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Analytical Methods

HPAEC-PAD oligosaccharide analysis to detect adulterations of honey with sugar syrups

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Abstract

A method previously validated in our laboratory to study the oligosaccharide profile of honey was used in this work to detect adulterations of corn syrups (CS) and high fructose corn syrups (HFCS) in genuine honey samples. High molecular weight oligosaccharides (DP3-DP16) of 9 sugar syrups and 25 honey samples were analysed by HPAEC-PAD. Samples were previously treated with activated charcoal to remove mono and disaccharides. This method enabled the detection of honey adulterations with CS down to 5%. Adulterations of honeys with HFCS with different degrees of isomerisation (20% and 40%) were also detected.

Keywords: Oligosaccharides; Honey; Syrup; Adulteration; HPAEC-PAD

1. Introduction

Honey is a natural food elaborated by honeybees and mainly constituted by carbohydrates. It has been considered to be a valuable product since ancient times and different properties such as prebiotic (Sanz et al., 2005), antioxidant (Frankel, Robinson, & Berenbaum, 1998), antibacterial (Weston & Brocklebank, 1999) and antimutagenic properties (Wang, Andrae, & Engeseth, 2002), among others, have been attributed to its constituents.

As a result of the high nutritional value and the unique flavour characteristics of natural bee honey, its cost is much greater than that of any other sweetener and it can, therefore, be a target of adulteration for economic gains (Sivakesava & Irudayaraj, 2002). Some honey frauds involve the addition of preparations based on simple and complex sugars which can be modified to simulate the natural carbohydrate profile of honey. Inexpensive sweetening products such as corn syrups (CS), invert syrups (IS) or high fructose corn syrups (HFCS), among others, have been found to be employed to that aim (Swallow & Low, 1994). However, the variations in honey carbohydrates and the similarities with sugar syrup composition make it difficult to detect these adulterations (Kushnir, 1979).

Recently, guaranteeing honey quality is becoming increasingly important for consumers, producers and regulatory authorities. The European Commission (Council directive 2001/110/EC) encourages the use of analytical methods to determine the authenticity of honeys. Although different procedures such as isotopic analysis (Cotte, Casabianca, Chardon, Lheritier, & Grenier-Loustalot, 2003; White, 1992) or spectroscopic (Kelly, Downey, & Fouratier, 2004; Kelly, Petisco, & Downey, 2006; Sivakesava & Irudayaraj, 2002) and calorimetric methods (Cordella et al., 2002) have been used to determine honey authenticity, several authors have proposed studying carbohydrates, the main constituents of honey, by chromatographic techniques (Cordella, Militao, Clement, Drajnudel, & Cabrol-Bass, 2005; Low & South, 1995; Swallow & Low, 1994). Most of these works have aimed to determine honey authenticity in terms of its botanical or geographical origin

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(Cotte et al., 2003; Peña Crecente & Herrero Latorre, 1993), whereas studies related to honey adulteration with different syrups are quite scarce (Serra Bonvehi & Gómez Pajuelo, 1986) and mainly focused on studying mono-, di- and trisaccharide relationships (Horvath & Molnar-Perl, 1998).

Different chromatographic techniques such as HPLC (Robinson, Bergstrom, Seymour, & Thomas-Oates, 2007) or GC–MS (Sanz, Sanz, & Martinez-Castro, 2004; Terrab, Vega-Pérez, Diez, & Heredia, 2001) have been used for carbohydrate analysis. HPAEC-PAD is one of the most useful techniques for oligosaccharide determination, although the large amounts of monosaccharides (60–70%) and the relatively high contents of disaccharides (10%) in honey make these analyses difficult.

A simple and easy method based on activated charcoal treatment to fractionate honey carbohydrates followed by analysing the oligosaccharide fraction by HPAEC-PAD has been recently developed in our laboratory (Morales, Sanz, Olano, & Corzo, 2006). In the present work, the utility of this method to detect honey adulterations with corn syrups (CS) and high fructose corn syrups (HFCS) is evaluated.

2. Materials and methods

2.1. Standards

Malto-oligosaccharides from glucose (G1) to maltoheptaose (G7) were obtained from Sigma (St. Louis, MO, USA).

2.2. Samples

Twenty-five honey samples were used in this study: 17 artisanal honeys directly obtained from beekeepers and eight commercial honeys purchased at local markets.

