SHORT COMMUNICATION

The phenolic profile of strawberry tree (Arbutus unedo L.) honey

ANDREJA JURIČ1, UROŠ GAŠIĆ2*, IRENA BRČIĆ KARAČONJI1**, KARLO JURICA3 and DUŠANKA MILOJKOVIĆ-OPSENICA4#

1Institute for Medical Research and Occupational Health, Ksavarska cesta 2, HR-10001 Zagreb, Croatia, 2Department of Plant Physiology, Institute for Biological Research “Siniša Stanković” – National Institute of Republic of Serbia, University of Belgrade, Bulevar despotov Sea 142, 11060, Belgrade, Serbia, 3Ministry of the Interior, Ulica grada Vukovara 33, HR-10000 Zagreb, Croatia and 4University of Belgrade – Faculty of Chemistry, P.O. Box 51, 11158 Belgrade, Serbia

(Received 17 December 2019, revised and accepted 30 March 2020)

Abstract: Despite of the many beneficial health effects of strawberry tree (Arbutus unedo L.) honey, due to its strong antioxidant activity derived mostly from polyphenols, a detailed phenolic profile has not been previously studied. The aims of this study were to identify the phenolic compounds, determine the total phenolic content (TPC) and evaluate the radical scavenging activity (RSA) of strawberry tree honey from south Croatia. Fifty-two polyphenolics (twenty-seven phenolic acids and twenty-five flavonoids) were identified using ultra-high-performance liquid chromatograph coupled to a hybrid mass spectrometer (LTQ Orbitrap MS). Our overall results point to the higher TPC (1038 mg gallic acid equivalents per kg of honey) and the stronger RSA (3.32 mmol Trolox equivalents per kg of honey) compared to the other monofloral honeys. Due to the presence of large quantities of polyphenolic compounds, strawberry tree honey may have great potential as a health promoting food.

Keywords: polyphenolics; UHPLC-LTQ Orbitrap MS; TPC; RSA.

INTRODUCTION

Strawberry tree (Arbutus unedo L.) is a wild evergreen shrub that typically grows in the Mediterranean area. All of its plant parts (leaves, fruits, bark and root) have been used in folk medicine as an antiseptic, diuretic, and laxative, as well as for treating cardiovascular, urological and gastrointestinal diseases.1 This plant has also shown significant antiproliferative properties and its health benefits

*,** Corresponding authors. E-mail: (*)uros.gasic@ibiss.bg.ac.rs; (**)ibracic@imi.hr
# Serbian Chemical Society member.

https://doi.org/10.2298/JSC191217018J

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are mainly attributed to phenolic compounds such as flavonoids, phenolic acids, and tannins.1–3

In addition, it is the floral source of strawberry tree honey, known as “bitter honey”, and produced in Sardinia, Corsica, some parts of Spain, Portugal and Croatia.4,5 The characterization of this rare honey is a very challenging task because of the low pollen content. Arbutus pollen is under-represented due to the upside-down position of the flowers and, therefore, melissopalynological analysis should be carefully performed and combined with sensory and physicochemical characteristics.6,7 Although strawberry tree honey is not described in the descriptive sheets of the main European unifloral honeys, its characteristic physicochemical parameters are given.8 This unifloral honey is very dark, shows high values of water and acidity and a low value of diastase activity. The European Directive concerning honey (2001/110/CE) includes Arbutus honey in a group whose electrical conductivity may go beyond the 0.8 mS cm−1 limit.8

Our previous study has suggested that strawberry tree honey consumption improved antioxidative status, increased serum iron level, decreased activity of liver enzymes, and increased leukocyte and platelet counts.9 A significant decrease in DNA damage in leukocytes of almost all participants who consumed strawberry tree honey was observed after an ex vivo challenge with H2O2 compared to the control group with no honey supplementation.10 Therefore, it is recognised as a health-promoting food due to its strong antioxidant activity mainly attributed to high polyphenol contents. The limited production and respected biological properties make this honey particularly appreciated.11

Although honeys of different botanical origin, namely polyfloral,12 lime,13 sage,14 acacia, sunflower, linden, basil, buckwheat, oilseed rape and goldenrod15 have previously been characterized on the basis of their phenolic fraction, to the best of the authors’ knowledge no previous studies regarding the detailed polyphenolic profile of strawberry tree honey has been published.

