DISTRIBUTION OF COUMAPHOS RESIDUES IN TURKISH-ISRAEL HIVES: A COLLABORATIVE STUDY

Türkiye-İsrail Kovanlarında Kumafos Kalıntısının Yaygınlığı: Ortak Bir Çalışma

(Genişletilmiş Türkçe Özet Makalenin Sonunda Verilmiştir)

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Key words: Coumaphos, residue, hive, Turkish, Israel

Anahtar Kelimeler: Kumafos, kalıntı, kovan, Türk, İsrail

ABSTRACT

A collaborative study was achieved to determine the distribution of coumaphos residues in beeswax and honey samples collected from hives in different parts of Turkey and Israel. Totally 170 samples were analyzed by Gas Chromatography / Mass Spectrometry (GC/MS). In Turkey and Israel no honey samples were contaminated over Maximum Residue Limit (MRL=100 ppb) but in Turkey 100 % of beeswaxes and in Israel 91.6% of positive beeswaxes were over MRL.

INTRODUCTION

Contamination of bee products with chemicals, which are originated from environmental sources or apicultural treatments, has been widely documented for many years. Most of the time, acaricide treatments such as coumaphos, amitraz and fluvalinate leave residues in hives. Acaricides are hydrophobic therefore they contaminate mostly the beeswax rather than the honey (Martin, 2004). In honey, residue levels are low, but accumulation of several pesticides in beeswax could lead to synergistic toxic effects on bees, also, the persistence of acaricides in beehive wax favor the appearance of acaricide resistant mites (Wallner, 1999b). The contamination of recycled beeswax during acaricide treatment is fast and it takes long time for residues to disappear. This brings economical damage to bee products, which should maintain the image of being natural, healthy and clean substances. Significant acaricide levels in wax and propolis damage their quality in view of their use in pharmacy and medicine (Kochansky, 2001).

Cleaning of recycled beeswax is very important on the process of decreasing the residue levels on beeswax. Chemical concentration does not decrease during regular beeswax recycling process of producing new wax from old combs. On the contrary, recycling of old beeswax during time increases the contaminants level. In order to reduce the contamination we need to develop efficient cleaning methods and tools for cleaning of the recycled beeswax (Martel, 2007).

Beekeepers have been putting acaricides in their hives for Varroa mite control for over a decade (Walner, 1999b; Martel et al., 2007; EPA, 2007; Karazafiris et al., 2008). Due to their non-polar nature, coumaphos and other acaricides mostly contaminate beeswax, while honey remains relatively

free of contaminants (PMRL 2008). The objective of this research was to determine the coumaphos residues of Turkish and Israeli beeswax and honey.

MATERIAL AND METHODS

This research was carried out in year 2009 and all samples were obtained from different parts of Turkey and Israel. They were analyzed in National Residue Control Laboratory in Beit-Dagan, Israel. Distribution of coumaphos in the contamination of honey and beeswax in hives were examined.

Sampling

Honey and beeswax samples from different sources in Turkey and Israel were analyzed for coumaphos residues. Totally 55 honey samples from Turkey, 38 honey samples from Israel and 10 beeswax samples from Turkey and 67 beeswax samples from Israel were analyzed.

Determination by gas chromatography

All samples were analyzed with Gas Chromatography/Mass Spectrometry (GC/MS). Coumaphos was extracted from 10 g of sample (honey or beeswax with 20 ml Acetonitril or Ethyl acetate correspondently), 1 µl honey or wax extract were injected by auto sampler in 30 m DB 1, J+W, 0.25 mm id, 0.25 µm film thickness. The GC analysis and quantification was done with an Agilent 7890A GC System equipped with a flame photometric detector (FPD).

The recoveries were between 80-100% and the detection limits were 0.005 mg/kg in honey and 0.25 mg/kg in wax for coumaphos.

Confirmation was done by 6890N gas chromatograph (GC) and configured with a 5975 inert mass-selective detector (MSD).

RESULTS

The counts of samples and the levels of residues are shown in Table 1.

In Turkey; 89.09 % (49/55) of honey samples are positive about coumaphos residue but none of them are over MRL. 100 % (10/10) of beeswax samples are positive and all of them are over MRL.

In Israel; 86.84 % (33/38) of honey samples are positive but none of them are over MRL. 89.55 % (60/67) of beeswax samples are positive and 91.66 % (55/60) of positive ones are over MRL.

Table 1. Counts of samples and levels of coumaphos residues in both countries

Country	Sample	n	Number of positivity	Number of over MRL (100 ppb)	Mean concentration of samples (ppb)
Turkey	Honey	55	49	0	30.89
	Beeswax	10	10	10	21395.90
Israel	Honey	38	33	0	46.10
	Beeswax	67	60	55	3076.41

Difference of the concentration of coumaphos residues between honey and beeswax can be seen in table. Mean level of coumaphos concentration in beeswax is obviously higher than honey samples.

Collaborative study between Israel and Turkey on residues in beeswax caused by acaricides such as coumaphos showed that there is a similar coumaphos contamination levels on both countries ' beeswax. However, all the beeswax samples from Turkey were over MRL. This should be taken in consideration that Turkish beeswax samples were less than Israeli ones.

DISCUSSION

The great majorities of synthetic acaricides, like coumaphos, are lipophilic and accumulate in beeswax, while honey residues are relatively low and mostly below the fixed maximum residue limit (MRL). As these acaricide is used for a long-term Varroa control, it is important to study the coumaphos (as representative acaricide) distribution in hive as well as the level in honey and beeswax after repeated use of the varroacides (Karazafiris et al., 2008). Beside the danger of residues of coumaphos for peoples, the resistance of Varroas to chemicals is important too. Resistance to chemical acaricides such as organophosphorous coumaphos (Checkmite® and Perizin®) has been reported in some European countries and U.S.A. (Martin, 2004; Pettis 2004).

