STANISŁAW SADŁO

CHANGES OF BROMOPROPYLATE AND CARBENDAZIM RESIDUES DURING PROCESSING OF APPLES INTO APPLE PUREE

ZMIANY POZOSTAŁOŚCI BROMOPROPYLATU I KARBENDAZYMU W TRAKCIE PRZEROBU JABŁEK NA KREMOGEN JABŁKOWY

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The study of changes of bromopropylate and carbendazim residues during apple processing was carried out. It was stated that bromopropylate residues on apples before and after washing stayed at similar levels (0.024 mg/kg) and then dropped by 60% during apple processing, while those of carbendazim remained at the level of 0.10 mg/kg during the whole process.

INTRODUCTION

The study of pesticide residues in food has the protection of human health as its primary objective. Before a pesticide is put on the market, it must undergo many toxicological tests to completely evaluate the short- and long-term effects which humans may be exposed to by the presence of its residues in food. On the basis of these studies, the FAO and WHO established the ADI (Acceptable Daily Intake, as mg/kg of body weight) which is the amount of a certain compound that a person can ingest during his lifetime without damage to his health. Depending on the ADI, and taking into account the amount of residue-containing food in the daily diet, competent authorities establish the Maximum Residue Limit (MRL) allowed in foods. As a rule, the MRLs concern unprocessed foods. In Poland, however, MRLs at the level of 0.01 mg/kg are proposed also for all foods destined for children. Similar restrictions have been imposed on pesticide residues in baby food in Germany.

The aim of the study was to estimate if bromopropylate and carbendazim residues, present in apples as a result of chemical treatment, dropped during apple processing to the rigorous level of 0.01 mg/kg in the final products.

MATERIALS AND METHODS

Pesticides tested.

Investigation included active ingredients (a.i.) of agricultural chemicals, which, according to grower's information, were used in fruit trees' protection: Neoron 500 EC (acaricide, a.i.-bromopropylate), applied on 7 May and 21 June and Benlate (fungicide, a.i.-benomyl), applied also twice on 22 July and 18 August. Tests were conducted

during apple processing into apple puree on 12 December, after a two-monthly period of storage of the apples.

Apple processing description.

After washing, apples were sorted on an inspection conveyer belt with water spray, ground in Rietz mill and then steamed in a finisher with sieve mesh diameter 1.2 mm and 0.4 mm. After deaeration and rapid pasteurization at 96–100°C within 60–90 seconds, apple puree was cooled down to 8–10°C and then frozen.

Sampling.

Samples were collected in specified below apple puree production stages:

— apples before washing (5 samples of raw fruits collected at random from various parts of several containers),

— washed apples (5 samples of fruits taken at 20-minute intervals from inspection conveyer belt) and,

— apple puree (5 samples taken at 20-minute intervals from a tank after cooling).

Extraction procedure.

100 g apple or apple puree subsamples were homogenized with 180 ml of acetone and then pesticide residues were extracted with dichloromethane, according a multiresidue method [1, 2]. The final extract (10 ml), equivalent to 20 g of the sample, was analyzed with the aid of a Gas-Chromatograph equipped with an electron capture detector on a column with 3% of OV 101 on Gas-Chrom Q 100–120 mesh and results obtained were then confirmed on a column with mixed stationary phase OV 17 + QF 1. After determination of bromopropylate residues, the extracts were concentrated to the volume of 2 ml and carbendazim residues were estimated with Thin Layer Chromatography [3].

RESULTS AND DISCUSSION

Benomyl, closely related to thiophanate methyl (Topsin M 70 WP), is a benzimidazole compound used as a curative, preventive, and systemic fungicide, very effective against diseases occurring on apples in storage. For this reason the compound, formulated as Benlate, is widely employed in apple orchards 2–3 weeks before harvest at the rate of 1.5 kg/ha. The biological activity of Benlate is mainly due to carbendazim, into which its active ingredient is rapidly converted with the decrease of molecular weight by 35%. In a monitoring survey conducted between 1985 and 1989, it was reported that carbendazim residues were present in 45% of samples of fresh apples [4]. In 5% of the samples, they exceeded 0.1 mg/kg, a level similar to those detected in apples used in the study. Bromopropylate is a new contact acaricide used both in greenhouses and outdoors. In apple orchards, the chemical is applied for the control of the mobile stages of phytophagous mites at the rate of 1.1–1.5 l/ha.

