

Sugar profiles and conductivity of stingless bee honeys from Venezuela

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Summary — The HPLC sugar profiles and the conductivity of 42 stingless bee honey samples from Venezuela were determined. Three of the honey types were produced by *Melipona* species ($n = 24$), while the rest belonged mainly to five *Trigona* species. The main sugars of the *Melipona* honeys were fructose and glucose, with an average of 36.7 g/100 g. The *Trigona* (*Frieseomelitta*) honeys had a completely different sugar spectrum. There the principal sugar was a disaccharide with the retention time of maltose with an average content of 32.3 g/100 g, while fructose and glucose had smaller concentrations: 24.4 and 18.1 g/100 g respectively. The *Melipona* honeys contained also small quantities of maltose and only traces of oligosaccharides, while the *Trigona* honeys had small but measurable amounts of turanose, trehalose and erlose. The conductivity values of the *Melipona* honeys varied from 0.32 to 0.44 mS/cm and were significantly lower than those of the non-*Melipona* ones with minimum and maximum values of 1.04 and 1.07 mS/cm.

honey / sugar / conductivity / HPLC / Meliponinae / Venezuela

INTRODUCTION

The carbohydrates are the major components of honey. The monosaccharides fructose and glucose are the dominant fraction and account for 85-95% of the honeybee honey sugars, the remainder being represented by a number of different di- and trisaccharides (Doner, 1977; Bogdanov and Baumann, 1988).

The sugar composition of stingless bee honeys has been studied occasionally. Nogueira-Neto (1953), Maurizio (1964) and Phadke (1968) presented fructose, glucose and sucrose values for few samples of *Melipona* and *Trigona* honeys. Roubik (1983) measured the sugar concentration of honey in 86 colonies of 27 stingless bee species from Panama, by refractometric Brix units converted into gram equivalents. Klink

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(1992) analysed enzymatically the glucose, fructose and sucrose content of stingless bee honeys from Costa Rica. Vit et al (1994) compared the reducing sugar- and apparent sucrose content of honeys from 40 colonies of nine stingless bee species from Venezuela, using the Codex alimentarius reducing sugar method. The pollen spectrum of these honeys was also investigated (Vit and Ricciardelli D'Albore, 1994).

The sugar profile and the conductivity are those quality criteria, which are best suitable for differentiating different sorts of honey. In the present study we measured the sugar content by HPLC and the conductivity of 42 stingless bee honey samples from Venezuela and discuss their role in elucidating the entomological origin of stingless bee honeys. However, we cannot correlate our measurements to the floral origin of the honeys, due to the very few monofloral samples (Vit and Ricciardelli D'Albore, 1994).

MATERIALS AND METHODS

Honey samples

Forty-two honey samples were extracted from sealed honey pots of stingless bee (Apidae, Meliponinae) hives located in different regions of Venezuela during 1987-1988. Due to the restricted number of honey samples from certain species, we can only refer separately to three *Melipona*: *M compressipes compressipes*, *M favosa favosa*, *M trinitatis* and to one *Trigona* species: *Frieseomelitta aff varia*. The other, non-*Melipona* (mostly *Trigona*) species, have one or two honey samples each and were grouped together. For further details concerning the honeys and their origin, see Vit et al, 1994.

Analysis

HPLC analysis was done according to Bogdanov and Baumann (1988): 10 μ L of filtered 20% (g/vol) honey solutions were directly injected on a 25 x

4.6 cm column filled with 3 mm Spherisorb-Amino mounted on a HP 1084 chromatographic system equipped with a Spectraphysics RI-detector 6040 with 80% acetonitrile as eluent. The temperature of the column and the refractometer was 40 °C. The following sugars were used as sugar standards (g/100 mL): 4% fructose and glucose, and 0.5% each of sucrose, turanose, maltose, trehalose, erlose, melezitose and raffinose. Except for erlose (Senn Chemicals, Dielsdorf, Switzerland), all sugars were purchased from Merck or Fluka (Switzerland). The detecting limit of the sugars is 0.1 g/100 g honey.

