Industrial Crops and Products 60 (2014) 86–91

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Lipophilic composition of eleven apple seed oils: A promising source of unconventional oil from industry by-products

Paweł Górnaś[a,*], Magdalena Rudzińska[b], Dalija Segliņa[a]

[a] Latvia State Institute of Fruit-Growing, Graudu 1, Dobele LV-3701, Latvia
[b] Poznan University of Life Sciences, Faculty of Food Science and Nutrition, Wojska Polskiego 28, 60-623 Poznan, Poland

ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 3 June 2014
Accepted 4 June 2014
Available online 26 June 2014

Keywords:
By-products
Apple seed oils
Fatty acids
Phytosterols
Squalene

ABSTRACT

The profile of lipophilic compounds was studied in oils obtained from seeds of five dessert and six crab apple cultivars. Apple seeds were collected from by-products generated during the preparation of fruit salads and in juice pressing. The oil yield in the apple seeds ranged from 12.06 to 27.49 g/100 g dry weight base. The average level of oil obtained from crab apple seeds was higher by 30% when compared to dessert apple seeds. The fatty acid composition was dominated by palmitic acid (5.78–8.33%), oleic acid (20.68–29.00%) and linoleic acid (59.37–67.94%). Among the six detected phytosterols β-sitosterol was predominant (51–94%). Total phytosterol concentration as well as squalene varied in different apple seed oils and amounted to 1.13–7.80 and 0.01–0.34 mg/g, respectively. Four significant correlations were found between oil yield and contents of oleic acid ($r = 0.822$, $p < 0.01$), α-linolenic acid ($r = 0.919$, $p < 0.0001$), β-sitosterol ($r = 0.931$, $p < 0.0001$) and total phytosterols ($r = 0.901$, $p < 0.001$) in apple seed oils.

1. Introduction

Due to the growing trend of replacing synthetic substitutes with their natural counterparts, changing consumer expectations and environmental protection concerns, a number of industries nowadays are returning to the use of natural ingredients obtained from natural raw materials. The greatest challenge for most commercial scale producers is connected with the management of by-products and reducing rising production costs. Therefore, in many cases proper utilization of by-products makes it possible not only to obtain natural bio-components, but also tangible financial benefits. A good example of the management of by-products generated by fruit industry is the use of seeds in oil production (Górnaś et al., 2013).

Apple juice production belongs to the branches of industry that produce large quantities of by-products in relation to the initial amount of processed fruits, estimated at 25% (Mahawar et al., 2012). Cider and fresh-cut fruit salad production also generates large amounts of valuable by-products, for instance seeds, which have no further use. The share of seeds in apples depends on the cultivar and may be as high as 0.7% of fresh fruit (Fromm et al., 2012). Furthermore, apple is one of the most popular fruit crops in the world with the global production reaching 76 million tons in 2011 (FAOSTAT, 2013). Despite the fact that not all apples are processed by industry, the amount of seeds that could be obtained from by-products and used as a valuable source of bio-compounds is impressive.

In recent years an increasing amount of publications have been released regarding various unconventional sources of seed oil and its phytochemical composition (Fromm et al., 2012; Górnaś et al., 2013; Nogala-Kalucka et al., 2010). Because of the fact that unconventional seed oils contain valuable natural compounds such as unsaturated fatty acids, squalene, phytosterols, carotenoids and tocopherols, they could be utilized in pharmaceutical and cosmetics industries (Górnaś et al., 2013; Nogala-Kalucka et al., 2010).

Both saturated and unsaturated fatty acids are very important integral components of biological membranes, where their influence on the hydrophobic–hydrophylic balance in the bilayer is essential. Saturated acyl chains provide a rigid membrane structure, while unsaturated acyl chains provide its liquid character. However, the presence of embedded specific biological compounds in the membrane, e.g. α-tocopherol, can change that balance (Dwiecki et al., 2007).

Phytosterols are steroid compounds, their structure and functions are similar to those of cholesterol. In the pharmaceutical and cosmetics industries phytosterols are recovered from cellulose processing or vegetable oil waste and they are utilized in the production of therapeutic steroids, creams or lipsticks (Fernandes and Cabral, 2007).

* Corresponding author. Tel.: +371 63707345; fax: +371 63781718.
E-mail address: pavel.gornas@lvai.lv (P. Górnaś).

http://dx.doi.org/10.1016/j.indcrop.2014.06.003
0926-6690/

Squalene is a natural isoprenoid molecule with an antioxidant activity, a precursor of steroid hormones, cholesterol and vitamin D. As an antioxidant, it is responsible for protection against oxidative DNA damage of mammary epithelial cells in humans (Warleta et al., 2010).

The aim of this study was to enhance knowledge on the composition of lipophilic ingredients such as fatty acids, phytosterols and squalene in seed oils of various dessert and crab apple cultivars, recovered from apple industrial by-products. Obtained results will promote the development, utilization and potential applications of apple processing by-products, seeds in particular.

