

Composition of flavonoids in Lithuanian honey and beebread

V. Čeksterytė¹, S. Kazlauskas²,

J. Račys³

^{1,3} Department of Apiculture,
Lithuanian Institute of Agriculture,
Instituto alėja 1, Akademija,
LT-58344 Kėdainiai district,
Lithuania
E-mail: violeta@lzi.lt

² Kaunas University of Medicine,
Mickevičiaus 9,
LT-44307 Kaunas,
Lithuania

Tests were done to study the composition and contents of flavonoids in different spring and summer honey and beebread. Spring honey was gathered from willows and orchards at the basis of the Lithuanian Institute of Agriculture. Summer honey was produced from the nectar of spring rape, clover, caraway, lime trees, and heather. The content of pollen from one plant species in this monofloral honey accounted for over 49.0%. The pollen of plants flowering in summer was prevalent in beebread: white clover (*Trifolium repens* L.) – 36.0%; red clover (*Trifolium pratense* L.) – 35.4%; spring rape (*Brassica napus* L. ssp. *oleifera annua* Metzg) 46.2%. The data indicated that in spring and summer honey the total content of flavonoids was $281.5 \pm 30.8 \mu\text{g}/100 \text{ g}$ and $3019.2 \pm 1817.9 \mu\text{g}/100 \text{ g}$ and in beebread $3141.0 \pm 935.4 \mu\text{g}/\text{g}$. The average content of the main antioxidant quercetin in spring and summer honey was $2.1 \pm 0.3 \mu\text{g}/100 \text{ g}$, $6.7 \pm 1.4 \mu\text{g}/100 \text{ g}$, respectively and in beebread $399.7 \mu\text{g}/\text{g}$. The content of hyperoside in willow honey in which willow pollen dominated (73.8%) accounted for the largest share ($178.8 \mu\text{g}/100 \text{ g}$). The content of the flavonoid vitexin in caraway and lime honey was the highest compared to the other kinds of honey and constituted $4188.9 \mu\text{g}/100 \text{ g}$ and $10270.0 \mu\text{g}/100 \text{ g}$. Consequently, hyperoside may be used as a floral marker for willow honey and vitexin for caraway and lime honey.

Key words: honey, beebread, pollen, flavonoids

INTRODUCTION

Honey, plant pollen and beebread are used as food supplements. They influence antioxidative processes in the body, human immune and blood systems [1, 2]. Studies of the effects of plant pollen and honey on the antioxidative processes and immune system of oncological patients have shown a decrease of lipid peroxidation in the blood and an increase in lymphocyte count [3–5]. A mixture of beebread with honey is helpful for regulation of lipid metabolism and positively affects the immune system [6]. Analysis of artificial oxidation of low density lipids (LDL) in the blood of healthy volunteers showed that honey reduced formation of conjugated dienes in their blood. The evaluation of antioxidative potency of various kinds of honey with respect to oxygen radicals absorbance capability (ORAC) has shown that ORAC of honey was in the range 3.1–16.3 μmol of Trolox equiv/g honey [7]. Honey, plant pollen and beebread possess antioxidative properties and exhibit free radical scavenging capacity. As a result, these products can be recommended as a food supplement with a positive curative effect on human health [8–10]. The clinical experiments suggest that beebread mixed with honey has a positive effect on patients suffering from chronic joint and cardiovascular

diseases and facilitates the regulation of disordered lipid metabolism [11].

Recently we have identified that activity of catalase, as one of the antioxidant enzymes, was higher in heather honey compared with spring, rape or clover honey [12]. The antioxidative properties of honey are related to flavonoids, phenolic acids, α -tocopherol and β -carotene present in honey [13–16].

The aim of this study was to elucidate the differences in the composition and content of flavonoids in various kinds of Lithuanian honey and beebread. The flavonoids as possible floral markers of the botanical origin of monofloral honeys were identified in this study. The data of melissopalynological analysis suggest that honey and beebread collected at the Lithuanian Institute of Agriculture apiary was monofloral and polyfloral. Beebread has a higher flavonoid content than spring and summer honey and can act as a remedy.