The aim of this study was to determine, for the first time, a characteristic polyphenolic profile of strawberry tree honey by the UHPLC-LTQ Orbitrap MS technique. In addition, the TPC and RSA of honey sample were determined.

EXPERIMENTAL

Chemicals

Acetonitrile and acetic acid (both MS grade), gallic acid, phenolic standards, and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were obtained from Sigma–Aldrich (Steinheim, Germany), while 2,2-diphenyl-1-picrylhydrazyl (DPPH•) was purchased from Fluka AG (Buch, Switzerland). Folin–Ciocalteu reagent, hydrochloric acid, methanol (HPLC grade), and sodium carbonate were obtained from Merck (Darmstadt, Germany). Standard solutions and dilutions were prepared using ultrapure water (TKA Germany MicroPure water purification system, 0.055 µS cm⁻¹). Syringe filters (25 mm, nylon membrane 0.45 µm) were purchased from Supelco (Bellefonte, PA, USA). The cartridges for
solid-phase extraction (SPE) were Strata C18-E (500 mg/3 mL) obtained from Phenomenex (Torrance, CA, USA).

**Sample**

Honey was collected in Dalmatia, Pelješac peninsula (Croatia) in 2014. Detailed melisso-palynological and sensory assessments of the honey sample were performed. Apart from strawberry tree pollen found at 7% in the analysed sample, the rest of the identified pollen originated from species belonging to the families Ericaceae, Cistaceae, Fagaceae, Lamiaceae, Oleaceae and Amaryllidaceae. The strawberry tree honey’s botanical origin was additionally confirmed by determining the specific chemical marker homogentisic acid (HGA). The mass fraction of HGA in this honey sample, determined by gas chromatography-mass spectrometry, was 280.6 mg kg\(^{-1}\).\(^{16}\)

**Total phenolic content (TPC)**

The TPC determined by a modified method reported by Gašić et al.\(^{12}\) Fifty µL of honey diluted with ultrapure water (1:10) was mixed with 1.4 mL of ultrapure water and 100 µL of 2 M Folin–Ciocalteu reagent. The reaction mixture was incubated at room temperature for 5 min and mixed with 1.5 mL of sodium carbonate solution (6%). Absorbance was measured at 765 nm after 30 min at 40 °C on Cary 50 UV–Vis spectrophotometer (Varian, Mulgrave, Australia) and the results were expressed as mg of gallic acid equivalents (GAE) per kg of honey.

**DPPH (2,2′-diphenyl-1-picrylhydrazyl) radical scavenging activity (RSA)**

RSA was determined by a method proposed by Tariba Lovaković et al.\(^{11}\) One hundred µL of honey diluted with ultrapure water (1:10) was mixed with 1.9 mL of methanol. Then, 1.5 mL of DPPH methanolic solution (0.18 mM) was added and vortexed vigorously. The mixture was incubated in the dark for 30 min at 25 °C. The absorbance was measured at 517 nm on a Cary 50 UV–Vis spectrophotometer (Varian, Mulgrave, Australia) and the results were expressed as mmol of the Trolox equivalents (TE) per kg of honey.

**Honey sample preparation for the analysis of polyphenolic compounds**

The honey sample (5 g) was mixed with 5 mL of ultrapure water, adjusted to pH 2 with 0.1 % hydrochloric acid and homogenised in an ultrasonic bath (30 min at room temperature). The sample was filtered through filter paper. An SPE cartridge was conditioned (3 mL of acetonitrile and 9 mL of ultrapure water). The filtrate was passed through a cartridge, which was then washed with 6 mL of acidified water to remove all sugars and other polar constituents of honey. The adsorbed compounds were eluted with acetonitrile (1.5 mL). The extracts were filtered through a 0.45 µm PTFE membrane filter before analysis.