From the data reported in Table I it can be seen that carbendazim and bromopropylate residues in raw, unprocessed apples after two sprayings were, on average, 0.10 and 0.024 mg/kg, respectively. Differences between their values may be linked to different preharvest intervals which elapsed from the last treatments. However, their presence in apples after such a long period of time indicated that the two compounds are persistent ones. After washing, their average residues stayed at similar levels what

additionally proved that bromopropylate, though nonsystemic compound, is strongly absorbed on the fruit surfaces. In the apple puree carbendazim residues remained unchanged but concentration of bromopropylate decreased by 60%. However, the decrease of bromopropylate residues does not mean that the compound undergoes degradiation during apple processing because the apple skins retained on the sieves were not analyzed.

Table I. Bromopropylate and carbendazim residues (mg/kg)* in apples and apple puree
Pozostałości bromopropylatu i karbendazymu w jabłkach i kremogenie jabłkowym

Processing stage	Bromopropylate		Carbendazim	
Apples:				
– before washing	0.012–0.035	0.024±0.005	0.08–0.14	0.10±0.022
– after washing	0.008–0.040	0.024±0.011	0.11–0.14	0.13±0.012
Apple puree	0.012–0.010	0.010±0.001	0.12–0.14	0.12±0.008

* The reported values are residue ranges and their average levels ± standard deviations of duplicate analyses from five replications.

After washing the apples to eliminate impurities, processing method comprised grinding and steaming, followed by pressing, whereby puree was separated from the skin (about 10% of the total mass of apples used). On an average, 0.3 kg of apple puree is needed to produce 1 litre of juice, and therefore any pesticide residues, if completely transferred from the apples to the puree, can undergo about a 3-fold dilution in juice. The data reported in Table I indicated that carbendazim behave in this way. Hence, apples supplied from orchards sprayed with Benlate or Topsin 2–3 weeks before harvest should be carefully checked for carbendazim residues because apple processing do not ensure reduction of its amount in the final product, even after 3-fold dilution, as it takes place in the case of juice production, carbendazim residues may exceed the level of 0.01 mg/kg. Apples, coming from orchards in which Neoron was applied should be also analyzed on the presence of bromopropylate. However, due to a longer preharvest interval and reduction of its content in fresh apples during apple processing, it is almost impossible for bromopropylate residues in apple puree to exceed the level of 0.01 mg/kg.

S. Sadło

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Streszczenie

Celem badań było sprawdzenie czy pozostałości bromopropylatu i karbendazymu spadną w produktach końcowych poniżej poziomu 0,01 mg/kg. Przeprowadzono je 12 grudnia, po dwumiesięcznym przechowywaniu jabłek. Próby jabłek przed i po myciu oraz kremogenu po

schłodzeniu homogenizowano z acetonem a następnie pozostałości pestycydów ekstrahowano dwuchlorometanem. Ekstrakt końcowy analizowano za pomocą chromatografu gazowego wyposażonego w detektor wychwytu elektronów a po oznaczeniu bromopropylatu zawartości karbendazymu określano metodą chromatografii cienkowarstwowej. Pozostałości karbendazymu i bromopropylatu w nie przetworzonych jabłkach po dwukrotnych opryskach wyniosły średnio 0,10 i 0,024 mg/kg i po myciu nie uległy zmianie. W kremogenie jabłkowym pozostałości karbendazymu utrzymały się także na niezmienionym poziomie podczas gdy stężenie bromopropylatu obniżyło się o 60%. Uzyskane wyniki wskazują, że jabłka dostarczane z sadów chronionych preparatami Benlate i Neoron 500 EC powinny być dokładnie przebadane na zawartości karbendazymu i bromopropylatu. Pozostałości karbendazymu, nawet po trzykrotnym rozcieńczeniu kremogenu jabłkowego podczas produkcji soków, mogą przekraczać poziom 0,01 mg/kg.

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