Sugar composition of depectinized apple juices

Composição de açúcares em sucos de maçãs despectinizados

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Abstract

Apple juice, the second in the world consumption ranking, has glucose, fructose and sucrose as the main sugar components in fairly known proportion. Intentional adulteration maintaining such feature is possible by addition of high fructose syrup or inverted sugar and this attitude reflects losses from both economical and healthy aspects. The sugar profile in apple juices, although depending of the maturation degree, feature of cultivar and effect from growing places, may give some information in what concerns their authenticity. This article deals with the sugar composition of authentic depectinized apple juice made with selected samples 26 cultivars harvested in different growing places from 1994 to 2006. Total reducing sugar average content was 14.19±1.18 $g.100mL^{-1}$, comprehending glucose (1.86±0.66 $g.100mL^{-1}$, fructose (6.69±1.51 $g.100mL^{-1}$) and sucrose (3,06±1,39 $g.100mL^{-1}$). The relationship between the sugar concentration found was glucose: fructose: sucrose:: 1: 3,51: 1,64 what is in perfect agreement with the specialized literature. Sugar composition depends of the cultivars but the effects of growing places were not statistical significant in Brazilian geographical context.
Key words: Glucose, fructose, sucrose, apple juice, adulteration

Resumo

Suco de maçã, o segundo mais consumido no mundo, apresenta glucose, frutose e sacarose como os principais açúcares em proporções praticamente definidas. Adulterações intencionais mantendo as características de proporções de açúcares são possíveis pela adição de xarope com altos teores de frutose ou açúcar invertido, mas pode resultar em diminuição da qualidade sensorial e nutricional dos sucos. O perfil de açúcares em sucos de maçã, embora dependente do grau de maturação, da característica do cultivar e do efeito do local de crescimento pode dar algumas informações no que diz respeito à sua autenticidade. Este artigo avalia a composição de açúcares de sucos despectinizados autênticos de 26 cultivares de maçãs colhidas em diferentes locais nas safras 1994 – 2006. O teor médio de açúcar redutor total foi de 14.19±1.18 $g.100mL^{-1}$, compreendendo glicose (1.86±0.66 $g.100mL^{-1}$), frutose (6.69±1.51 $g.100mL^{-1}$) e sacarose (3,06±1,39 $g.100mL^{-1}$). A proporção dos açúcares encontrados nas amostras foi glucose: frutose: sacarose :: 1,00: 3,51: 1,64 o que está em perfeito acordo com a literatura especializada. A composição de açúcar depende do cultivar, mas os efeitos dos locais de cultivo não foram estatisticamente significativo no contexto geográfico brasileiro.
Palavras-chave: Glucose, frutose, sacarose, suco de maçã, adulteração, autenticidade

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Introduction

Apple production, a quite recent agriculture activity in Brazil, began in the 1960's with the first investigations concerning the installation commercial orchards somewhere in Southern States. In the 1970's, with the cooperative work of farmers and scientists supported by Federal laws, it was started the installation of the first commercial orchards in Fraiburgo SC and the *per capita* consumption raise from 2 to 5 kg/year/habitant, simultaneously with an increase in the cultivated area, in the production and in the productivity.

Today, the production of 1.000.000 ton of apple in Brazil supplies the domestic market with fruits of top quality and delivers around 300.000 ton of industrial apples, which can partially being processing in juice or apple wine. From such production around 97% are from the varieties Gala and Fuji and so every trial for processing should consider their physical-chemical properties in order not to fail, although there are many research projects dealing with the development of new varieties more resistant to insects, illness, phenologycal instability or demands of hibernal cold. Many of these new varieties are spontaneous mutations of the main cultivars and so is supposed to be found some similarities among the physical-chemical features of them (ALMEIDA; ALVES, 2006; WOSIACKI; NOGUEIRA, 2005).

The most common adulteration methods for apple juice include dilution with water, addition of sugars [cane and beet sucrose (BS), invert or medium invert syrup, high fructose corn syrup (HFCS), and hydrolyzed inulin syrup)], addition of pulpwash solids, or addition of a less expensive fruit juice (NAGY, 1997; LOW, et al., 2006). Adulteration of fruit juice is likely to remain a problem while the price of sugar and syrups is significantly cheaper than the juice itself. Besides the importance of sugar composition in respect of authenticity, it also has an effect on the sensory properties and nutritional values of apple products and has to be considered carefully in the preparation of the diet for diabetic patients (KELLY; DOWNEY, 2005; KARADENIZ; EKS, 2002).