Conductivity was measured on 20% (g/g by dry weight) honey solutions at 20 °C (Swiss food manual, 1996) and is expressed in millisiemens (mS) per cm.

The statistical significance of the differences between the various parameters of each honey group was determined with Fischer's least-significant-difference test of a Systat software package.

RESULTS

The results of our analysis are summarised in table I, typical sugar profiles of the two types of HPLC profiles honeys are shown in figure 1.

The *Melipona* honeys had fructose and glucose as predominating sugars and only traces of disaccharides (fig 1 A, table I). On the other hand, the *Trigona* and most of the non-*Melipona* honeys had a completely different sugar spectrum (fig 1, B). There the main sugar is a disaccharide having the retention time of maltose, reaching the concentration of a principal sugar (table I). Besides maltose ($P < 0.001$), turanose, trehalose and erlose ($P < 0.01$) in the *Trigona*- and the non-*Melipona* honeys were also significantly higher than in the *Melipona* honeys. Besides erlose, no other trisaccharide was found in the honeys analysed.

The conductivity of the *Trigona* and the non-*Melipona* honeys was also significantly higher ($P < 0.01$) than that of the *Melipona* honeys.

Table 1. Sugars and conductivity of stingless bee honeys (average sugar values in g/100 g honey, standard deviation in brackets).

	Melipona compressipes	Melipona Trinitatis	Melipona favosa	Frieseomelitta aff varia	Other non-Melipona
<i>n</i>	5	5	14	8	10
Fructose	36.6 (1.0)	36.8 (1.8)	34.8 (2.5)	24.4 (4.1)	30.4 (8.0)
Glucose	36.3 (2.8)	36.9 (2.1)	36.9 (2.7)	18.1 (6.9)	26.4 (8.6)
Sucrose	0.1	–	0.1	0.2	0.1
Turanose	0.1	0.2 (0.1)	0.1	0.4	0.4
Maltose	3.2 (0.6)	2.5 (1.6)	2.8 (1.0)	32.3 (11.4)	19.7 (16.0)
Trehalose	–	–	–	0.2 (0.2)	0.1
Erlöse	0.1 (0.1)	–	–	0.5 (0.3)	0.1
Sum of all sugars	76.3 (3.1)	76.3 (2.8)	74.7 (3.5)	76.0 (2.4)	75.2 (2.0)
Cond mS/cm	0.32 (0.06)	0.32 (0.05)	0.44 (0.33)	1.04 (0.26)	1.07 (0.62)

DISCUSSION

The sugar profile of the *Melipona* honeys is similar to the profile of those *A mellifera* honeys, which are poor in oligosaccharides, eg, rape, sunflower. While the sugar profiles of *Melipona* and *Trigona* honeys are different, their content in reducing sugars is not (Vit et al, 1994). This confirms that the disaccharide, tentatively characterized as maltose, has a reducing capacity. With the amino column used in the present study it is not possible to differentiate between the two reducing disaccharides maltose and maltulose, as both sugars have almost the same retention time (Bogdanov and Baumann, 1988). The identity of the *Trigona* disaccharide should thus be confirmed with other sugar characterization methods, such as ion chromatography (Swallow and Low, 1990) or some other sugar determination

method such as GC-MS or NMR. The origin of the high 'apparent' maltose content of the *Trigona* honey should be investigated in further studies. To our knowledge there is only one finding of a honey with extremely high maltose value: in one Mexican honeydew honey, 23% of maltose were found (C Lüllmann, Bremen, personal communication). The somewhat higher values of turanose and trehalose in the *Trigona* honeys is not a characteristic feature of honeydew honeys (Bogdanov and Baumann, 1988). Erlöse is contained in higher amounts in honeydew than in blossom honeys (Bogdanov and Baumann, 1988; Sabatini et al, 1990) with the exception of some unifloral honeys like acacia and rhododendron (Sabatini et al 1990). However, the honeydew *A mellifera* honeys contained mostly more erlose (average 1.4%) than the *Trigona* honeys (average 0.5%).

