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Inositols and carbohydrates in different fresh fruit juices

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Abstract

Juices from different fresh fruits (grapefruit, lemon, lime, mandarin, orange, guava, kiwifruit, apple, mango, peach, pear, pineapple, banana, bilberry, raspberry, strawberry, redcurrant and grape) were prepared in the laboratory. Inositols were analysed by GC as their trimethylsilyl derivatives; their identities were confirmed by GC-MS and retention of pure standards. *Myo*-inositol was present in most juices, (excepting those of redcurrant and banana, where no inositols were detected) varying from traces in raspberry up to 153 mg/100 g in kiwifruit. *Chiro*-inositol was present in all examined citrus juices and ranged from 7 mg/100 g in lemon up to 108 mg/100 g in mandarin. *Scyllo*-inositol was present in both grapes and citrus juices, appearing as traces in orange and attaining 15 mg/100 g in grapefruit.

Keywords: Fruit juices; *Myo*-inositol; *Chiro*-inositol; *Scyllo*-inositol

1. Introduction

Nutritionally, fruit juices are an important source of energy in the form of sugars glucose, fructose and sucrose being the most abundant in fruit and fruit products. It is well known that the compositions of fruit juice vary according to varieties or species of fruit, with maturity, and as a result of environmental and climatic effects of the growing season (Brown, Katz, & Cohen, 1988). Inositols are present in the vegetable kingdom as minor components of plants, and some of them have positive physiological effects in humans (McLaurin, Golomb, Jurewicz, Antel, & Fraser, 2000; Nestler, Jakubowicz, Reamer, Gunn, & Allan, 1999).

Myo-inositol is a minor component of fruits (Belitz & Grosch, 1997; Bieleski, Clark, & Klages, 1997). *Scyllo*-inositol, which has been detected in grapes, has been proposed, along with *myo*-inositol, to control the genuineness of the concentrated rectified grape must (Monetti, Versini, Dalpiaz, & Reniero, 1996; Versini, dalla Serra, & Margheri, 1984); this proposal has been partially adopted by the EC (European Union Regulation, 1990) and only the presence of *myo*-inositol has been finally considered as a quality parameter. *Myo*-inositol content and *myo*-inositol/fructose ratio have been found to provide information on the quality and genuineness of orange juice (Villamiel, Martínez-Castro, Olano, & Corzo, 1998). To the best of our knowledge, the presence of other inositols has not been reported in fruit juices, although *scyllo*- and *chiro*-inositol have been detected in ethanol stillage from citrus waste (Dowd, Johansen, Cantarella, & Reilly, 1994).

In the present work the occurrence and contents of inositols in fresh juices from different fruits have been investigated in an attempt to contribute to the knowledge of fresh juice composition. Major carbohydrates have also been determined.

2. Materials and methods

2.1. Samples

Good quality ripe fruits were purchased at local markets. Citrus juices (grapefruit, lemon, lime, mandarin and orange) were prepared using a domestic juicer (Braun Citromatic). Guava, kiwifruit, apple, mango,

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peach, pear, pineapple, banana, bilberry, raspberry, strawberry, redcurrant and grape juices were crushed after removing skins (and seeds when necessary) and centrifuged at 10,000 rpm during 20 min at 5 °C. The supernatant was filtered to remove any suspended solid material. Every juice was prepared from several individual fruits.

2.2. Chromatographic analysis

0.5 ml of juice and 0.7 ml of phenyl-β-D-glucoside (1 mg/ml) were mixed and diluted to 25 ml with 70% methanol; 0.5 ml of the solution was evaporated under vacuum. Sugar oximes were formed using 2.5% hydroxylamine chloride in pyridine and heated to 75 °C for 30 min. After reaction, samples were persilylated using hexamethyldisilazane (HMDS) and trifluoroacetic acid (TFA) at 45 °C for 30 min (Brobst & Lott, 1966) and centrifuged at 7000*g* for 5 min at 5 °C (Li & Schumann, 1981). Gas chromatographic separation was carried out using a SPB-1 fused silica capillary column, 25 m × 0.25 mm i.d., 0.25 μm film thickness from Supelco (Bellefonte, PA), installed in a Perkin–Elmer Autosystem GC equipped with a flame ionisation detector (Perkin–Elmer, Norwalk, Con). The temperatures of injector and detector were 250 and 280 °C, respectively; the oven temperature was held at 200 °C for 20 min, programmed to 270 °C at a heating rate of 15 °C min^{-1} and held for 40 min. Nitrogen was used as carrier gas. Injections were made in split mode, with a split flow of 20 ml/min. Chromatographic peaks were measured using a ChromCard 1.20 acquisition system (CE Instruments, Milan, Italy). GC-MS analysis was carried out using the same capillary column, installed in a HP5890 series with a MD 5971 quadrupole mass detector (both from Hewlett-Packard, Palo Alto, CA, USA) working in EI mode at 70 eV and using helium as carrier gas. Chromatographic conditions were the same as above. Chromatographic peaks were measured using HPChem Station software (Hewlett-Packard, Palo Alto, CA, USA).