A significant challenge in the detection of adulterated apple juice is the natural variation in authentic samples, a result of differences in species, maturity, climate, growing regions, seasons, processing, and storage conditions. Ranges in component compositions can be used to flag suspicious samples. Carbohydrates account for >98% of the total soluble solids in apple juice; fructose, glucose, and sucrose are the main carbohydrates with an approximate ratio of 6:3:2 and ranges from 5 to 8, 1 to 4, and 0 to 5% w/w, respectively (BRAUSE, 1998). Three commercially available sweeteners that approximate the carbohydrate composition of apple juice are fully inverted beet/cane sugar, HFCS, and hydrolyzed inulin syrup (KELLY; DOWNEY, 2005).

As a partner who joints the scientist group during the phase of rapid development of pomiculture many samples of apple from several places, different crops and distinct cultivars were collected in order to qualify the authentic processed juice from a physical-chemical point of view.

Material and Methods

Material

Samples of commercial or experimental apple (10 kg), harvested by specialized personnel, were collected in the Southern Paraná, Central Region of Santa Catarina and Serra Gaúcha in Rio Grande do Sul, the main sub-tropical area fitted to pomiculture, during the season from 1994 to 2006. The fruits were cleaned and stored at 4^{o}C overnight before processing.

Methods

Juice processing

After stored overnight at 4^{o}C, apple samples (10 kg) were sorted, cleaned, ground and the juice, extracted through pressing at 3 kgf/5 min, were treated with pectinase (Pectinex 100L) at ratio of 3ml/hL at 45^{o}C during 120 min. The clear supernatant, siphoned, filtered through qualitative paper and bottled, was microbiologically stabilized through a thermal treatment (80°C; 20 min) and stored at room temperature (WOSIACKI et al., 1989). Before analysis, the bottled juice was filtered through qualitative paper to obtain a clear sample.

Physical-chemical analysis

Sucrose was hydrolyzed with 0,5N HCl (65°C/5 min), and reducing sugar were determined through the classical method of Somogyi (1945) as modified by Nelson (1944), expressed as glucose in g/100 mL. Glucose was determined by the glucose oxidase / peroxidase method (ref.). The differences between total reducing sugar and reducing sugar represent the sucrose concentration and between reducing sugar and glucose, that of fructose, both expressed as monosaccharide in g/100 mL. Relative amount of total fructose was calculated with the expression Fructose%= 100*[((0,5*Sucrose) +(Fructose))/(Total reducing sugar)]

Apple fields

Samples were harvested preferentially in **Southern *Paraná***, *Porto Amazonas* (S 25º 32'49.26" W 49º 54'54.00" A 2,652 ft), in *Santa Catarina*'s **Central Region**, *Caçador* (S 26º 46'37.52" W 51º 01'19.95" A 3,160 ft) and in the ***Serra Gaucha*** of *Rio Grande do Sul*, *Vacaria* (S 28º 29'59.14" W 50º 55'46.88" A 3,122 ft). Climatic data were gave by Iapar Station in *Ponta Grossa* (PR), Epagri Station in *Caçador* (SC) and Embrapa Station in *Vacaria* (RS).

Statistic analysis

The raw data were treated by statistical tools to be shown as actual descriptors in both tables or graphics.

Results and Discussion

Main discussion in the literature concerning soluble sugars refers to apple juice adulteration with high fructose syrup. This discussion focuses economic implications of adulteration of fruit juices, acid hydrolysis of inulin to produce a high fructose syrup and its use to adulterate apple juices. The author report the development of an oligosaccharide fingerprinting method for detection of such syrup in apple juice using capillary GC with flame ionization detection with application to a wide range of apple juice samples (GIESE, 1997).

Evans (1996), through the utilization of multi component chemical analysis based on RSK procedures, had already reported novel methods for detecting adulteration of apple juices with high fructose syrups derived from inulin, especially capillary GC indicating 2 fingerprint oligosaccharide peaks. Balmer and McLellan (1996) at that time also reported how to detect the adulteration of apple juice with high fructose syrup from inulin by HPLC-PAD, as an alternative to the capillary-GC method. Indeed, there are many other possibilities to be explored regarding adulteration and how to detect it but, at a first glance, it is necessary to determine the standard of quality of authentic apple juices, specially concerning the soluble sugars.