MATERIALS AND METHODS

The honey and beebread were collected in the basis department of apiculture of the Lithuanian Institute of Agriculture. During the period 2002–2004, five kinds of spring honey, seven kinds of summer honey and three kinds of

beebread were collected from different locations of Kėdainiai district and assayed. The botanical composition of honey and beebread was identified according to pollen content by the method of melissopalynology [17]. The estimation of botanical composition of pollen from honey is based on the frequency of pollen from specific nectar-producing plants. The pollen was identified using the atlas of pollen [18] and a reference pollen collection prepared at the Lithuanian Institute of Agriculture by comparing it under a microscope with identical samples from the atlas or collection at a magnification of 400 times. Two to three hundred of pollen was counted per specimen. In the specimens that contained pollen only from two plants, the minimum counted number of pollen was 200. The number of pollen from plants not producing nectar was subtracted from the total number of pollen. The quantity of pollen in the honey and beebread was expressed in percent age. The pollen from the nectar plants that in the total composition did not exceed 3.0% was counted jointly and denominated as "single" in the results.

The content and quantities of flavonoids were estimated at the faculty of Pharmacy of Kaunas University of Medicine by the HPLC method.

Extraction of flavonoids from honey. Honey and beebread samples (25–50 g each) were mixed with five parts of water (pH 2 acidified with HCl) and filtered through cotton to remove solid particles. The filtrate was passed through a column (25 cm × 2 cm) of Amberlite XAD – 2 (Fluka Chemie; pore size 9 nm, particle size 0.3–1.2 mm) where phenolic compounds were separated from sugars. Sugars and other polar compounds were eluted with 300 ml acid water (pH 2), afterwards with water (pH 7). The phenolic fraction was eluted with 250 ml methanol, subsequently concentrated and dried at 40 °C under 0.8 MPa pressure. The residue was dissolved in 5 ml water, extracted with diethyl ether (5ml × 3). The ether fractions were mixed and dissolved in 0.5 ml of methanol for HPLC analysis.

HPLC analysis of honey flavonoids. Flavonoids were identified and quantified using the HPLC-MS techniques. The apparatus consisted of separation module Waters 2690 with PDA (photo – diode array) detector. Chromatographic separation of the flavonoids from the honey was carried out with Oasis HLB 3cc solid phase columns [19]. Elution of flavonoids was achieved with 1% acetic acid and 10 % of methanol. The gradient elution method was used [20, 21]. The resolution of flavonoids was stepwise starting with 30% methanol in water, and over 30 min its concentration was increased to 100%. The solvent composition remained constant for 6 min; a 30% methanol concentration was used from min 36–40. The solvent flow rate was 0.8 ml/min. For the assay of flavonoid calibration curves, external standards for each flavonoid were created. HPLC standards were purchased from Sigma Chemical Co., Sigma–Aldrich Sp. z o o. The samples of different flavonoids and standard solutions of vitexin-*o*-rhamnoside, vitexin, rutin, hyperoside (quercetin-3-galac-

toside, quercitrin (quercetin 3-rhamnoside), quercetin, izorhamnetin, kempherol were analyzed by HPLC with photo–diode array detector in the UV spectra from 254 to 400nm. Quantification of honey flavonoids was done by measuring the peak areas of calibration plots and by matching their UV spectra with those of standards. The content of identified flavonoids was expressed by µg/100 g in honey and by µg/g in beebread.

Statistical analysis. The experimental data were expressed as mean values ± standard deviation SD computed, and the coefficient of variance (CV) was calculated for all representative experiments. Statistical differences were estimated among different kinds of honey and beebread at $p = 0.01$.