Kovats retention indices (*I*) were calculated from the retention times of TMS oximes of disaccharides and suitable *n*-alkanes. Hold-up time was measured by injecting *n*-pentane.

Quantitative values were calculated from FID peak areas. Standard solutions, containing different proportions of each compound, were prepared to calculate response factors (RF) relative to internal standard over the expected range. Detection limit was calculated following the method described by Foley and Dorsey (1984).

3. Results and discussion

Quantitative data (g/100 ml) of major carbohydrates, along with the ratio glucose/fructose in the different juices studied, are given in Table 1. The amounts of glucose, fructose and sucrose were very different, depending on the type of fruit analysed. These data were broadly similar to those reported by other authors for edible fruit juices (Chan & Kwok, 1975; Belitz & Grosch, 1997; Lee & Coates, 2000; Villamiel et al., 1998).

Kovats retention indices (*I*) and mass spectra of *allo*-, *muco*-, *chiro*-, *scyllo*-, *epi*- and *myo*-inositol were determined. *I* values were calculated at 180, 200 and 220 °C. Table 2 shows *I* values for each compound at 200 °C and their increments per 10 °C. Although elution orders of all TMS ethers of inositols have been reported (Sherman, Goodwin, & Gunnell, 1971), Kovats indices

Table 1
Contents (g/100 ml) of fructose, glucose and sucrose in fresh juices from different fruits

Sample	Fructose	Glucose	Sucrose	Glucose/fructose
Grapefruit	2.73 ± 0.01	2.66 ± 0.05	2.21 ± 0.03	0.97
Lemon	0.52 ± 0.04	0.50 ± 0.05	0.08 ± 0.01	0.96
Lime	1.18 ± 0.40	1.41 ± 0.3	0.26 ± 0.02	1.19
Mandarin	2.44 ± 0.07	2.22 ± 0.05	6.16 ± 0.46	0.91
Orange	1.90 ± 0.09	1.75 ± 0.10	4.71 ± 0.38	0.92
Grape	11.4 ± 0.06	9.72 ± 0.01	0.03 ± 0	0.85
Bilberry	4.91 ± 0.36	4.80 ± 0.30	0	0.98
Strawberry	2.08 ± 0.02	1.82 ± 0.01	1.73 ± 0.10	0.88
Guava	2.74 ± 0.26	0.95 ± 0.08	0.57 ± 0	0.35
Kiwifruit	5.33 ± 0.24	4.79 ± 0.23	0.66 ± 0.03	0.90
Apple	8.67 ± 0.30	2.62 ± 0.09	2.04 ± 0.10	0.30
Mango	2.47 ± 0.15	0.26 ± 0.01	4.50 ± 0.06	0.11
Peach	1.05 ± 0.08	0.69 ± 0.01	9.60 ± 0.40	0.66
Pear	11.2 ± 4.10	1.35 ± 0	0.26 ± 0.05	0.12
Pineapple	3.86 ± 0.19	3.51 ± 0.08	0.99 ± 0.07	0.91
Raspberry	2.51 ± 0.13	2.18 ± 0.14	0	0.87
Banana	3.54 ± 0.23	5.62 ± 0	13.9 ± 0	1.59
Redcurrant	4.46 ± 0.18	3.66 ± 0.14	0	0.82

Table 2
Kovats retention indices (I) at 200 °C of trimethylsilyl-inositols and their increments per 10 °C

Compound	I (200 °C)	$\Delta I/10$ °C
Allo-inositol	1944	1.75
Muco-inositol	1981	1.75
Chiro-inositol	2017	0.00
Scyllo-inositol	2085	3.25
Epi-inositol	2082	−0.75
Myo-inositol	2152	1.25

are only available for three of them (Binder & Haddon, 1984).

Fig. 1(a) and (b) show the chromatographic profiles of grapefruit and guava juices, respectively. The identities were assigned by comparison of retention times with standard substances and confirmed by GC-MS. *Myo*-inositol was observed in all analysed samples except redcurrant and banana juices. *Scyllo*-inositol was found in grape and in all citrus juices, whereas *chiro*-inositol was only present in raspberry and citrus samples. Other inositols were not detected in any of the studied juices.

Inositol content is reported in Table 3. *Myo*-inositol was present in variable amounts, from traces in raspberry to 153 mg/100 ml in kiwifruit. This value was similar to that reported by Bieleski et al. (1997), although we found that it was only 1.42% of soluble sugars. *Myo*-inositol content in orange juice (146 mg/100 ml) was within the ranges 119–162 and 130–170 mg/100 ml reported by Villamiel et al. (1998) and Belitz and Grosch (1997), respectively. *Myo*-inositol in grape juice (16.0 mg/100 ml or 756 mg/kg sugars) was higher than the minimum limit (750 mg/kg sugars) suggested by Versini et al. (1984) to control the genuineness of must. This compound was also previously found in other fruits, such as guava (Mowlah & Itoo, 1982), lemon and mandarin (Cataldi, Margiotta, & Zambonin, 1998), peach (Nickel & Maruyama, 1983), pear (Akhavan, Wrolstad, & Richardson, 1980) and strawberry (Macias-Rodriguez, Quero, & López, 2002). No data have been found about *myo*-inositol contents in apple, bilberry, mango and pineapple juices.