There are no discussion in the specialized literature concerning the three main sugars found in depectinized apple juice, glucose, fructose and sucrose (RICHTWERTE UND SCHWANKUNGSBREITEN KENNZAHLEN - RSK, 1987), although some authors include sorbitol, a poliol, in the same set probably because this compound is involved in the fructose: glucose balance. According to Beruetter et al (1997), who studied the carbon partitioning of sucrose and sorbitol in apples, glucose derived from disaccharide more readily enters the hexose phosphate pool than fructose derived either from sucrose or sorbitol. The selective utilization of glucose, dependent on the cleavage of sucrose by sucrose synthase, favours its diversion to starch while fructose is accumulated in the vacuole of the parenchyma cell.

Although some scientists (KARADENIZ; EKSI, 2002) have chosen maximum 3.5% sucrose and minimum 1.6 fructose: glucose ratio as standard of authenticity for apple juice however, it is not ease to generalize rules for apples considering the variability of genotypes and the many factors affecting the chemical composition even when only three compounds are in concern.

There are many new apple cultivars in study aiming to find out whether they could satisfy the consumer.

But with a production cost lower than that of Gala and Fuji, the main varieties cultivated in Brazil.

As a result from the research upon many new cultivars to determine those able to be cultivated as commercial, both as producers or as pollinators, their sugar composition is shown here comprehending many crops and many different climatic conditions.

In the specialized literature is possible to find some article which deals with the same subject and may be used as references (FULEKI; PELAYO; PALABAY, 1994; FOURIE; HANSMANN; OBERHOLZER, 1991; WILL; SCHULTZ; LUDWIG; OTTO; DIETRICH, 2002; KARADENIZ; EKSI, 2002).

The sugar composition of depectinized apple juices: a survey from Brazil

The Table 1 depicts the statistical descriptive analysis of sugar composition of Brazilian authentic apple juices made with 26 different cultivars during the crops 1994 up to 2006.

Table 1. Statistical descriptive analysis of sugar composition of Brazilian apple juice

g/100mL	N	Mean	-95%	+95%	Median	Min.	Max.	Std. deviation	C.V%
Total reducing sugar	84	11.51	11.25	11.76	11.50	8.65	14.19	1.19	10.34
Reducing sugar	84	8.51	8.17	8.85	8.30	5.42	12.22	1.58	18.57
Glucose	84	1.87	1.73	2.02	1.65	0.83	4.10	0.68	36.36
Fructose	84	6.63	6.31	6.95	6.42	3.33	10.78	1.48	22.32
Sucrose	84	3.07	2.78	3.36	2.90	0.58	6.05	1.35	43.97
Fructose: glucose	84	3.97	3.60	4.33	3.72	1.06	11.20	1.67	42.06
Fructose%	84	70.95	69.50	72.40	71.23	50.83	86.98	6.67	9.40

Total reducing sugar content found in experimental depectinized apple juice has an average value of 11.51±1.19 g/100 mL (CV= 10%) as depicted in Table I. This is a ratter small variation considering the many causes of fluctuation and, as a matter of fact, the fruits were ever harvested by specialized personnel to have at least some homogeneity in the degree of maturity. Such value represents the result of the analysis, in triplicate, of 26 varieties and experimental apple juice made with fruits from several crops (from 1994 up to 2006) in three different regions (Paraná, Santa Catarina and Rio Grande do Sul). In the set of samples analyzed 90% are within the range 9.13-13.89 g/100 mL, with amplitude (minimum to maximum values) of 8.65-14.19 g/100 mL. Such results are in agreement to the values mentioned by Fuleki, Pelayo and Palabay (1994), who reported a survey of 21 articles, published since 1912 up to 1992, comprehending authentic juices from 151 cultivars. Lower minimum and higher maximum values were reported by Eisele and Drake (2005) in what concerns 175 apple varieties although the average was not so far (10.31 g/100 mL) from that here reported but it includes also sorbitol in this amount. The average value reported by Karadeniz and Eksi, (2002), of 12.93 g/100 mL, and also the values found for minimum and maximum, were slightly higher than that here reported but the variation coefficient was of the same magnitude (8.5%). High values of total reducing sugar are desirable both for consumption *in natura* as for juice fermentation and it can be easily and quickly measured as total soluble solids with a refractometer with slight deviations especially due to difference in temperature and should be referred to as 20ºC (TANNER; BRUNNER,1979). Both total sugar concentration and total soluble solids represent a good tool in what concerns to define the degree of maturity of apple.