RESULTS AND DISCUSSION

In this study, the flavonoid composition and content of five spring (I–V), seven summer (VI–XII) honey and three kinds of beebread BB (I, II, III) were estimated. The flavonoids in honey and beebread (vitexin-*o*-rhamnoside, vitexin, rutin, hyperoside, quercitrin, quercetin, izorhamnetin, kempherol) were identified and quantified (Tables 1, 2). Willow honey is presented in samples I–III, orchard in IV and mixed honey in V. The honey sample V contained 55.0% of pollen from plants blooming in spring, and the other part was from summer plants. Summer honey samples are VI–XII. The honey sample VI consisted of mixed summer and sprig honey. Pollen from plants flowering in summer contained the highest part (66.0%) in this honey. The other summer honey was produced mainly from one plant species and was classified as monofloral (unifloral) honey. The summer honey came from spring rape (VII), caraway (VIII), lime (IX), red clover (X), heather (XI), and red clover (XII). The botanical origin of spring and summer honey and beebread was identified by pollen analysis (Table 4). We found that the same flavonoids were present in spring and summer honey, but their content depended mainly on the floral source. The average sum of flavonoids in spring (I–V) honey was 282.8 ± 16.2 µg/100 g, the coefficient of variance (CV) being 22.4% (Table 1). The highest content of hyperoside (76.1 to 178.8 µg/100 g) and quercitrin (88.2 to 96.7 µg/100 g) was determined in willow (I–III) honey.

The average sum of flavonoids in the summer honey (VI–XII) gathered in Lithuania was significantly higher ($p < 0.01$) compared to spring honey and reached 3017.4 ± 995.3 µg/100 g, (CV–151.2%) (Table 2). The greatest differences in the content of vitexin-*o*-rhamnoside vitexin, rutin and hyperoside were determined in summer honey; the CV% for these flavonoids was 169.4%, 158.3%, 207.1%, and 195.1%, respectively. Lime honey had a significantly ($p < 0.01$) higher content of flavonoids compared to the other kinds of honey. Honey from different floral sources and geographical regions shoed a great variability in the quantity of flavonoids [22, 23]. The quercetin content in rape honey from different localities of Germany was

Table 1. Content of flavonoids in spring honey, $\mu\text{g}/100\text{ g}$

Flavonoids	Kind of honey					CV%
	I	II	III	IV	V	
Vitexin-o-rhamnoside	23.7 \pm 0.3	19.0 \pm 0.2	14.0 \pm 0.2	15.8 \pm 0.2	20.1 \pm 0.1	19.06
Vitexin	27.6 \pm 0.1	35.8 \pm 0.4	27.6 \pm 0.2	34.4 \pm 0.2	127.0 \pm 0.2	75.21
Rutin	17.9 \pm 0.1	16.5 \pm 0.1	15.8 \pm 0.2	15.0 \pm 0.2	0.6 \pm 0.0	50.00
Hyperoside	178.8 \pm 0.4	74.1 \pm 0.2	76.1 \pm 0.1	25.6 \pm 0.1	7.0 \pm 0.1	85.40
Quercitrin	96.7 \pm 0.2	97.4 \pm 0.2	88.2 \pm 0.1	90.2 \pm 0.1	96.3 \pm 0.1	4.20
Quercetin	2.2 \pm 0.1	3.2 \pm 0.1	1.2 \pm 0.1	2.0 \pm 0.1	1.8 \pm 0.1	33.81
Izorhamnetin	30.7 \pm 0.1	18.2 \pm 0.1	7.8 \pm 0.2	5.3 \pm 0.1	26.6 \pm 0.1	58.42
Kempferol	13.0 \pm 0.2	18.1 \pm 0.1	11.6 \pm 0.1	19.1 \pm 0.1	5.5 \pm 0.1	37.71
Total	390.6 \pm 1.0	282.3 \pm 1.0	242.3 \pm 0.9	207.4 \pm 0.9	284.9 \pm 0.3	22.24