CS and HFCS with 20% and 40% of isomerisation (20HFCS and 40HFCS, respectively) were a gift from Cerestar S.A. (Barcelona, Spain); HFCS with 80% isomerization (80HFCS) was a donation from Moreno Dolera S.A. (Murcia, Spain). Also, five commercial syrups (S1–S5) were purchased at local markets.

Adulterated samples were prepared by adding 5%, 10% and 20% of syrup to an artisanal honey (H1).

2.3. Oligosaccharide analysis

2.3.1. Sample preparation

Oligosaccharides were extracted from honeys, adulterated honeys and syrups following the method of Morales et al. (2006). In brief, 0.5 g of honey was dissolved in 100 mL ethanol: water 10:90 (v/v) and stirred with 3 g activated charcoal Darco G60, 100 mesh (Sigma) for 30 min to remove mono- and disaccharides. This mixture was filtered through Whatman No. 1 filter paper under vacuum and the activated charcoal was further washed with 25 mL ethanol: water 10:90 (v/v). Oligosaccharides adsorbed onto activated charcoal were extracted by stirring for 30 min in 100 mL ethanol:water 50:50 (v/v). The activated charcoal was removed by filtering as previously described and the ethanol was evaporated under vacuum at 30 °C. The sample was dissolved with 5 mL of deionised water and filtered through 0.22 μm filters (Millipore).

2.3.2. High performance anion-exchange chromatography-pulsed amperometric detection (HPAEC-PAD)

Oligosaccharides of honey samples were analysed using a Dionex DX-300 equipment containing a gradient pump and an eluent degas module. Separation of carbohydrates was carried out on a CarboPac PA 100 guard column (4 × 50 mm) and a CarboPac PA-100 anion-exchange column (4 × 250 mm) and 20 μL was injected. The flow rate was 0.7 mL min^{-1} and carbohydrates were detected by pulsed amperometric detection (PAD) (Concorde Waters) with a gold working electrode and a hydrogen reference electrode using triple pulsed amperometry with the following potentials and durations: $E_1 = +0.15$ V ($t_1 = 400$ ms), $E_2 = +0.75$ V ($t_2 = 200$ ms) and $E_3 = -0.8$ V ($t_3 = 200$ ms). Sampling time (t_s) was 20 ms. Carbohydrates were eluted by a gradient prepared from 1 M sodium acetate (eluent A), deionized water (eluent B) and 1 M sodium hydroxide (eluent C). Eluent C was constant (10%) during the whole process and eluent A changed from 3% to 10% at 30 min and increased to 20% at 70 min. This proportion was kept constant till 85 min, when it recovered the initial conditions.

Quantification of malto-oligosaccharides were carried out by an external standard method using a mixture containing from maltotriose to maltoheptaose (G3–G7) in a concentration from 0.0156 to 0.778 mg mL^{-1} each. Malto-oligosaccharides from G8 to G16 were quantified using the G7 calibration curve due to lack of commercial standards.

All analyses were carried out in duplicate.

3. Results and discussion

Chromatographic profiles of oligosaccharides obtained after charcoal treatment of CS, 20HFCS, 40HFCS and 80HFCS were studied by HPAEC-PAD (Fig. 1). CS profile showed a high number of oligosaccharides. Peaks with retention times from 10 to 45 min were identified as maltose (G2), maltotriose (G3), maltotetraose (G4), maltopentaose (G5), maltohexaose (G6) and maltoheptaose (G7) by comparison with commercial standards. Peaks with retention times longer than 45 min, could be assigned to malto-oligosaccharides from G8 to G16, whereas peaks eluting among malto-oligosaccharides could correspond to branched glucooligosaccharides from starch. These oligosaccharides can present linkages different from $\alpha 1 \rightarrow 4$ which are not hydrolysed by the enzymes used during the conversion of corn starch to corn syrup (Low, 1998; Reeve, 1992). In 20HFCS, malto-oligosaccharides from G2 to G9

