THE DETERMINATION OF THE FLUVALINATE RESIDUES IN THE BELGIAN HONEY AND BEESWAX

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Introduction

In the recent years, Apistan has been used in Belgium for the control of *Varroa jacobsoni.* This product has been accepted since 1988 and it is prefered by the great majority of the beekeepers because of its non-toxicity for the utilizer and of its efficiency. But its regular utilization may negatively influence the innate qualities of the beehive products, by the formation of residues. Because of its lipophilous characteristics, the fluvalinate is easily incorporated in the beeswax. On the contrary, in honey, only few residues could be detected (SLABESKI, 1990; PECHHAKKER, 1991; TACCHEO BARBINA, 1988).

In the State Institute of Nematology and Entomology in Gent, in 1989, an examination of the fluvalinate residues in the honey and beeswax samples was started. In collaboration with the phytopharmacy of the Gent University, we elaborated a procedure of analysis of the fluvalinate residues in the honey and beeswax samples.

Material and Methods

The Sample Prelevation

From 1989 to 1993, every year, in June, therefore after the honey crop, we have regularly extracted 50 samples of honey and beeswax from various beehives, where Apistan had been legally used, namely 2 stripes in autumn for 6—8 weeks and, whenever necessary, a new application in spring. From the new honey crop, a 100 g honey sample was prelevated. Also, a 10 x 10 cm beeswax sample was cut from a comb and wrapped in plastic. The data referring to the treatment (dose, time and place) and the position of the beeswax sample in the bee colony were written down. From each apiary, we took a honey sample and a beeswax sample. Up to the time of analysis, all the samples were deposited at a temperature of —20°C. Since 1989, 24, 29, 43, 51 and 68 honey samples and respectively, 12, 23, 49, 44, and 63 beeswax samples have been examined.

The Analysis

10 g of honey dissolved in 10 ml of water were poured down an Extrelut 20 (M 11737) column and eluated in 200 ml hexane. The extract was dried in a rotative vaporiser and solved again in 5 ml hexane. A 5 g beeswax sample was dissolved in 50 ml hexane in a water bath and centrifugalized for 20 minutes at 3000 rpm. 10 ml of the

above-mentioned hexane solution were introduced in a separative funnel and extracted 4 times with 10 ml of N, N'-dimethylformamide (DMF). 200 ml sodium sulphate (5%) and 20 ml hexane were added to the DMF layers and the entire composition was thoroughly aggitated. 10 ml of the hexane layer were poured down a fluorisyl column (60 — 100 mesh) for decantation, and the residues were eluated with 200 ml hexane (50%)-dichloromethane (50%). The extract was dried and was solved again in 5 ml hexane. The gaseous chromatography analysis was effected by means of an ECD detector endowed with a 3700 Varian. The column was 1 m long and contained 5% OV210 + 2% OV17. The temperature of the column was 240°C. The limit of detectability of the fluvalinate in honey was of 0.001 ppm and of 0.1 ppm in the beeswax.

Results

Analysis Procedures

The procedures used for the extraction of the honey and beeswax samples are very sensitive to the determination of the fluvalinate residues (a 95—100% determination). The procedure of honey extraction by means of Extrelut columns is the most suitable for the routine analysis, being rapid and sensitive.

The Analysis of the Honey and Wax Samples

In only one of the 215 samples of honey which we examined, we detected a fluvalinate residue of 0.004 ppm. But every year, we detected residues in the beeswax. Table 1 offers a general view on the residues in the beeswax: the number

