – 21.0
35590-31	Tebuconazole	1.42	1.25 ± 0.060	1.21 – 1.63
	Imazalil	1.90	1.77 ± 0.14	1.61 – 2.19
35590-32	Prothioconazole	8.84	8.04 ± 0.68	7.96 – 9,72

All tested fungicides comply with the declared content of the controlled active ingredient.

The results from the performed measurements for the content of desthio prothioconazole are listed in Table 1.5.

Table 1.5 Documented content of desthio prothioconazole in the analysed samples

TI sample no.	Degradation product	Content in w/w-%
35590-20	Desthio prothioconazol	0.056 ± 0.0059
35590-32	Desthio prothioconazol	-
Limit of detection		0.005

"-" means that the result is below the limit of detection of the applied analytical method.

2 Conclusions

Three different groups of products covered by the pesticide and biocide regulation were included in the 2010 analytical authority control:

1. Wood preservatives containing propiconazole, tebuconazole and IPBC
2. Rodenticides containing bromadialone, difethialon and difenacoum
3. Fungicides containing propiconazole, tebuconazole, prothioconazole and imazalil

All products were examined for content of the active ingredients.
25 different pesticide products were analysed. The content of the active ingredient of 14 products comply with the labelled content.

The measured content of IPBC was under the declared content in all four examined wood preservatives, whereas the content of propiconazole and tebuconazole did comply with the declared content in all four products.

Three out of five tested rodenticides based on bromadiolone had content below the declared value of the active ingredient. All products but one containing difethialone comply with the declared content and all three examined rodenticides based on difenacoum had contents below the declared value.

All tested fungicides comply with the declared content of the controlled active ingredient.

3 Appendix

Pesticide and biocide samples collected from the Danish market for the authority control in 2010.

Table 3.1 Collected woodpreservatives

TI sample no.	Name of product	Company	Active ingredient
35590-1	Gori 22 trægrunder (30-70)	Dyrup	Propiconazole, tebuconazole, IPBC
35590-2	Gori 11 trægrunder (30-37)	Dyrup	Propiconazole, IPBC
35590-3	Pinotex superbase trægrunder (106-112)	Akzo Nobel	Propiconazole, IPBC
35590-4	Domestic grundingsolie (220-18)	Brifa	Propiconazole, IPBC

Table 3.2 Collected rodenticides

TI sample no.	Name of product	Company	Active ingredient
35590-6	Rentokill Bromard mod mus (2-84)	Rentokil	Bromadiolone
35590-7	Brota musekorn (9-6)	Mortalin	Bromadiolone
35590-8	Brota Koncentrat (9-40)	Mortalin	Bromadiolone
35590-9	Brota rottegift (9-52)	Mortalin	Bromadiolone
35590-10	Kirk Bromadiolon rottegift (10-90)	Kirk Chemical	Bromadiolone
35590-11	Dita rottegift (9-50)	Mortalin	Difethialone
35590-12	Difalon D400 (58-16)	Kiltin	Difethialone
35590-13	Kiltin Kilbox muselokkeboks (58-17)	Kiltin	Difethialone
35590-14	Rentokil difenard mod mus (2-70)	Rentokil	Difenacoum
35590-16	Ratak musekorn (528-8)	Sorex Trinol A/S	Difenacoum
35590-17	Ridak Blok (528-13)	Sorex Trinol A/S	Difenacoum

Table 3.3 Collected fungicides

TI sample no.	Name of product	Company	Active ingredient
35590-5	Bumper 25 EC (396-1)	Makhteshim	Propiconazole
35590-18	Zenit 575 EC (1-155)	Syngenta Crop	Propiconazole
35590-19	Stereo 312 EC (1-128)	Syngenta	Propiconazole
35590-20	Proline (18-473)	Bayer	Prothioconazole
35590-21	Folicur EC 250 (18-391)	Bayer	Tebuconazole
35590-22	Baymat Ultra Rosesprøjtemiddel (18-403)	Bayer	Tebuconazole
35590-23	Baymat Ultra Klar-til-brug (18-476)	Bayer	Tebuconazole
35590-24	Orius 200 EW, (396-24)	Makhteshim	Tebuconazole
35590-31	Raxil IM 035 ES	Bayer	Tebuconazole, imazalil
35590-32	Redigo FS 100	Bayer	Prothioconazole

4 References

Statutory Order on Pesticides. Statutory Order from the Ministry of the Environment, No. 533 of June 18, 2003 incl. revisions. Miljøministeriet (2003): Bekendtgørelse om bekæmpelsesmidler. Miljøministeriets bekendtgørelse nr. 533 af 18. juni 2003, inkl. revisioner

Danish EPA, 2009. List of approved Pesticides 2009, Danish Environmental Protection Agency. The list is in Danish

Tomlin, C.D.S (2009): The Pesticide Manual, fifteenth Edition. British Crop Protection Council. United Kingdom.

Miljøstyrelsen (2009): Oversigt over godkendte bekæmpelsesmidler 2009

http://www.mst.dk/Virksomhed_og_myndighed/Bekaempelsesmidler/Pesticider/Regulering/Godkendte_bekaempelsesmidler.htm

http://www.pesticideinfo.org

DANAK retningslinjer vedr. validering af analysemetoder, RL 1

CIPAC-method no. 494 - Tebuconazole

CIPAC-method no. 408 - Propiconazole

CIPAC-method no. 335 - Imazalil

CIPAC-method no. 371 - Bromadiolone