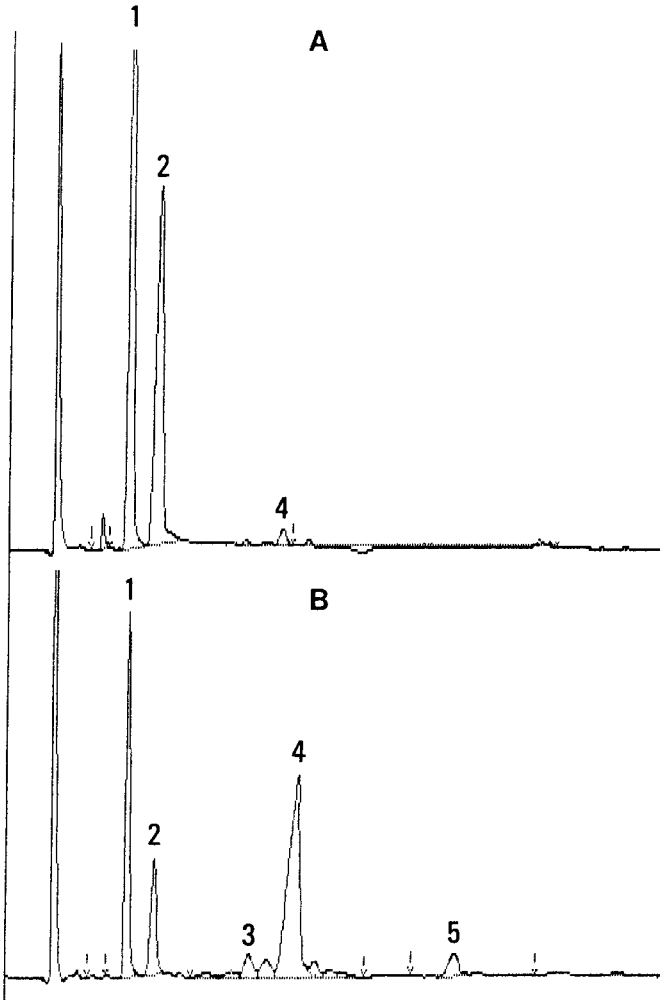


Fig 1. HPLC patterns of stingless bee honeys. **A.** *Melipona* honey, 1. fructose, 2. glucose, 4. maltose. **B.** *Trigona* (*Frieseomelitta*) honey, 1. fructose, 2. glucose, 3. turanose, 4. maltose, 5. erlose. For experimental details, see Methods.

In *A mellifera* honeys the conductivity is a very good criterion of honey origin. Generally, in flower honeys it is lower than in honeydew honeys. The finding of this paper, that the *Melipona* and *Trigona* honeys differ in their conductivity is similar to the finding of our previous paper (Vit et al, 1994), that the ash content of these honey groups is also different. In *A mellifera* honeys it is considered that honeys having conductivity values greater than 0.7 mS/cm

have a honeydew origin (Talpay, 1985). Exceptions are for some monofloral honeys like chestnut and eucalyptus honeys. If this were true also for the stingless bee honeys, then these honeys should be classified as honeydew honeys. However, except in three *Trigona* honeys (Vit and Ricciardelli D'Albore, 1994) no honeydew particles could be found in the *Trigona* and in the non-*Melipona* honeys. To our knowledge honeydew *mellifera* honeys from the tropic

regions of South America have not been characterised. Their nectar seems to be the main honey source (Wilms, 1996).

Whether the high conductivity and 'apparent' maltose values of the *Trigona* and the non-*Melipona* honeys has its explanation in the origin of these honeys or/and in the specific enzymatic transformation of nectar by the *Trigona* species, should be the subject of future investigations.