Table 2. Content of flavonoids in summer honey, $\mu\text{g}/100\text{ g}$

Flavonoids	Kind of honey							CV%
	VI	VII	VIII	IX	X	XI	XII	
Vitexin-o-rhamnoside	31.4 \pm 1.1	32.3 \pm 0.7	476.9 \pm 4.9	1295.5 \pm 6.6	19.8 \pm 0.8	16.8 \pm 1.0	23.1 \pm 1.6	169.4
Vitexin	169.8 \pm 2.6	342.3 \pm 5.2	4188.9 \pm 11.7	10270.0 \pm 23.7	580.5 \pm 11.1	179.1 \pm 7.6	237.0 \pm 10.6	158.3
Rutin	16.7 \pm 0.6	65.6 \pm 1.8	71.3 \pm 1.0	966.0 \pm 9.5	4.1 \pm 0.1	12.0 \pm 0.6	3.4 \pm 0.1	207.1
Hyperoside	27.9 \pm 1.2	0.5 \pm 0.1	33.6 \pm 0.7	461.6 \pm 13.4	20.3 \pm 1.2	3.3 \pm 0.1	25.1 \pm 2.6	195.1
Quercitrin	98.3 \pm 2.1	116.0 \pm 2.0	222.6 \pm 1.8	202.8 \pm 10.1	92.3 \pm 3.7	104.2 \pm 5.1	108.6 \pm 5.2	37.0
Quercetin	3.2 \pm 0.1	8.9 \pm 0.5	10.5 \pm 0.6	5.9 \pm 0.1	9.3 \pm 0.8	0.4 \pm 0.1	9.1 \pm 0.1	53.4
Izorhamnetin	43.6 \pm 1.3	78.7 \pm 1.6	73.1 \pm 1.0	7.9 \pm 0.1	80.4 \pm 8.3	43.9 \pm 3.9	37.1 \pm 3.9	49.6
Kempferol	21.4 \pm 0.9	37.8 \pm 1.4	24.3 \pm 0.6	13.5 \pm 0.4	35.1 \pm 2.4	25.7 \pm 3.0	45.4 \pm 4.6	37.2
Total	412.2 \pm 9.3	674.4 \pm 13.2	5092.5 \pm 22.5	13219.7 \pm 56.3	842.0 \pm 24.8	394.4 \pm 12.9	488.0 \pm 19.6	151.2

54 and 87.6 $\mu\text{g}/100\text{ g}$, and from Denmark 12.3 and 122.7 $\mu\text{g}/100\text{ g}$. Kempferol constituted 28.5 and 53.2 $\mu\text{g}/100\text{ g}$ in lime honey from different localities of the Netherlands. The content of kempferol in heather honey from two localities of Germany was 48.9 and 68.2 $\mu\text{g}/100\text{ g}$ and from the Netherlands and England 14.3 and 455.7 $\mu\text{g}/100\text{ g}$, respectively [22]. However, the authors did not show the data on the content of quercetin in lime and heather honey, and the content of vitexin and vitexin-o-rhamnoside, hyperoside (quercetin-3-galactoside), quercitrin (quercetin 3-rhamnoside) in other kinds of honey. The concentration of flavonoids in Australian honey ranged from 20 to 901.2 $\mu\text{g}/100\text{ g}$ [24, 25]. Specific differences in the flavonoid profiles can be detected in honey of different botanical origin, therefore different flavonoids can serve as markers of the botanical origin of honey [26].

It is well known that antioxidant activity of honey depends on the flavonoid composition and content. The flavonoids hyperoside, rutin, quercetin, vitexin, vitexin rhamnoside and phenolic acids from herbs reduce the level of blood lipids, improve blood circulation, and

alleviate hypertension [27, 28]. Based on our results, we can conclude that honey gathered in Lithuania was of high quality. Flavonoids and their glycosides are present in Lithuanian honey. Lime and willow honey contained the flavonoid hyperoside (quercetin-3-galactoside) in higher amounts compared to the other kinds of honey tested, and its level was 461.6 \pm 13.4 $\mu\text{g}/100\text{ g}$ and 178.8 \pm 0.4 $\mu\text{g}/100\text{ g}$, respectively. The content of hyperoside in the spring rape honey was the lowest (0.5 \pm 0.1 $\mu\text{g}/100\text{ g}$). The amount of quercitrin (quercetin 3-rhamnoside) in caraway, lime, spring rape honey amounted to 222.6 \pm 1.8 $\mu\text{g}/100\text{ g}$, 202.8 \pm 10.1 $\mu\text{g}/100\text{ g}$, 116.0 \pm 2.0 $\mu\text{g}/100\text{ g}$, respectively. The honey from lime, caraway, red clover, spring rape had large contents of vitexin (10270.0 \pm 23.7; 4188.9 \pm 11.7; 580.5 \pm 11.1; 342.3 \pm 5.2 $\mu\text{g}/100\text{ g}$, respectively). However, the amount of rutin was the highest in lime honey (966.0 $\mu\text{g}/100\text{ g}$).