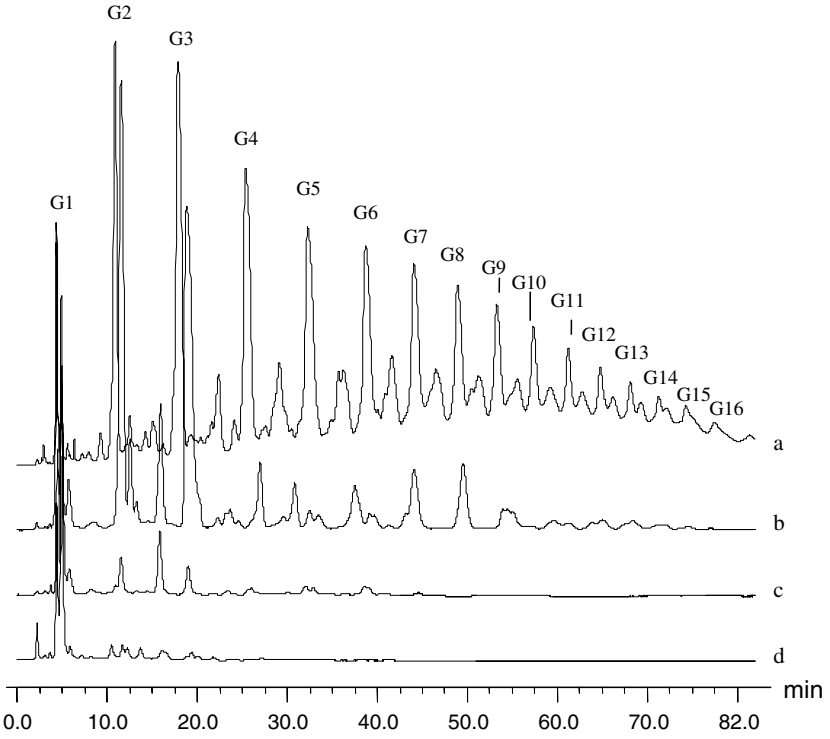

Fig. 1. HPAEC-PAD chromatographic profiles of oligosaccharide fraction of CS (a), 20HFCS (b), 40HFCS (c) and 80HFCS (d). G1: glucose; G2: maltose; G3: maltotriose; G4: maltotetraose; G5: maltopentaose; G6: maltohexaose; G7: maltoheptaose; G8–G16: maltrodextrins from 8 until 16 units of glucose.

were easily detected although peaks with minor areas corresponding to G10–G15 could also be appreciated. According to our previous work (Morales et al., 2006), charcoal treatment removed 86% of disaccharides from samples; therefore, the presence of a high amount of G2 in both CS and 20HFCS indicates the high initial content of disaccharides in these syrups.

Simpler chromatographic profiles were observed in 40HFCS and 80HFCS samples where only oligosaccharides from G2 to G7 were found. The small number of higher oligosaccharides in these two syrups can be the result of the isomerisation and hydrolysis of oligosaccharides during the production of HFCS (Low, 1998).

Quantification of malto-oligosaccharides (g/100 g product) for each analysed syrup was carried out (Table 1). G2 was not quantified in this study because it had been partially removed during the extraction of oligosaccharides. The greatest value of these oligosaccharides was found for CS followed by 20HFCS with malto-oligosaccharides G7 and G8 in the highest proportion. In 40HFCS and 80HFCS samples, only small amounts of malto-oligosaccharides from G3 to G6 could be quantified.

Similarly, HPAEC-PAD oligosaccharide profiles of five commercial syrups of unknown origin (S1–S5), obtained after charcoal treatment, were also studied. Chromatographic profiles of S1, S4 and S5 were comparable to that of CS, whereas chromatographic profiles of S2 and S3 could correspond to HFCS with a low level of isomerization. Minimum, maximum and mean values of malto-oligosaccharide contents found in these syrups are shown in Table 2. Oligosaccharides with a degree of polimerization (DP) from 3 to 16 (G3–G16) were quantified in all samples analysed. In

Table 1
Malto-oligosaccharide content (g/100 g of sample) found in CS, 20HFCS, 40HFCS and 80HFCS samples analysed by HPAEC-PAD

Syrups	Malto-oligosaccharides (g/100 g of sample)														
	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15	G16	Total
CS[a]	1.14	1.16	2.22	2.78	4.85	3.80	2.94	2.08	1.39	1.12	0.78	0.63	1.09	0.54	26.52
20[b]HFCS[c]	1.22	0.21	0.32	0.71	2.09	1.91	0.38	0.06	0.21	0.31	0.38	0.18	0.05	tr	8.03
40HFCS	0.08	0.06	0.07	0.14	tr	tr	–	–	–	–	–	–	–	–	0.35
80HFCS	0.01	0.01	0.03	0.01	tr	tr	–	–	–	–	–	–	–	–	0.06

All samples were analysed by duplicate. tr: traces; (–): not detected.