Table 1

The Annual Development of the Fluvalinate Residues in the Beeswax Samples

	The number of the beeswax samples with residue									
	1989		1990		1991		1992		1993	
	n	%	n	%	n	%	n	%	n	%
Residues below 1 ppm	0	0	0	0	20	40,8	15	34,0	15	23,8
Residues between 1 and 10 ppm	3	25,0	8	34,7	17	34,6	22	50,0	37	58,7
Residues between 10 and 50 ppm	0	0	4,3	4	8,2	2	4,5	6	9,5	
Residues between 50 and 100 ppm	0	0	0	0	1	2,0	1	2,3	1	1,6
Residues over 100 ppm	0	0	0	0	1	2,0	0	0	1	1,6
Examined beeswax samples	12		23		49		44		63	
Positive samples	3		9		43		40		60	
% positive	25%		39%		87%		91%		95%	

n: beeswax samples with residues
% : % beeswax samples with residues

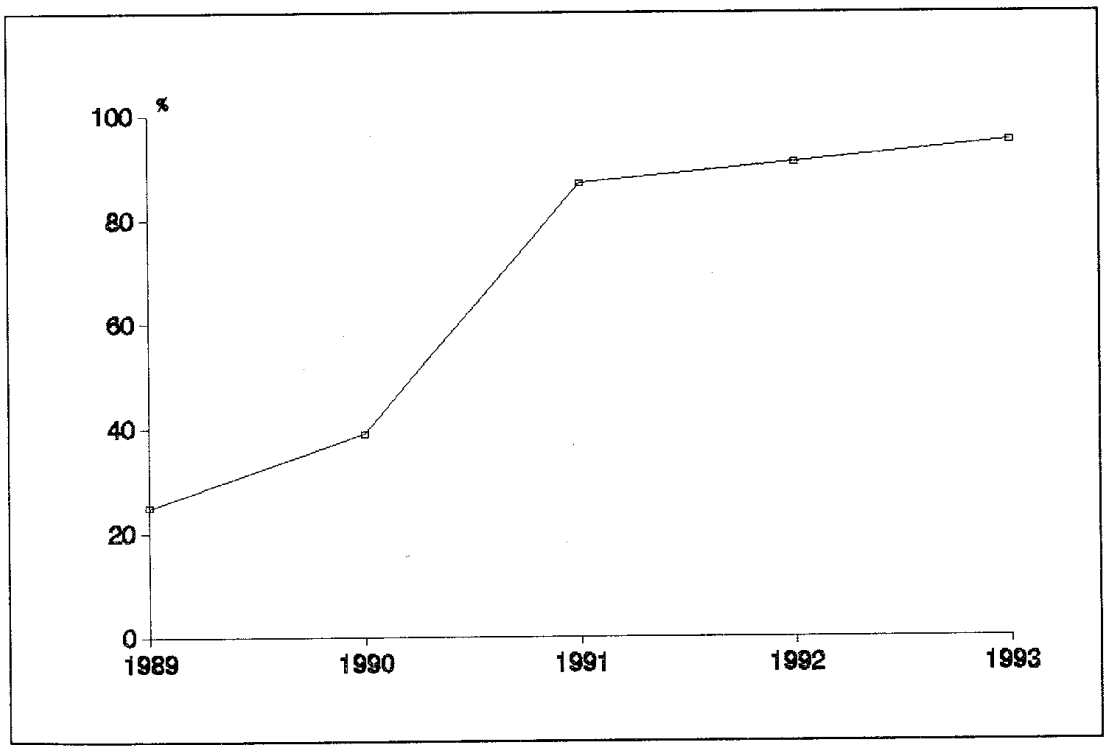

Fig. 1 — The annual increase of the percentage of the positive beeswax samples

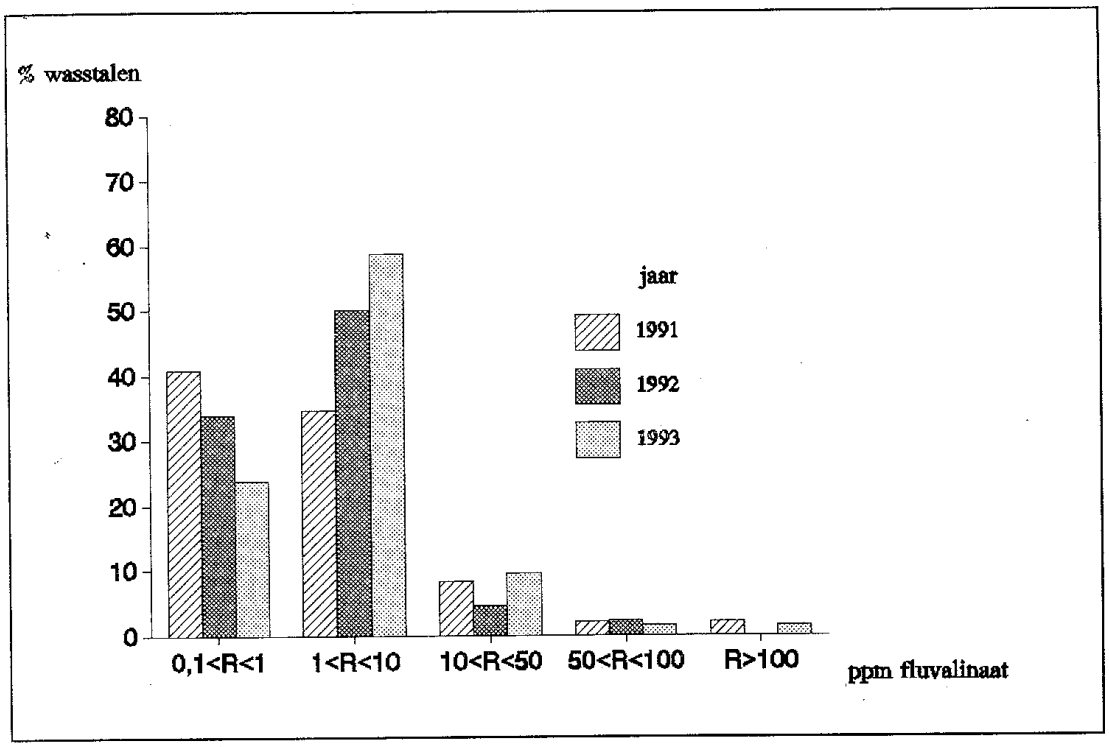

Fig. 2 — The evolution of the ppm fluvalinate in the beeswax samples

and the percentage of the positive samples per year and the classification of the positive samples according to the value of the ppm. The annual increase of the positive samples is certain, (fig. 1) as well as an increase of the samples with residues between 1 and 10 ppm and a decrease of those between 0.1 and 1 ppm (fig. 2). The beeswax samples with a residue of over 50 ppm are exceptions.

Discussions

The results of this examination confirm that, in case of the utilization of the Apistan stripe, residues of fluvalinate appear in the beeswax and, only in exceptional cases, in honey. The annual increase of the residues in the beeswax samples confirms the results obtained by other authors with regard to the accumulation of fluvalinate in the beeswax (BOGDANOV, 1990; WALLNER, 1992; LODESANI, 1992). But, there still does not exist any procedure of removal of the residues in