Substantial differences in the quantitative composition of flavonoids in Lithuanian beebread were determined (Table 3). The average amount of flavonoids in the beebread was 3139.5 \pm 467.9 $\mu\text{g}/\text{g}$, CV% being 44.7%.

The level of quercetin in beebread ranged from 274.1 ± 2.8 to 495.8 ± 3.9 $\mu\text{g/g}$ and were comparable to the levels found in fruit and vegetables. The level of quercetin in vegetables is below 10 mg/kg, in onions which are the major source of quercetin 284–486 mg/kg, in apples 21–72 mg/kg and in berries 20 mg/kg [29, 30]. It is well known that quercetin prevents the low density lipoproteins (LDL) by scavenging free oxygen radicals [31]. Vinson et al. have shown that flavonoids extracted from different plants and fruits studied in *vitro* using different

models of oxidation were more powerful antioxidants than the traditional vitamins C and E [32].

The dependence of the origin of honey and beebread on the season is presented in Table 4. In spring, mainly the monofloral willow and orchard honey and in summer rape, heath, caraway and lime honey were collected. Pollen from one plant species was prevailing in the monofloral honey and accounted for no less than 45% of the total pollen number. Monofloral honey possessed also specific chemical and organoleptic properties [33]. According to

Table 3. Content of flavonoids in beebread, $\mu\text{g/g}$

Flavonoids	Kind of beebread			
	BB(I)	BB(II)	BB(III)	CV%
Vitexin-o-rhamnoside	295.2 ± 2.5	116.3 ± 1.6	305.5 ± 3.3	38.6
Vitexin	309.3 ± 5.6	676.8 ± 4.2	597.3 ± 4.2	31.8
Rutin	41.1 ± 1.1	219.6 ± 3.5	798.3 ± 4.3	97.1
Hyperoside	55.8 ± 1.7	1150.0 ± 9.1	345.3 ± 2.8	94.9
Quercitrin	115.5 ± 2.1	337.6 ± 3.7	144.5 ± 1.5	52.5
Quercetin	274.1 ± 2.8	495.8 ± 3.9	429.2 ± 3.9	24.7
Izorhamnetin	337.5 ± 4.1	1210.1 ± 10.4	437.5 ± 2.9	62.7
Kempherol	39.9 ± 1.1	496.8 ± 3.6	195.6 ± 1.6	82.4
Total	1468.4 ± 17.5	4703.0 ± 40.2	3253.2 ± 19.9	44.7

BB (I) – beebread from clover, BB(II) – beebread from spring rape, BB (III) – polyfloral beebread.

Table 4. Botanical composition of honey and beebread according to pollen content (%)