[a] CS: corn syrup.

[b] % of isomerization.

[c] HFCS: high fructose corn syrup.

Table 2
Minimum, maximum and mean malto-oligosaccharide content (g/100 g of sample) of commercial syrups determined by HPAEC-PAD

	Malto-oligosaccharides (g/100 g of sample) (commercial syrups $n = 5$)													
	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15	G16
Minimum	0.50	0.46	2.00	2.75	2.67	0.77	0.73	1.14	0.80	0.59	0.47	0.30	0.30	0.29
Maximum	1.04	1.32	3.74	3.57	4.74	4.01	2.93	2.25	1.04	1.01	0.77	0.88	0.82	0.53
Mean	0.83	1.04	2.78	3.15	3.25	3.08	2.21	1.59	0.92	0.81	0.65	0.60	0.58	0.45
SD[a]	0.23	0.40	0.87	0.34	0.99	1.55	1.02	0.47	0.10	0.18	0.14	0.25	0.21	0.11

All samples were analysed by duplicate.
[a] SD: standard deviation.

general, the malto-oligosaccharides found in greater amount (G5–G8) were the same as those of CS and 20HFCS. Besides, the G16 content ranging from 0.29 to 0.53 g/100 g product could even be quantified in these samples.

In order to study the oligosaccharide composition of honeys, 25 honey samples were analysed by HPAEC-PAD after charcoal treatment. Peaks corresponding to oligosaccharides with retention times similar to malto-oligosaccharides were quantified and minimum, maximum and mean values are summarised in Table 3. Only oligosaccharides with retention times similar to G3–G7 were detected and their contents were relatively low and variable among samples.

An artisanal honey (H1) was selected as a representative sample and was intentionally adulterated with different percentages (5%, 10% and 20%) of CS, 20HFCS, 40HFCS and 80HFCS, to determine if it was possible to detect the addition of these syrups to honey. Fig. 2 shows the chromatographic profiles of honey H1 and H1 adulterated with 20% of CS, 20HFCS and 40HFCS. Important changes were observed in the oligosaccharide profiles of honey adulterated with 20% CS (Fig. 2a), even with only 5% addition. A high increase in oligosaccharides from G2 to G6 was detected and also malto-oligosaccharides from G7 to G16 could be observed. Adulterations with 20HFCS (Fig. 2b) could also be noticed from oligosaccharide profiles; malto-oligosaccharides from G3 to G15 increased with the addition of this syrup. However, slighter variations could be observed after adulterations of honey with 40HFCS (Fig. 2c) and no changes were detected when honey H1 was supplemented with 80HFCS, due to the low amount of oligosaccharide present in the syrup. Table 4 shows the content (g/100 g of product) of malto-oligosaccharides found in the adulterated honey. When H1 was adulterated with CS, total malto-oligosaccharide content increased from 0.09 g/100 g product in genuine honey to 0.85 g/100 g product in 5% adulteration and these carbohydrates steadily increased to reach values of 1.99 and 9.79 for additions of 10% and 20%, respectively. Oligosaccharide contents were lower for samples adulterated with HFCS. Adulterations of H1 carried out using 20HFCS increased the content of total malto-oligosaccharides from 0.36 g/100 g product (5% addition) to 1.39 g/100 g product (20% addition), while these carbohydrates increased slightly with 10% and 20% adulterations of 40HFCS (to 0.12 and 0.15 g/100 g product, respectively). No changes in malto-oligosaccharide content were observed when 80HFCS was used as an adulterant.

Since studies of adulteration were carried out in only one sample, in order to have more information about the possible oligosaccharide content of adulterated honeys, a mathematical simulation was performed. With this purpose, the maximum content of malto-oligosaccharides from G3 to G7 found in the analysed honey samples (Table 3) was considered as a starting point and additions of the corresponding percentages of each syrup were carried out depending on the adulteration; i.e. for an adulteration of 5%, the 5% of oligosaccharide content in syrup was added to the 95% maximum content of oligosaccharides in honeys. CS and 20HFCS were easily detected when a calculated contribution of 5% was assumed for these syrups, while 40HFCS was only detected for contributions of 20% or higher using concentration values of malto-oligosaccharide G6.