2. Materials and methods

2.1. Apple seeds

Seeds of six crab apple cultivars (inter-species hybrids of *Malus* sp.) ('Kerr', 'Kuku', 'Riku', 'Ritika', 'Ruti' and 'Quaker Beauty') were obtained from apple pomace supplied by a local producer of cider (Lejaskerzeni, Valmiera, Latvia). Seeds of five dessert apple cultivars (*Malus* × *domestica*) ('Antej', 'Beforest', 'Kent', 'Sinap Orlovskij' and 'Zarja Alatau') were obtained as a by-product during the preparation of fruit salads at the processing facility of the Latvia State Institute of Fruit-Growing (LSIFG). Both dessert and crab apples were collected in September 2012 in Dobele, at the LSIFG, GPS location: N: 56° 36′ 39″, E: 23° 17′ 50″. The apple trees were cultivated in soil, varying from haplic luvisol (super eutric) to luvisol (hypereutric), while in terms of soil texture – loam and sandy clay loam. The sustainable growing system and the planting distance of 1.5 × 4 m for crab apple trees and 5 × 3 m for dessert apple trees, without irrigation system were used. Grass was mowed several times (5–6) during the growing season and the rows were kept clean using herbicides in the first part of the vegetation season. The present study was conducted as a part of an experiment designed to evaluate suitability of different apple varieties for processing (cider and salad production). Samples were evaluated according to the scheme shown in Fig. 1. In brief, seeds were separated from apple flesh and cores, then oven-dried (5 h) in Orakas 5600 (Marlemi, Lemi, Finland) with forced hot air circulation at 55 ± 1 °C. Undamaged seeds were selected (~50 g) and milled with a Knifetec™ 1095 (Foss, Höganäs, Sweden) universal laboratory mill, then passed through a sieve of 0.75 mm mesh size to finally obtain a powder.

Dry weight basis (dwb) in a sample was measured gravimetrically according to Ruiz (2005).

2.2. Extraction of oil

Oil was extracted using the ultrasound technique (partially), which according to Cravotto et al. (2008) provides a higher oil yield in comparison to conventional methods. In brief, ground apple seeds (5 g) were supplemented with *n*-hexane (Sigma–Aldrich, Steinheim, Germany) at 25 ml in a centrifuge tube and vortexed on a Vortex REAX top (Heidolph, Schwabach, Germany) at 2500 rpm (1 min). Samples were subjected to ultrasound treatment in the Sonorex RK 510 H ultrasonic bath (Bandelin electronic, Berlin, Germany) (5 min, 35 °C) and centrifuged on a Centrifuge 5804 R (Eppendorf, Hamburg, Germany) (10,000 × g, 5 min, 21 °C). The supernatant was collected in a round bottom flask and the remaining solid residue was re-extracted (twice) as described above. The combined supernatants were evaporated in a Laborota 4000 vacuum rotary evaporator (Heidolph, Schwabach, Germany) at 40 °C until constant weight.

2.3. Fatty acid composition

The fatty acid composition of apple seed oils was estimated using gas chromatography according to AOCS (2005). Fatty acid methyl esters were separated using a Hewlett-Packard 5890 II gas chromatograph equipped with a Supelcowax 10 capillary column (30 m × 0.20 mm × 0.20 μm) and FID detector under programmed temperature conditions: from 60 °C, at a rate of 12 °C/min to 200 °C – hold 25 min. Temperature of the injection port and the detector was held at 240 °C. Hydrogen was used as a carrier gas at a flow rate of 1.0 ml/min.

Fatty acids were identified out by retention times of standards of the fatty acid methyl ester mix (Supelco, Steinheim, Germany) and expressed as a percentage of the total peak area of all the fatty acids in the oil sample.

2.4. Contents of phytosterols and squalene

Contents of plant sterols and squalene were determined according to AOCS (1997). In brief, apple seed oil (50 mg) was saponified with 1 M KOH in methanol for 18 h at room temperature, and then unsaponifiables were extracted trice with hexane/methyl *tert* butyl ether (1:1, v/v). After silylation using a Sylon BTZ (Supelco, Bellefonte, PA, USA) phytosterols were separated on a HP 6890 gas chromatograph equipped with a DB-35MS capillary column (25 m × 0.20 mm × 0.33 μm; J&W Scientific, Folsom, CA). Samples of 0.5 μl were injected in a splitless mode. Column temperature was held at 100 °C for 5 min, then programmed to 250 °C at 25 °C/min, held for 1 min, then further programmed to 290 °C at 3 °C/min and held for 20 min. Detector temperature was set at 300 °C. Hydrogen was used as a carrier gas at a flow rate of 1.5 ml/min. An internal standard, 5α-cholestane, was used for sterol quantifications. Phytosterols and squalene were identified by comparing retention data of standards previously verified by mass spectrometry. Samples from autonomous series were analyzed in triplicate.

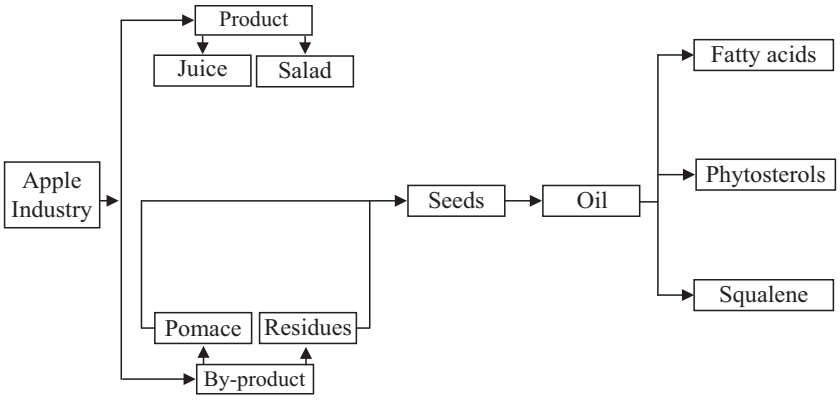

Fig. 1. Scheme for potential utilization of seeds of different crab and dessert apple cultivars.