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Chemical compositional characterization of some apple cultivars

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Abstract

Eight commercially harvested apple cultivars were analysed by gas chromatography and high-performance liquid chromatography, in particular the composition and level of sugars, organic acids, amino acids, phenolic compounds and fatty acids. The results showed great quantitative differences in the composition of the apple cultivars, particularly in their phenolic contents. Fructose was the most dominant sugar in the different apple cultivars, followed by glucose and sucrose, while malic acid was the principal organic acid. The C16:0, C18:0, C18:1, C18:2 and C18:3 fatty acids were the most abundant fatty acids, and the C18 family accounted for more than 70% of the total fatty acids content. Asparagine and serine were the principal amino acids. Chlorogenic acid and protocatechuic acid were the dominating phenolic compounds. The results provide important information on how to make the best use of the apple cultivars investigated, for both technological research and processing practice.

Keywords: Apple cultivars; Chemical composition; Gas-chromatography; High–performance liquid chromatography

1. Introduction

Apples are one of the most frequently consumed fruits. In China, commercial apple production in recent years amounted to 24 million t/year, of which most (~70%) were used for direct consumption, and the others (~30%) were processed to produce juice concentrates. Apples constitute an important part of the human diet, as they are a source of monosaccharides, minerals, dietary fibre, and various biologically active compounds, such as vitamin C, and certain phenolic compounds which are known to act as natural antioxidants. Some researchers also consider polyphenols to be antimutagenic and anticarcinogenic compounds (Lee & Mattick, 1989; Miller & Rice-Evans, 1997). Along with sugars and organic acids, phenolics determine the quality of apples (Dolenc & Stampar, 1997; Fuleki, Pelayo, & Palabay, 1994). They have important roles in providing taste characteristics, such as flavour, bitterness and astringency, and also colour (Bengoechea, Sancho, & Bartolome, 1997; Miller & Rice-Evans, 1997). The concentration of these phenolic compounds, which is strongly dependent on the variety of apples and their maturity, is closely associated with the nutritional and sensory qualities of the fruits. Low concentrations may protect apples from oxidative deterioration, for instance during juice production. High concentrations of phenolics and their oxidation products may cause discolouration of fruit products and haze formation in juices, as a result of the interaction of proanthocyanidins (condensed tannins) with proteins, carbohydrates or minerals (Ayaz, Kadioglu, & Reunanen, 1997). The susceptibility of apples to browning depends on the relative concentrations of different groups of phenolic compounds. The most reactive are catechins and both chlorogenic and caffeic acids (Amiot, Tacchini, Aubert, & Nicolas, 1992; Simon, Ilzarbe, & Hernandez, 1992). Phenolic compounds, and particularly flavanols, appear to be important for the classification of different apple cultivars

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into groups, with respect to their uses. For cider production, apples with a high phenolic content are preferred, while for naturally cloudy juices a low level of phenolics is required. Apples for direct consumption should be rich in biologically active compounds, such as ascorbic acid, and phenolic compounds, particularly flavanols, including catechins and proanthocyanidins. Furthermore, free amino acids and fatty acids, which are nutritive components of many fruit and vegetables also play important roles in human health and maintaining fruit quality (Schieber, Keller, & Carle, 2001). The roles of fatty acids and amino acids in fruit aroma have been reported in previous research. It has been reported that tyrosine and phenylalanine were substrates for the formation of volatile components (Jie & ji Zhong, 2002).

No comprehensive data have been reported on the chemical composition of different cultivars cultivated and processed in China. As China is the biggest cider producer and exporter, detailed research on raw materials is necessary, to ensure good product quality. Therefore, this research is focused on analysis and comparison of the chemical compositions, such as monosaccharides, organic acids, amino acids, phenolic compounds and fatty acids of different apple cultivars. A more detailed knowledge of the variability of the compositions of different cultivars will be of benefit in the future selection of apple genotypes with improved nutritional quality and suitable processing characteristics for the manufacture of apple juice concentrate (Edgar, Allen, & Roy, 1996).