Following the same procedure as that mentioned above, a mathematical simulation of adulteration of honeys with commercial syrups (S1–S5) was also carried out. Contribution of G3–G16 was calculated assuming 5% and 10% additions of the syrups. Even for syrups with the lowest

Table 3
Malto-oligosaccharide content (g/100 g of sample), determined by HPAEC-PAD, in artisanal and commercial honeys

	Malto-oligosaccharides (g/100 g of sample) (honey samples $n = 25$)				
	G3	G4	G5	G6	G7
Minimum	0.00	0.00	0.00	0.00	0.00
Maximum	0.05	0.02	0.04	0.02	0.02
Mean	0.02	0.01	0.03	0.01	0.00
SD[a]	0.01	0.00	0.02	0.01	0.01

All samples were analysed by duplicate.
[a] SD: standard deviation.

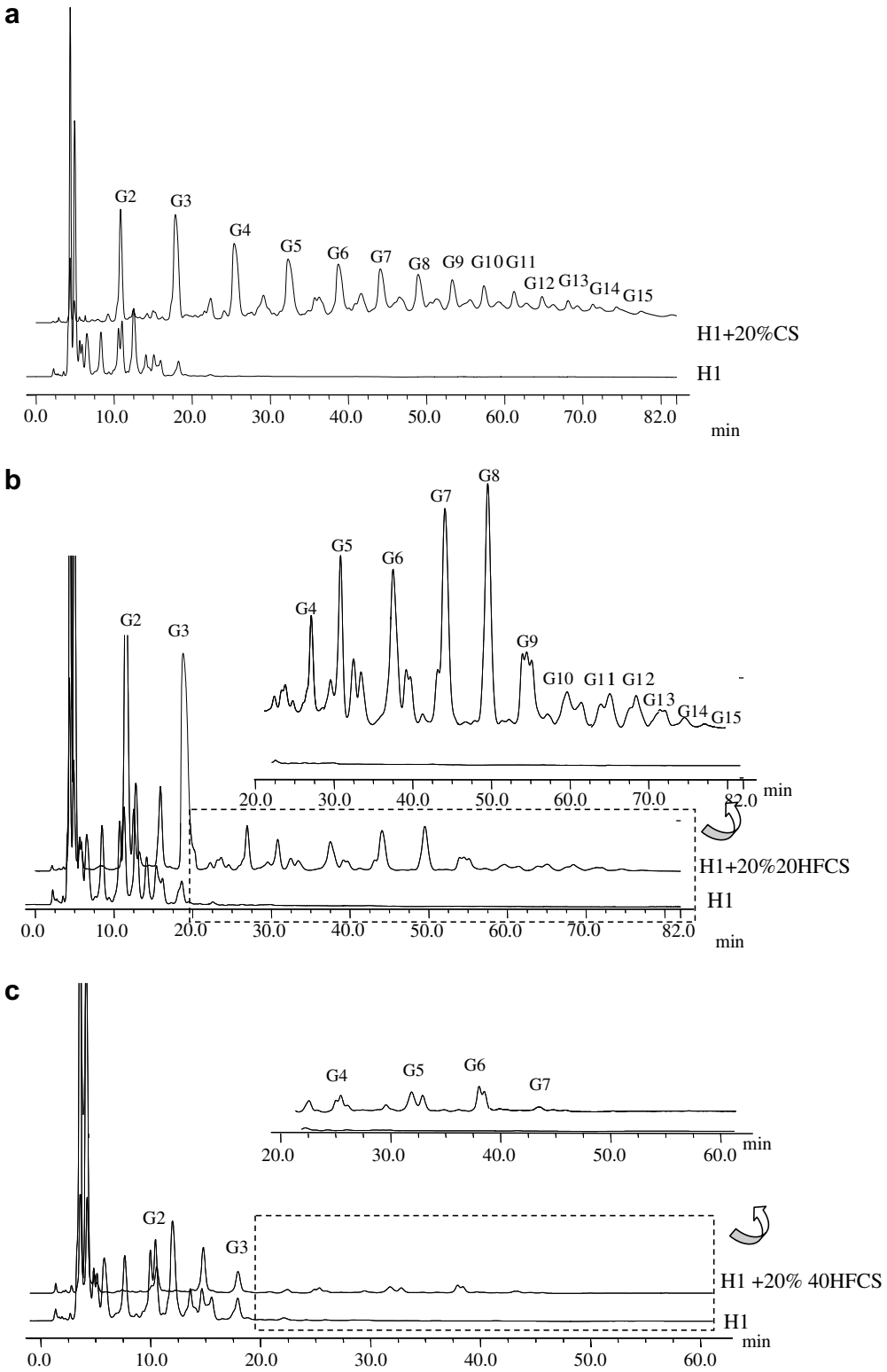

Fig. 2. HPAEC-PAD chromatographic profiles of oligosaccharide fraction of a honey sample H1 and H1 adulterated with 20% of (a) CS; (b) 20HFCS and (c) 40HFCS.