Reducing sugar content represents the sum of both monosaccharide glucose and fructose and this feature is seldom referred in the literature, indeed because it is a preliminary result in the analysis procedure, in order to calculate the amount of fructose since glucose was known. It was observed that the clarified juices showed high content of fructose, followed by sucrose and glucose. Glucose average concentration is rather than small, 1.87±0.68 g/100 mL and the set of samples is also heterogeneous (36.36%) as compared with total reducing sugar. Fructose, the main sugar, with an average concentration of 6.63±1.48 g/100 mL also as a high variation coefficient (22.32%), the sum of both represents the reducing sugar, which has an average concentration of 8.51±1.58 g/100 mL (CV=18.57%), and their ratio, the supremacy of fructose over glucose, which has an average value of 3.97± 1.67 (42.06%). Relative total fructose amount was specifically 70.95%±6.67 %, (CV=9.40%) the feature in which the set of samples of apple was more homogeneous (9.40%). Sucrose, the non reducing disaccharide, shows an average value of 3.07±1.65 g/100 mL (43.97%) and is the most dispersive sugar from the set.

It was verified that the relationship glc: fru: suc: in the aapple juice made with fruits harvested in the States of Paraná, Santa Catarina and Rio Grande do Sul was: 1.0: 3.54:1.64 respectively. These results are in agreement with those from Berueter, Studer Feusi e Rueedi (1997) in what concerns the higher amount of fructose. An average value for such relationship in the literature points to 1,0: 3,61: 1,64 but with high standard deviation due to the degree of maturation, to varietal variations and to the effect of growing places (FOURIE; HANSMANN; OBERHOLZER, 1991; FULEKI; PELAYO; PALABAY, 1994; KARADENIZ; EKSI, 2002; ROCHA; MORAIS, 2003; EISELE; DRAKE, 2005). All these values are in agreement with that disseminated (RICHTWERTE UND SCHWANKUNGSBREITEN KENNZAHLEN - RSK, 1987) in the late's 1980. Apple is so a fruit with high amount of fructose, sugar and with sucrose in concentration with high variability.

The distribution of simple sugars in depectinized apple juices

The amount of glucose in the set of 84 samples is shown in Figure 1, both as histogram and as probability distribution function considering a normal distribution. It is depicted in these graphics that the distribution has a shift toward high values as mean value (1.87 g/100 mL) is higher than median (1.67 g/100 mL), with a large amplitude and variation coefficient (36.36%).

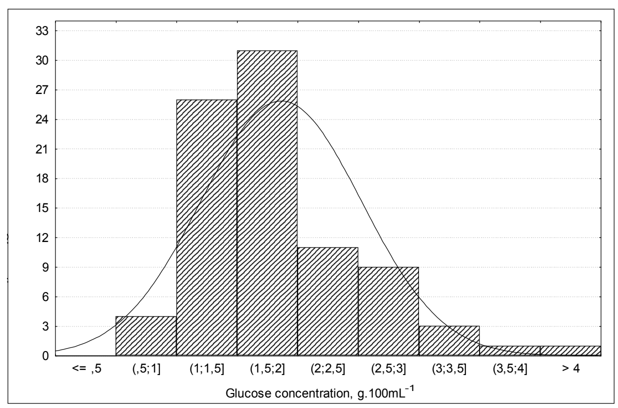

Figure 1. Histogram of glucose in authentic apple juices

The amount of fructose in the set of 84 samples is shown in Figure 2, both as histogram and as probability distribution function considering a normal distribution. It is depicted in these graphics that the distribution also has a shift toward high values as mean value (6.63 g/100 mL) is higher than median (6.42 g/100 mL), but with a smaller variation coefficient (22.32%).