No.	Spring honey
I	Willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 73.8; apple-tree (<i>Malus domestica</i> Borkh.) – 7.2; red clover (<i>Trifolium pratense</i> L.) – 6.9; white clover (<i>Trifolium repens</i> L.) – 5.3, single 6.8.
II	Willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 66.4; apple-tree (<i>Malus domestica</i> Borkh.) – 31.9, single 1.7.
III	Willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 61.9; apple-tree (<i>Malus domestica</i> Borkh.) – 30.1; winter rape (<i>Brassica napus</i> var. <i>oleif. F. biennis</i> Thellung) – 5.3, single – 2.7.
IV	Apple-tree (<i>Malus domestica</i> Borkh.) – 49.3; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) 36.7; spring rape (<i>Brassica napus</i> var. <i>oleif. F. biennis</i> Thellung) – 14.0.
V	Dandelion (<i>Taraxacum officinale</i> L.) – 21.0; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 17.0; apple (<i>Malus domestica</i> Borkh.) – 17.0; white clover (<i>Trifolium repens</i> L.) 10.0; raspberry (<i>Rubus idaeus</i> L.) – 10.0; charlock (<i>Sinapis arvensis</i> L.) – 9.0; red clover (<i>Trifolium pratense</i> L.) – 4.0; bluebottle (<i>Centaurea cyanus</i> L.) – 4.0, single – 8.0.
	Summer honey
VI	White clover (<i>Trifolium repens</i> L.) – 39.0; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) 34.0; charlock (<i>Sinapis arvensis</i> L.) – 9.5; raspberry (<i>Rubus idaeus</i> L.) – 12.0; red clover (<i>Trifolium pratense</i> L.) – 3.0; caraway (<i>Carum carvi</i> L.) – 2.5.
VII	Spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 100.
VIII	Caraway (<i>Carum carvi</i> L.) – 53.3; spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) 36.5; apple-tree (<i>Malus domestica</i> Borkh.) – 5.1; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 5.1; honeydew – 15.4.
IX	Lime (<i>Tilia</i> L.) – 50.0; white clover (<i>Trifolium repens</i> L.) – 32.7; melilot (<i>Melilotus albus</i> Medic.) – 7.3; caraway (<i>Carum carvi</i> L.) – 4.8; red clover (<i>Trifolium pratense</i> L.) – 2.5; honeydew – 7.3, single – 2.7.
X	Red clover (<i>Trifolium pratense</i> L.) – 75.0; spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 19.4; white clover (<i>Trifolium repens</i> L.) – 2.4, single – 3.1.
XI	Heather (<i>Calluna vulgaris</i> L.) – 58.0; spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 25.0; raspberry (<i>Rubus idaeus</i> L.) 7.0; alder (<i>Frangula</i> L.) 6.0, single – 4.0.
XII	Red clover (<i>Trifolium pratense</i> L.) 56.8; heather (<i>Calluna vulgaris</i> L.) – 18.2; white clover (<i>Trifolium repens</i> L.) – 6.8; charlock (<i>Sinapis arvensis</i> L.) – 4.7; spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 4.2; thistle (<i>Cirsium</i> L.) – 3.1; honeydew 3.0, single – 6.2.

Continuation of Table 4. **Botanical composition of honey and beebread according to pollen content (%)**

No.	Beebread
I	White clover (<i>Trifolium repens</i> L.) – 36.0; red clover (<i>Trifolium pratense</i> L.) – 35.4; charlock (<i>Sinapis arvensis</i> L.) – 12.0; spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 11.2; dandelion (<i>Taraxacum officinale</i> L.) – 3.1, single – 2.3.
II	Spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 37.9; caraway (<i>Carum carvi</i> L.) – 23.9; bluebottle (<i>Centaurea cyanus</i> L.) – 16.3; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 7.3; charlock (<i>Sinapis arvensis</i> L.) – 7.6; red clover (<i>Trifolium pratense</i> L.) – 7.0.
III	Spring rape (<i>Brassica napus</i> L. ssp. <i>oleifera annua</i> Metzg) – 46.2; bluebottle (<i>Centaurea cyanus</i> L.) – 19.9; willow (<i>Salix alba</i> L., <i>Salix caprea</i> L.) – 12.2; coltsfoot (<i>Tussilago farfara</i> L.) – 5.6; charlock (<i>Sinapis arvensis</i> L.) – 4.8; red clover (<i>Trifolium pratense</i> L.) – 4.6; thistle (<i>Cirsium</i> L.) – 4.4, single – 2.3.