the beeswax. FAUCON (1992) proved that the processings used for the fabrication of the artificial combs cannot remove the residues. The residues in honey may come from small beeswax particles, which have been sifted, or from the penetration of the fluvalinate molecules in beeswax into honey (WALLNER, 1992). BALAYANNIS (1992) established that the fluvalinate is eliminated from honey during a period of 28 weeks. Thus, the residue which is subsequently detected is so small that it does not endanger people's life, as it is at the limit of detectability, according to the toxicological experiments. The fluvalinate has an ADI value of 0.01 mg/kg of body weight (Zoecon Corporation), namely, a person who weighs 60 kg may ingest 0.6 mg fluvalinate a day, without suffering any harm.

Yet, it is desirable that we have beekeeping products which would be free of residues, especially as regards the honey destined to human consumption, because thus, we may defend the quality of these natural products.

Summary

Since 1989, we have annually examined 50 samples of honey and beeswax from the point of view of the existence of the fluvalinate residues. The samples come from apiaries where we have applied Apistan, according to the given indications. The number of beeswax samples with residues increased from 25% in 1989 to 95% in 1993. The majority of the beeswax samples have a residue between 1 and 10 ppm. From the 215 honey samples which we have examined, in only one of them we have detected a residue of 0.004 ppm. In order to carry out this examination, we have elaborated a procedure of analysis. The procedure elaborated for the analysis of honey is very favourable to the routine examinations, being rapid and sensitive.

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