Scyllo-inositol ranged from traces in orange to 15.2 mg/100 ml in grapefruit; it was present in all citrus fruit examined. Although *scyllo*-inositol has already been detected in musts (Monetti et al., 1996; Versini et al., 1984), no presence of this inositol has been previously described in other juices.

Chiro-inositol varied from traces in raspberry to 108 mg/100 ml of mandarin. These levels are high enough to

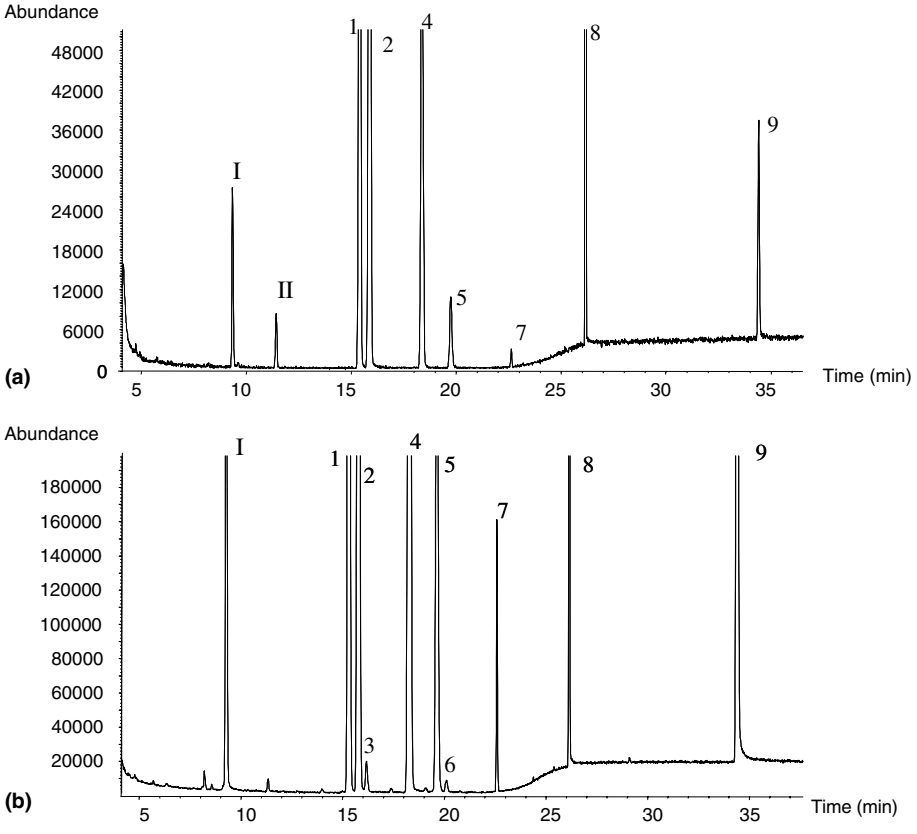

Fig. 1. Chromatographic profiles of TMS inositols and sugar oximes of guava (a) and grapefruit (b): (1) and (2) fructose; (3) *chiro*-inositol; (4) and (5) glucose; (6) *scyllo*-inositol; (7) *myo*-inositol; (8) phenyl-β-D-glucoside; (9) sucrose. Peaks eluting before fructose were carboxylic acids: (I) citric acid; (II) quinic acid.

Table 3
Contents (mg/100 ml) of *chiro*-, *scyllo*- and *myo*-inositols in fresh juices from different fruits

Sample	*Chiro*-inositol	*Scyllo*-inositol	*Myo*-inositol
Grapefruit	28.6 ± 0.07	15.2 ± 0.64	114 ± 4.97
Lemon	6.76 ± 0.17	7.39 ± 0.63	32.5 ± 1.97
Lime	21.7 ± 0.89	9.71 ± 2.24	58.7 ± 16.30
Mandarine	108 ± 8.72	11.4 ± 0.03	112 ± 0.62
Orange	55.8 ± 3.20	Traces	146 ± 10.61
Grape	0	8.04 ± 0.02	16.0 ± 0.52
Bilberry	0	0	14.1 ± 1.31
Strawberry	0	0	35.5 ± 6.57
Guava	0	0	26.1 ± 1.45
Kiwifruit	0	0	153 ± 2.59
Apple	0	0	41.3 ± 1.08
Mango	0	0	26.6 ± 2.22
Peach	0	0	54.1 ± 1.49
Pear	0	0	21.3 ± 0.43
Pineapple	0	0	29.9 ± 0.18
Raspberry	Traces	0	Traces
Banana	0	0	Not detected
Redcurrant	0	0	Not detected

consider citrus as an interesting dietary source of *chiro*-inositol. To the best of our knowledge this is the first evidence of the presence and content of *chiro*-inositol in fruit juices.

Although more research is necessary, besides some nutritional interest, the above presented data could afford important information on adulteration of fruit juices. Thus, the presence of the three inositols: *chiro*-, *scyllo*- and *myo*-inositol could contribute, together with other parameters, such as citric acid, to the detection of citrus in other kinds of juices.

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