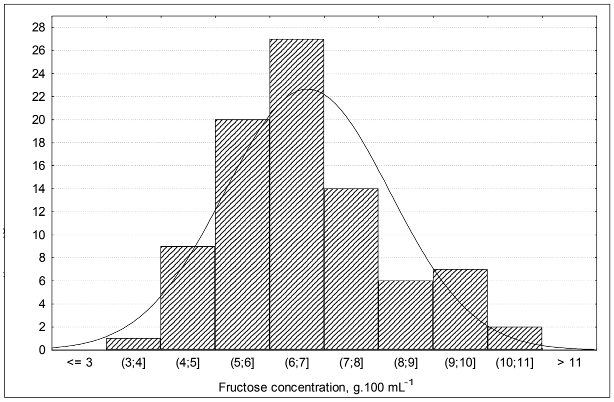

Figure 2. Histogram of fructose in authentic apple juice

The amount of sucrose in the set of 84 samples is shown in Figure 3, both as histogram and as probability distribution function considering a normal distribution. It is depicted in these graphics that the distribution also has a shift toward high values as mean value (3.07 g/100 mL) is higher than median (2.90 g/100 mL), but with the highest variation coefficient (44%).

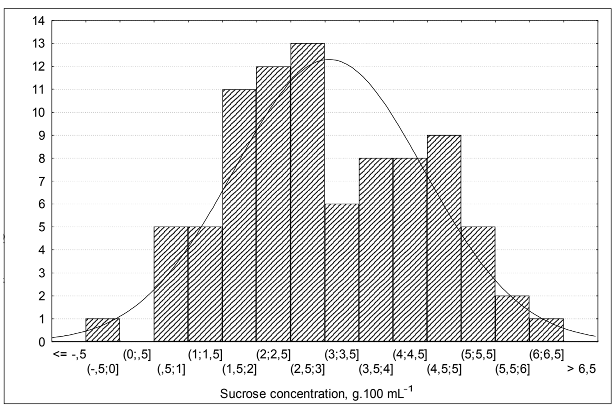

Figure 3. Histogram of sucrose in authentic apple juices

Effect of growing region on sugar composition

In the Table 2 are shown the average sugar level and their standard deviation as found in the juices made with apple growing in Paraná, Santa Catarina and Rio Grande do Sul. It is clear that there are differences between them but not statistically significant. It seems reasonable to accept that these states have medium temperature decreasing in the Southern direction, especially in the high altitudes where apple are cultivated. So it is possible to accept also some popular statements as "cold places, less sucrose" although not confirmed by statistical analysis.

This fact becomes more understandable by observing Figure 4 where the relative amounts of the three soluble sugars are depicted.

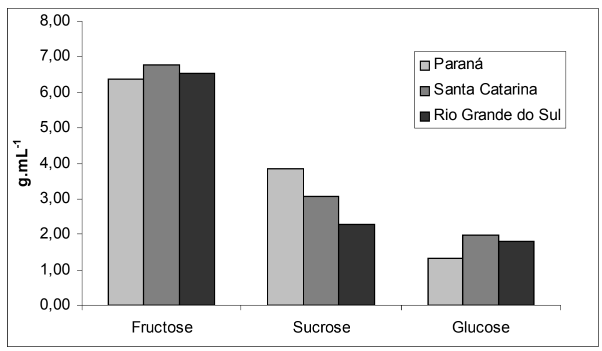

Figure 4. Partition of simple sugars in depectinized apple sugars from different States

Table 2. Effect of growing region on sugar composition of depectinized juice of 84 samples from 26 apple cultivars

Region	Glucose g/100 mL	Fructose g/100 mL	Sucrose g/100 mL
Paraná	1.343±0.436	6.353±1.408	3.848±1.419
Santa Catarina	1.961±0.680	6.770±1.626	3.060±1.375
Rio Grande do Sul	1.796±0.515	6.541±0.824	2.274±1.120

Conclusions

The concentration of total reducing sugar in authentic Brazilian apple juices in a set covering at least 14 crops was 11.51±1.19 g/100 mL with a small variation coefficient, of around 10%. The relationship between all sugars based in glucose was 1.0: 3.54:1.64 and confirms the predominance of fructose, which is present as 71%. Fructose: Glucose ratio of 3,95 was the average for the 84 samples of analyzed juices.

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