**Analysis of polyphenolic compounds**

Analyses were carried out using Accela UHPLC system connected to a hybrid mass spectrometer (LTQ Orbitrap MS) with a HESI (heated electrospray ionization) probe (Thermo Fisher Scientific, Bremen, Germany). The analytical column used for separation was Synergon C18 (100 mm x 2.1 mm, 1.7 µm particle size). The mobile phase consisted of (A) water containing 0.01 % acetic acid and (B) acetonitrile. The gradient program was as follows: 0.0–1.0 min 5 % B, 1.0–16.0 min from 5 to 95 % (B), 16.0–16.1 min from 95 to 5 % (B), then 5 % (B) for 4 min. Flow rate was set to 0.300 mL min\(^{-1}\) and the injection volume 5 µL.\(^{17}\)

The mass spectrometer was operated in negative ionisation mode covering a range from 100 to 1000 m/z. Ion source parameters were determined as previously described by Gašić et al.\(^{14}\) The ions of interest were isolated in the ion trap and activated with 35 % collision energy levels (CEL). Full scan analysis was employed to calculate the monoisotopic mass of
unknown compounds, while the fragmentation pathway was obtained by MS<sup>n</sup>. Phenolics were identified according to the corresponding spectral characteristics: mass spectra, accurate mass, characteristic fragmentation and characteristic retention time.<sup>17</sup>

RESULTS AND DISCUSSION

Polyphenolic profile

Fifty-two polyphenolics (twenty-seven derivatives of phenolic acids and twenty-five flavonoid glycosides and aglycones) were identified according to their [M–H]<sup>−</sup> exact masses (Table I) and fragmentation pattern (Table S-I of the Supplementary material to this communication). The base peak chromatogram of <i>A. unedo</i> honey polyphenolics is shown in Fig. 1.

### TABLE I. Phytochemical fingerprint of strawberry tree (<i>Arbutus unedo</i> L.) honey from Croatia using UHPLC-LTQ Orbitrap MS

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Flavonoids and their derivatives

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The presence of twenty-eight compounds was confirmed by comparison with commercial analytical standards, while the other twenty-four compounds were identified using high resolution mass spectrometry (HRMS) in combination with MS^4 fragmentation. Phenolic acids were represented as hydroxy derivatives of
benzolic and cinnamic acids. In addition to free phenolic acids, some of their derivatives were identified in the form of hexosides (loss of 162 Da) and esters with quinic acid and shikimic acid. In addition to twenty-three identified flavonoids (twelve of them were glycosides and eleven were aglycones), two B type proanthocyanidins were also identified. It is interesting to note that only one flavonoid C-glycoside was identified in this honey sample, namely vitexin (apigenin 8-C-glucoside), and its presence was confirmed by an appropriate standard. The other flavonoid glycosides were identified as O-glycosides, mainly with the glycosidic unit at 3-O position. Two compounds (37 and 40) were identified as 7-O glycosides, showing specific fragmentation to support this claim.18

Fig. 1. Base peak chromatogram of polyphenolics identified in strawberry tree (Arbutus unedo L.) honey (peak number corresponding to Table I).

The base peak chromatogram (Fig. 1) shows the peaks of the most represented phenolic compounds found in the investigated honey. Thus, compound 32 (639 m/z and 6.19 min) showing an MS2 base peak at 315 m/z and MS3 base peak at 300 m/z (Table S-I) was identified as methoxy kaempferol 3-O-(2”-hexosyl)-hexoside. The fragmentation of this compound has already been described in the literature, as it has been identified in honeydew honey from Croatia.17 The second most abundant compound (33) found in investigated honey at a retention time 6.26 min and molecular ion 609 m/z, was identified as kaempferol 3-O-(2”-hexosyl)-hexoside. It gave an MS2 base peak at 285 m/z (deprotonated kaempferol) and a secondary MS2 peak at 447 m/z ([M–H–162]–) and 429 m/z ([M–H–180]–). The presence of fragment ion at 429 m/z ([M–H–162–18]–) indicated that the interglycosidic linkage between the two sugars in this glycoside is type 1→2.19 The detailed fragmentation pathway of compound 33 is depicted in Fig. 2.