2. Materials and methods

2.1. Sample preparation

Eight apple cultivars (Delicious, Golden Delicious, Ralls, Fuji, QinGuan, Jonagold, Granny Smith and Orin) grown in Shandong province of China were used for this study. The apples were harvested at commercial maturity. Fruits were loosely packed inside conventional modular bulk containers with polyliners and stored at 0 °C, 80–90% relative humidity. The humidity inside the polyliner was approximately 95%. The air was exchanged with fans four times daily to remove ethylene.

2.2. Chemical analysis

High-performance liquid chromatography (HPLC) was used for separation, identification and quantification of individual compounds in apple juice. The HPLC system consisted of Thermo Separation Products (TSP) equipment with a model K-1001pump and K-1500 solvent mixer. Solute elution was monitored using a variable wavelength UV detector (model K-2501, KNAUER CO., Berlin, Germany) and RI detector (model K-2301, KNAUER, Germany).

For sugar (glucose, fructose, sucrose) and organic acid (citric, fumaric and shikimic) determination, we used the modified HPLC method of Dolenc and Stampar (1997). Samples were prepared by extracting juice from cored fruit flesh using a commercial blender. Five to eight apples from each variety were pooled, and then filtered through filter paper. The fruit juice (5 ml) was diluted to 100 ml with redistilled water, centrifuged in a refrigerated centrifuge at 0 °C and at 3000*g* for 10 min, and then filtered through a 0.45 μm Millipore filter. Analiquot (20 ml) of the resultant supernatant was used for HPLC analysis.

Sugar analyses were performed isocratically on a ProtonotSIL, 120-10-Amino column (10.0 μm, 250 × 4.6 mm i.d., KNAUER, Germany) attached to a retractive index (RI) detector (model K-2301, KNAUER, Germany). The analysis was carried out at 30 °C at a flow rate of 1.5 ml/min with acetonitrite/water CH_3CN/H_2O (85:15) as the mobile phase. Sugars present in each sample were identified and quantified using external standards. The reproducibility of the chromatographic separation of the components was determined by making five injections of the standard solutions and apple samples. The results expressed as relative standard deviation (RSD%) are as follows: 0.67 for sucrose, 0.23 for glucose, and 0.20 for fructose.

Organic acids were determined by HPLC analysis using a ProntoSIL, 120-10-C_{18} (10.0 μm, 250 × 4.6 mm i.d., KNAUER, Germany) column, with 0.01 M $K_2HPO_4 \cdot 3H_2O$, pH 2.6 as mobile phase, with a flow rate of 0.5 ml/min, at 30 °C.

Organic acids were identified and quantified by comparison of their retention time and peak area with standard solutions of known organic acids, using a UV detector with wavelength set 210 nm (model K-2501, KNAUER, Germany). The results of the reproducibility study of chromatographic separation for organic acids, expressed as RSD%, are as follows: 0.013 for tartaric acid, 0.044 for quinic, 0.84 for malic acid, 0.004 for shikimic acid, and 0.041 for succinic acid.

The total soluble solids (TSS), expressed as %, was determined in the juice of each sample using an Atago digital refractometer at 21 °C.

As for phenolic acid analysis, 10 ml juice was extracted twice with 10 ml of ethyl acetate: fractions were pooled and evaporated to dryness, and the residue was dissolved in 1.0 ml of methanol (HPLC grade). The resultant solution was filtered through a 0.45 μm membrane filter prior to HPLC analysis (Spanos & Wrolstad, 1992).

Fatty acid analysis was performed using a Hewlett-Packard 5890 Gas Chromatography with flame ionization detector. Single aliquots of lipid extract (approximately 0.5 μL) were injected in splitless mode onto a DB-23 capillary column (60 × 0.25 mm i.d., 0.25 μm film thickness); Agilent, USA. The injector and detector temperatures were set at 250 °C and 270 °C, respectively. The oven was set at an initial temperature of 130 °C for 1 min, which was increased to 215 °C at a rate of 6 °C/min, maintained for 2 min, then raised to 230 °C at a rate of 40 °C/min, and held at 230 °C for 40 min. The flow rate was 32 cm/s, helium used as carrier gas, and the electronic pressure control set in the constant flow mode. A calibration mixture of