concentration of each malto-oligosaccharide, calculated values for G8–G16 (not present in honeys) could be detected, while G3–G7 concentrations presented a large increase compared with those of non adulterated honeys.

Therefore, the analysis of malto-oligosaccharides by HPAEC-PAD is a useful tool to detect adulterations of honey with industrial syrups (CS and low isomerizated HFCS), and is less time consuming and less expensive than

Table 4
Content of malto-oligosaccharides (g/100 g of sample) in genuine and adulterated honey samples

Samples	Adulteration (%)	Malto-oligosaccharides (g/100 g of sample)													
		G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15	Total
Honey H1		0.04	0.01	0.03	0.01	–	–	–	–	–	–	–	–	–	0.09
CS[a]	5	0.18	0.22	0.24	0.12	0.09	–	–	–	–	–	–	–	–	0.85
	10	0.55	0.43	0.34	0.22	0.24	0.13	0.08	tr[a]	–	–	–	–	–	1.99
	20	0.79	0.85	1.40	1.31	2.20	1.43	0.88	0.51	0.27	0.15	tr	–	–	9.79
20[b]HFCS[c]	5	0.10	0.02	0.04	0.03	0.09	0.07	0.01	tr	tr	tr	–	–	–	0.36
	10	0.16	0.04	0.06	0.08	0.20	0.17	0.03	tr	tr	tr	tr	–	–	0.74
	20	0.25	0.05	0.09	0.14	0.37	0.34	0.07	tr	0.03	0.05	tr	tr	tr	1.39
40HFCS	5	0.04	0.01	0.03	0.01	–	–	–	–	–	–	–	–	–	0.09
	10	0.05	0.02	0.03	0.02	tr	–	–	–	–	–	–	–	–	0.12
	20	0.05	0.02	0.04	0.04	tr	–	–	–	–	–	–	–	–	0.15
80HFCS	5	0.04	0.01	0.02	0.01	–	–	–	–	–	–	–	–	–	0.08
	10	0.04	0.01	0.03	0.01	tr	–	–	–	–	–	–	–	–	0.09
	20	0.04	0.01	0.03	0.01	tr	–	–	–	–	–	–	–	–	0.09

All samples were analysed by duplicate. tr: traces; (–): not detected.
[a] CS: corn syrup.
[b] % of isomerization.
[c] HFCS: high fructose corn syrup.

other methodologies previously described in the literature (Sivakesava & Irudayaraj, 2002; Swallow & Low, 1994).

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References

Cordella, C., Antinelli, J. F., Aurieres, C., Faucon, J. P., Carbol-Bass, D., & Sbirrazzuoli, N. (2002). Use of differential scanning calorimetry (DSC) as a new technique for detection of adulteration in honeys. I. Study of adulteration effect on honey thermal behavior. *Journal of Agricultural and Food Chemistry, 50*(1), 203–208.

Cordella, C., Militao, J. S. L. T., Clement, M. C., Drajnudel, P., & Cabrol-Bass, D. (2005). Detection and quantification of honey adulteration via direct incorporation of sugar syrups or bee-feeding: Preliminary study using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) and chemometrics. *Analytica Chimica Acta, 531*(2), 239–248.

Cotte, J. F., Casabianca, H., Chardon, S., Lheritier, J., & Grenier-Loustalot, M. F. (2003). Application of carbohydrate analysis to verify honey authenticity. *Journal of Chromatography, 1021*, 145–155.

Council Directive 2001/110/EC of 20 December 2001 relating to honey. EU Council (2002) Official Journal of European Communities L10, pp. 47–52.

Frankel, S., Robinson, G. E., & Berenbaum, M. R. (1998). Antioxidant capacity and correlated characteristics of 14 unifloral honeys. *Journal of Apicultural Research, 37*(1), 27–31.