tests, I–IV spring honey was monofloral, V being polyfloral, the summer honey VII–XII monofloral, VI polyfloral. In willow honey (I, II, III), willow (*Salix alba* L., *Salix caprea* L.) pollen prevailed (73.8%, 66.4% and 61.9%, respectively) (Table 4). The quantity of apple-tree pollen in this honey was 7.2%, 31.9% and 30.1%. Apple-tree (*Malus domestica* Borkh.) pollen prevailed in the IV kind of honey (49.3%), willow pollen in this honey comprised 36.7% and spring rape (*Brassica napus* var. *oleif. F. biennis* Thellung) pollen 14.0%. Although in the I specimen willow (*Salix alba* L., *Salix caprea* L.) pollen prevailed (73.8%), summer pollen was found in this honey, and this fact can explain a slight increase in the total flavonoids content 390.6 µg/100 g versus in the II, III and IV specimens (282.3, 242.3 and 207.4 µg/100g, respectively). In caraway honey, pollen of caraway (*Carum carvi* L.) prevailed (53.3%), and in lime honey pollen of lime (*Tilia* L.) reached 50%. Vitexin was present in those honey types in the highest content.

CONCLUSIONS

Our experimental evidence showed that in spring and summer honey the total content of flavonoids was 282.8 ± 16.2 and 3019.2 ± 995.3 µg/100 g and in beebread 3139.0 ± 467.9 µg/g. The results presented in this study show statistically significant differences in the qualitative content of flavonoids in spring and summer honey. The highest level of hyperoside in pure willow honey was 178.8 ± 0.4 µg/100 g and only lime honey possessed the highest hyperoside amount (461.6 ± 13.4 µg/100 g) compared to the other kinds of honey. The amount of vitexin in caraway and lime honey constituted 4188.9 ± 11.7 µg/100 g and 10270.0 ± 23.7 µg/100 g, respectively. In the other kinds of summer honey vitexin composed from 169.8 to 580 ± 11.1 µg/100 g and in spring honey from 27.6 ± 0.1 to 127.0 ± 0.2 µg/100 g. Thus, the flavonoid hyperoside can serve as a marker for only one kind of spring honey that comes from willow. Also, we suggest that the flavonoid vitexin may be used as a marker for the identification of caraway and lime honey.

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V. Čeksterytė, S. Kazlauskas, J. Račys

FLAVONOIDŲ SUDĖTIS LIETUVOS MEDUJE IR BIČIŲ DUONELĖJE

Santrauka

Tirta flavonoidų sudėtis ir kiekis skirtingame pavasario ir vasaros meduje bei bičių duonelėje. Lietuvos žemdirbystės instituto Bitininkystės skyriaus bityne buvo surinktas pavasarinis karklų ir sodų medus. Vasaros medus buvo surinktas iš rapsų, dobilų, kmynų, liepų, viržių. Šiame monofloriniame meduje vienos rūšies augalų žiedadulkių buvo daugiau kaip 49,0%. Bičių duonelėje daugiausia vyravo vasarą žydinčių augalų žiedadulkės: baltųjų dobilų (*Trifolium repens* L.) – 36,0%, raudonųjų dobilų (*Trifolium pratense* L.) – 35,4%, pavasariinių rapsų (*Brassica napus* L. ssp. *oleifera annua* Metzg) – 46,2%.

Pavasario ir vasaros meduje bendra flavonoidų suma sudarė $281,5 \pm 30,8$ $\mu\text{g}/100$ g ir $3019,2 \pm 1817,9$ $\mu\text{g}/100$ g, bičių duonelėje – $3141,0 \pm 935,4$ $\mu\text{g}/\text{g}$. Pagrindinio antioksidanto, kvercetino, vidutinis kiekis pavasario, vasaros meduje – atitinkamai $2,1 \pm 0,3$ $\mu\text{g}/100$ g ir $6,7 \pm 1,4$ $\mu\text{g}/100$ g, bičių duonelėje – $399,7$ $\mu\text{g}/\text{g}$. Didžiausias hiperozido kiekis ($178,8$ $\mu\text{g}/100$ g) rastas gryname karklų meduje, kuriame karklų žiedadulkių buvo daugiausia – 73,8 %. Viteksino kiekis kmynų bei liepų meduje buvo didžiausias ir sudarė $4188,9$ $\mu\text{g}/100$ g ir $10270,0$ $\mu\text{g}/100$ g. Hiperozidas gali būti žymeklis karklų medui, o viteksinas – kmynų ir liepų medui atpažinti.