Phenolic compounds in strawberry tree honey have previously been identified only in hydrolysed honey extracts by high performance liquid chromatography with a diode array detector (HPLV-DAD) that revealed two phenolic acids and seven flavonoids.20 The identified phenolic compounds that correspond
to those previously described and HGA content higher than 200 mg kg⁻¹, as proposed by Cabras et al.⁶ and confirmed by Brčić Karačonji and Jurica,¹⁶ contributed to the confirmation of the botanical origin of strawberry tree honey despite its low pollen content.

Fig. 2. Proposed fragmentation pathway of compound 33 (kaempferol 3-O-(2″-hexosyl)-hexoside).

**Total phenolic content and radical scavenging activity**

Strawberry tree honey showed high total phenolic content (1038 mg GAE kg⁻¹) and strong DPPH scavenging activity (3.32 mmol TE kg⁻¹) in accordance with previous studies.⁴,⁵,²¹–²⁷ Moreover, strawberry tree honey was the richest in total phenols when compared to other honeys (e.g., eucalyptus, sunflower, lavender, thyme, rosemary, orange, lime, acacia, black locust, coriander, chestnut, asphodel and thistle).²¹,²³–²⁵,²⁷,²⁸

**CONCLUSION**

Hyphenated techniques that combine chromatographic with high resolution and high mass accuracy spectral methods, such as UHPLC-LTQ OrbiTrap MS⁴, are very useful in getting information about phenolic structures with high reliability. Using this technique, large numbers of phenolic acids and their derivatives as well as flavonoid aglycones and flavonoid glycosides in A. unedo honey were determined. The obtained phenolic profile can be used for further analysis of the content of the particular phenolic substances in strawberry tree honey for the purpose of its complete characterization.

Our results indicate that strawberry tree honey has great potential as a health promoting food due to the presence of a large number of phenolic compounds.
Acknowledgements. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant no. 172017 and by the Ministry of Science and Education of the Republic of Croatia, Institutional financing no. 418.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/index, or from the corresponding author on request.

ИЗВОД

ПОЛИФЕНОЛНИ ПРОФИЛ МЕДА ОД ОБИЧНЕ ПЛАНИКИ (Arbutus unedo L.)

ANDREJA JURIĆ1, UROŠ GAŠIN1, IRENA VRKIĆ KARAĆONJI1, KARLO JURICA1

1Institute for Medical Research and Occupational Health, Ksaverska cesta 2, HR-10001 Zagreb, Croatia
2Odveze za fiziološku bijak, hipertenzija i za biološku istraživanja „Сима Шаћковић” – Национални институт Републике Србије, Универзитет у Београду, Булевар десетог Светог Ћеорѓеа 142, 11060, Београд, 3Ministry of the Interior, Ulica grada Vukovara 33, HR-10000 Zagreb, Croatia и 4Хемијски факултет Универзитета у Београду, П. њ. 51,11158 Београд

Упркос многим благотворним здравственим ефektима меда од обичне планике (Arbutus unedo L.), због снажног антиоксидативног деловања које потиче највећим делом од полифенола, детаљни полифенолни профил овог меда није препреко проучен. Циљеви овог рада биле су идентификација полифенолних јединица, одређивање садржаја укупних фенола и процена антиоксидативне активности меда од обичне планике из јужног дела Хрватске. Педесет два полифенола (двадесет и седам фенолних киселина и два десет пет флавоноида) идентификовано је утврђено са хромато-спектрометром (LTO Orbitrap MS). Наши резултати указују на већи садржај укупних фенола (1038 mg еквивалент галне киселине по kg меда), као и знатну антиоксидативну активност (3,32 mmol Trolox еквивалента по kg меда) у поређењу са другим монофлоралним медовима. Због присуства велике количине полифенолних јединица, мед од обичне планике може имати велики потенцијал као храна благотворна за здравље.

(Примљено 17. децембра 2019, ревидирано и прихваћено 30. марта 2020)

REFERENCES

THE PHENOLIC PROFILE OF *Arbutus unedo* L. HONEY