Horvath, K., & Molnar-Perl, I. (1998). Simultaneous GC–MS quantitation of *o*-phosphoric, aliphatic and aromatic carboxylic acids, proline, hydroxymethylfurfurol and sugars as their TMS derivatives: In honeys. *Chromatographia, 48*(1/2), 120–126.

Kelly, J. F. D., Downey, G., & Fouratier, V. (2004). Initial study of honey adulteration of honey by sugar solutions using midinfrared (MIR) spectroscopy and chemometrics. *Journal of Agricultural and Food Chemistry, 52*(1), 33–39.

Kelly, D., Petisco, C., & Downey, G. (2006). Potential of near infrared transflectance spectroscopy to detect adulteration of Irish honey by beet invert syrup and high fructose corn syrup. *Journal of Near Infrared Spectroscopy, 14*(2), 139–146.

Kushnir, I. (1979). Sensitive thin-layer chromatographic detection of high fructose corn sirup and other adulterants in honey. *Journal of the Association of Official Analytical Chemists, 62*(4), 917–920.

Low, N. H. (1998). Oligosaccharides analysis. In P. R. Ashurst & M. J. Dennis (Eds.), *Analytical methods on food authentication* (1a Ed., pp. 97–136). London: Blackie Academic and Professional Ed.

Low, N. H., & South, W. (1995). Determination of honey authenticity by capillary gas chromatography. *Journal of Association of Official Analytical Chemists, 78*(5), 1210–1218.

Morales, V., Sanz, M. L., Olano, A., & Corzo, N. (2006). Rapid separation on activated charcoal of high oligosaccharides in honey. *Chromatographia, 64*(3/4), 233–238.

Peña Crecente, R., & Herrero Latorre, C. (1993). Pattern recognition analysis applied to classification of honeys from two geographic origins. *Journal of Agricultural and Food Chemistry., 41*, 560–564.

Reeve, A. (1992). Starch hydrolysis: Process and equipment. In F. W. Schenk & R. F. Hebeda (Eds.), *Starch hydrolysis products* (pp. 79–120). VCH Publishers Inc.

Robinson, S., Bergstrom, E., Seymour, M., & Thomas-Oates, J. (2007). Screening of underivatized oligosaccharides extracted from the stems of Triticum aestivum using porous graphitized carbon liquid chromatography-mass spectrometry. *Analytical Chemistry, 79*(6), 2437–2445.

Sanz, M. L., Polemis, N., Morales, V., Corzo, N., Drakoularakou, A., Gibson, G. R., et al. (2005). In vitro investigation into the potential prebiotic activity of honey oligosaccharides. *Journal of Agricultural and Food Chemistry, 53*(8), 2914–2921.

Sanz, M. L., Sanz, J., & Martinez-Castro, I. (2004). Gas chromatographic–mass spectrometric method for the qualitative and quantitative determination of disaccharides and trisaccharides in honey. *Journal of Chromatography A, 1059*, 143–148.

Serra Bonvehi, J., & Gómez Pajuelo, A. (1986). Determination of adulteration in honey. *Alimentación, Equipos y Tecnología, 5*(4), 143–147.

Sivakesava, S., & Irudayaraj, J. (2002). Classification of simple and complex sugar adulterants in honey by mid-infrared spectroscopy. *International Journal of Food Science and Technology, 37*(4), 351–360.

Swallow, K. W., & Low, N. H. (1994). Determination of honey authenticity by anion exchange chromatography. *Journal of Association of Official Analytical Chemists, 77*, 695–702.

Terrab, A., Vega-Pérez, J. M., Diez, M. J., & Heredia, F. J. (2001). Characterization of Northwest Moroccan honeys by gas chromatographic–mass spectrometric analysis of their sugar contents. *Journal of Science and Food Agriculture, 82*, 179–185.

Wang, X. H., Andrae, L., & Engeseth, N. J. (2002). Antimutagenic effect of various honeys and sugars against Trp-p-1. *Journal of Agricultural and Food Chemistry, 50*(23), 6923–6928.

Weston, R. J., & Brocklebank, L. K. (1999). The oligosaccharide composition of some New Zealand honeys. *Food Chemistry, 64*, 33–37.

White, J. W. Jr., (1992). Internal standard stable carbon isotope ratio method for determination of C4 plant sugar in honey: Collaborative study and evaluation of improved protein preparation procedure. *Journal of the AOAC International, 75*(3), 543–548.