Due to a previous research, results show that significant coumaphos residues were remain for a long

time in wax (Efrat et al 2009). All these residues fall within the "tolerance“ (Kochansky et al 2001) set by the EU (MRL=100 ppb), according to USDA/ARS program using coumaphos, research results also requiring precautions to prevent contact of coumaphos with combs used for extracted honey (EPA, 2007). This finding is important to beekeepers using coumaphos to control hive pests. Concentrations in honey were similar to those in syrup for higher concentrations of coumaphos in wax, reaching 430 ppb after 26 weeks, but could not be determined in honey in contact with wax containing only 10 ppm (PMRL 2008).

In our point of view, most likely, coumaphos residue of honey is contaminated by combs and Wallner's (1999a) data support our outcomes. Because of the contamination of combs is higher than from honey, it is very important to not to use old combs and to change them with new ones at least every two years. As a prevention of unhealthy situations, consumers should prefer liquid honey from markets.

There is a need to improve preventive methods to reduce or avoid accumulation of contaminants in the apiary infrastructure in aim to produce clean honey and apiary products. Studying residues in beeswax is relevant to several apicultural issues: colony health, economic reasons as well as scientific and ecological purposes.

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GENİŞLETİLMİŞ ÖZET

Çevresel etkilerin ve zirai ilaç kullanımının arı ürünlerinde kimyasal kalıntılara yol açtığı uzun yıllardan beri bilinmektedir. Çoğu zaman 'coumaphos' (Checkmite, Perizin), 'amitraz' ve 'fluvalinate' ile yapılan akarisit tedavileri kovanda kalıntılara yol açmaktadır. Akarisitler hidrofobik yapıya sahip oldukları için bal dışında petekte birikme özelliği gösterirler. Balda kalıntı miktarı düşük düzeyde olmasına rağmen, petekte kalıntı miktarının yüksek olması arılar üzerinde sinerjik toksik etkiye sebep olmakta ve akarisitlere dayanıklı akarların gelişmesine yol açmaktadır. Geri dönüşümü yapılarak kullanılan peteklerde kalıntı oranı çok hızlı bir şekilde artmakta ve bu kalıntıların yok olması çok uzun zaman almaktadır. Bu olay, doğal, saf, temiz ve yenmesi son derece sağlıklı olarak bilinen bal ve diğer arı ürünlerine ekonomik zararlar vermektedir. Eski peteklerin geri dönüştürülmesiyle yeni petek elde etme işlemleri, kumafos kalıntılarının seviyesini azaltmaya yardımcı olmamakta, tam aksine eski peteklerin sürekli geri dönüştürülmesi peteklerde kumafos seviyesinin artmasına neden olmaktadır.

Peteklerde ve ballarda kumafos kalıntı miktarının belirlenmesine yönelik Türkiye ve İsrail arasında ortak gerçekleştirilen bu çalışmada, her iki ülkenin çeşitli yerlerinden toplanan bal ve petek örnekleri İsrail'de bulunan Tarım Bakanlığına bağlı Kimron

Veteriner Enstitüsü Ulusal Kalıntı Kontrol Laboratuarına getirilmiştir. Toplam 170 örnek burada bulunan Gaz Kromatografi/Kütle Spektrometri (GC/MS) cihazında analiz edilmiştir. Böylece bal ve balmumu örneklerindeki milyarda bir (ppb) kumafos miktarı belirlenmiştir. Avrupa Birliği'ne bağlı Çevre Koruma Ajansı (EPA), arı ürünlerindeki kumafosun en fazla kalıntı sınırını (MRL) milyarda 100 birim (MRL=100 ppb) olarak belirlemiştir. Bu sınıra göre analiz sonuçları değerlendirildiğinde Türkiye'den toplanan peteklerin tamamının, İsrail'den toplanan peteklerde kumafos pozitif olanların % 91,6'sının kumafos ile yüksek oranda bulaşık olduğu görülmüştür. Her iki ülkeden toplanan ballarda ise sınır değer üzerinde kalıntı bulunmamıştır. İki ülkeye ait peteklerdeki yüksek orandaki kalıntı miktarları ve ballardaki düşük miktarlar Tablo 1'de görülmektedir. Bu durum bize ballardaki kumafos kalıntısının peteklerden bala geçtiğini, baldaki küçük petek parçalarının balın kumafos kalıntı değerini yükselttiği kanısını uyandırmaktadır.

Tablo 1. Her iki ülkeden toplanan örneklerin sayıları ve kumafos kalıntı miktarları

Ülke	Örnek	n	Pozitif örnek sayısı	MRL'nin üzerindeki örnek sayısı (100 ppb)	Ortalama kalıntı miktarları (ppb)
Türkiye	Bal	55	49	0	30.89
	Petek	10	10	10	21395.90
İsrail	Bal	38	33	0	46.10
	Petek	67	60	55	3076.41

Hem sağlıklı bal–arı ürünleri elde etmek hem de ekonomik olarak kazanç sağlamak için petekleri kumafos kalıntısız, en azından maksimum seviyenin altında bir kalıntı değerinde tutmak gerekmektedir. Bu amaçla akar mücadelesinde kullanılacak kumafos ve diğer ilaçlar, uygun dozda, belirli sürelerde ve tekrarlarda kullanılmalı, eskiyen petekler en az iki senede bir yenisiyle değiştirilmelidir. Bir sağlık önlemi olarak da, tüketiciler süzme balı petek bala tercih etmelidirler.