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Résumé — Profils glucidiques et conductibilité des miels des abeilles sans dard du Vénézuéla. Les profils glucidiques obtenus par HPLC et la conductibilité de 42 échantillons de miels d'abeilles sans dard du Vénézuéla ont été déterminés. Les miels provenaient principalement de trois *Melipona* ($n = 24$), les autres étant produits par cinq espèces de *Trigona* (non-*Melipona*), principalement *Frieseomelitta* ($n = 8$). Les résultats sont présentés dans le tableau I, les profils glucidiques typiques sur la figure 1. La composition glucidique des miels de *Melipona* est uniforme : le fructose et le glucose représentent 96 % des sucres. La teneur moyenne en fructose varie entre 34,8 et 36,8 g/100 g, celle du glucose entre 36,3 et 36,9 g/100 g. Le maltose n'est présent qu'en petites quantités et les oligosaccharides à l'état de traces. Le spectre glucidique des autres miels (*Frieseomelitta* et autres non-*Melipona*) est totalement différent. Le sucre principal est un dissaccharide qui a le même temps de rétention que le maltose. Sa teneur moyenne est de 32,3 g (*Frieseomelitta*) et de 19,7 g (autres non-

Melipona). Le fructose et le glucose ont des teneurs moyennes plus faibles, respectivement de 24,4 et 18,1 g/100 g (*Frieseomelitta*), 30,4 et 26,4 g/100 g (autres non-*Melipona*). Les miels de *Melipona* ne renferment que de petites quantités de maltose et des traces d'oligosaccharides ; les miels des non-*Melipona* renferment de petites quantités des oligosaccharides suivants : turanose, tréhalose et erlose. La conductibilité des différents miels de *Melipona* n'est pas significativement différente ; les valeurs moyennes sont comprises entre 0,32 et 0,44 mS/cm. Elles est en revanche significativement plus basse que celle des miels de *Frieseomelitta* (1,04 en moyenne) et des autres non-*Melipona* (1,07).

miel / glucide / conductibilité / HPLC / Meliponinae / Vénézuéla

Zusammenfassung — HPLC Profile und Leitfähigkeit von venezuelischen Honigen aus stachellosen Bienen (Hymenoptera, Apidae). Die HPLC Profile und die Leitfähigkeit von 42 Honigen aus Völkern stachelloser Bienen wurden bestimmt. Die Honige stammten hauptsächlich von 3 *Melipona* ($n = 24$) und 5 *Trigona* Arten, hauptsächlich *Frieseomelitta* ($n = 8$). Die Resultate der Analysen sind in Tabelle I, typische HPLC Profile sind in Abb 1 wiedergegeben. Die Zuckerzusammensetzung der *Melipona* Honige war praktisch gleich: 96% aller Zucker waren Fruktose and Glukose. Der Durchschnittsgehalt der Fruktose variierte in den 3 *Melipona* Honigen zwischen 34.8 und 36.8 g/100 g, derjenige von Glukose zwischen 36.3 und 36.9 g/100 g Honig. Es gab dort nur kleine Mengen von Maltose und Spuren von Oligosacchariden. Das Zuckerspektrum der *Frieseomelitta* - und der übrigen nicht-*Melipona* - Honige war ganz verschieden. Hauptzucker mit Durchschnittsgehalt von 32.3 g/100 g (*Frieseomelitta*) und 19.7 g/100 g (übrige nicht-*Melipona*) war ein Disaccharid mit der

Retentionszeit von Maltose. Fruktose und Glukose hatten kleinere durchschnittliche Konzentrationen: 24.4 und 18.1 g/100 g (*Frieseomelitta*), 30.4 und 26.4 g/100 g (übrige nicht-*Melipona*). Die nicht-*Melipona* Honige enthielten auch kleine Mengen der Oligosaccharide Turanose, Trehalose und Erlöse. Die Leitfähigkeit der verschiedenen *Melipona* Honige war nicht signifikant unterschiedlich, wobei die Durchschnittswerte zwischen 0.32 bis 0.44 mS/cm variierten. Die Leitfähigkeit der *Trigona* und nicht-*Melipona* Honige war signifikant höher: Durchschnitt 1.04 (*Frieseomelitta*) und 1.07 mS/cm (übrige nicht-*Melipona*).

Honig / Zucker / HPLC / Leitfähigkeit /Meliponinae / Venezuela

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