J Food Sci Technol (September 2017) 54(10):3366–3369
DOI 10.1007/s13197-017-2771-9

SHORT COMMUNICATION

Fatty acid profile of pecan nut oils obtained from pressurized *n*-butane and cold pressing compared with commercial oils

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Revised: 10 July 2017 / Accepted: 20 July 2017 / Published online: 22 August 2017

Abstract This short note compares the chemical profile of pecan nut oil samples obtained from pressurized *n*-butane and cold pressing with two commercial oils. The conventional cold pressing technique yielded 58.9 wt%, while pressurized *n*-butane yielded from 53 to 65 wt%, being the highest yield at 55 °C, and pressure of 40 bar. The *n*-butane behaves nearly like a piston fluid within the experimental conditions used. The results showed that the extraction variables had a slight influence on the fatty acid composition of the samples. Extraction with *n*-butane thus showed to be a promising alternative technique to conventional extraction methods, as very mild operating conditions and eco-friendly solvent can be used to provide good results without any residues in the final product.

Keywords Pecan nut oil · Extraction · Chemical characterization · *n*-butane · Cold pressing

Electronic supplementary material The online version of this article (doi:10.1007/s13197-017-2771-9) contains supplementary material, which is available to authorized users.

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Introduction

Oils obtained from pecan nuts are rich in oleic (49–76.5%) and linoleic (13–40%) acids and have small amounts of saturated fatty acids (6–17%) (Miraliakbari and Shahidi 2008; Block and Barrera-Arellano 2010). Pecan nut oil has been reported as one of the most interesting source of biologically active compounds (Bouali et al. 2014) and has considerable content of phytosterols mainly as β-sitosterol, and tocopherols that are present primarily as y- and α-tocopherol (Block and Barrera-Arellano 2010). Clinical studies showed that nuts-enriched diets may promote cardiovascular health. The high unsaturated fatty acids and low saturated fatty content may increase the high density lipoprotein (HDL-cholesterol) while lowering the low density lipoprotein (LDL-cholesterol). In addition, pecan nuts present high content of phenolic compounds with antioxidant and antiproliferative activity of cancer cells (Rosa et al. 2014). The positive effect of pecan nut consumption on health is probably associated with the synergistic effect of the bioactive compounds such as monounsaturated fatty acids, tocopherols, phytosterols and phenolic compounds (Alasalvar and Bolling 2015).

The pecan nut oil obtained by cold-pressing is primarily used for cooking and is considered a gourmet oil. Nevertheless, the main disadvantage of this method is the low yield of oil generally obtained. On the other hand, bioactives compounds such as tocopherols (vitamin E), phytosterols and phenolic compounds, and the organoleptic characteristics do not change.

The extraction process using organic solvents such as hexane can however afford higher extraction yields, but the oil must be refined, bleached and deodorized like all processed vegetable oil (Bouali et al. 2013; Prado et al. 2013; Ros 2010; Domínguez-Avila et al. 2015). Moreover, the processing conditions at high temperatures can alter the chemical composition of the oil from the nuts (Chandrasekara and Shahidi 2011). The replacement of hexane in the extraction of vegetable oils has been proposed due to increasing environmental concerns as well as process safety. Accordingly, there has been a great interest in the use of pressurized gases or highly volatile nonpolar solvents, as an alternative to the conventional solvents used. When gases at ambient conditions such as propane and *n*-butane are liquefied, its physicochemical properties become adequate for extraction purposes, and are considered non-toxic solvents (Yang et al. 2004). Another advantage is the complete removal of the solvent after the extraction by reducing pressure, resulting in solvent-free oil (Tres et al. 2014). *N*-butane is plenty available, cheaper and it can be used in much lower pressures compared to carbon dioxide. Besides, the mild temperature and pressure operating conditions, the use of short-chain hydrocarbons, like *n*-butane, allows reduction of extraction time, while improving the quality of the oil obtained.

In this context, the oils extracted from [*Carya illinoinensis (Wangenh) C. Koc*] (pecan nut) using pressurized *n*-butane and cold pressing were investigated and compared with two commercial pecan nut oils in terms of extraction yield and fatty acid profile.

Experimental

Materials

Pecan nuts were harvested in June 2015 from native plants in Erechim (Rio Grande do Sul, Brazil). Nuts were manually separated from the shells and kept under nitrogen atmosphere, protected from the light, in refrigeration (8 °C) until extraction. Pecan nuts employed in the extraction experiments presented a moisture content of 3.7 ± 0.31 wt%. Commercial pecan nuts oils were purchased in the local market.

Pecan nut extraction with pressurized *n*-butane

Before extraction, the nuts were crushed in slicer and sieved in order to obtain particles size of ≤2 mm. The equipment consisted of four components: a solvent gas cylinder, a high pressure pump, an extraction vessel, a micrometric valve and collection flask, and a temperature and pressure control systems. The *n*-butane with minimum purity of 99.5% in the liquid phase was purchased from White Martins S. A. After preliminary tests, the extraction condition for all assays was set as solvent flow rate of 3 mL/min and 2 h of extraction time for experimental runs. In fact, preliminary tests showed that extraction times greater than 2 h led to negligible gains of extract obtained and therefore above this time resulted in practice solvent losses with additional costs and unfruitful results. Effect of temperature and pressure parameters were assessed using a factorial 2^2 design with triplicate assays at the central point, resulting in seven experimental assays, comprising extraction temperature of 35, 45 and 55 °C and pressure of 40, 50 and 60 bar. Detailed discussion on the apparatus and extraction conditions can be found in the work of Novello et al. (2015) and Capeletto et al. (2016). For all extraction conditions using pressurized with *n*-butane pecan nut oils were collected in amber bottles and then stored under refrigeration (5 ± 2 °C).

Pecan nuts extraction with cold pressing

The pecan oil was obtained by cold pressing in a hydraulic press (Tecnal—TE-098, Ourinhos, São Paulo). The oil obtained was centrifuged in Daiki centrifuge model 80-2B (Akagidai, Japan) for 10 min and kept in amber bottles, under nitrogen atmosphere at −20 °C until analysis.

Fatty acid analysis by gas chromatography

The fatty acid profile was determine using a Shimadzu gas chromatograph model GC 2010 (Kyoto, Japan) equipped with a split-injection port, flame-ionization detector and a HP 88 capillary column (100 mm × 0.25 mm × 0.20 mm) was used. The chromatograph operating conditions were: split = 1: 150; column flux = 0.92 mL/min; detector temperature: 260 °C; injector temperature: 150 °C; oven temperature: 140 °C (6 min); 140–240 °C (4 °C/min), 240 °C (6 min); make up gas: nitrogen; carrier gas: helium; split ratio: 50:1; injected volume: 1.0 µL. The methyl esters were obtained according to O'Fallon (O'Fallon et al. 2007). The fatty acids were identified by comparison with retention times shown by the standards 20 A—NU-CHEK Elysian, USA and by comparison with the retention time of individual standards. Data were expressed as percentage of the area of each fatty acid.

Results and discussion

Overall extraction yield of pecan nut oil using cold pressing and pressurized *n*-butane were as follows: 52.9 wt% at 35 °C and 40 bar, 57.8 wt% at 35 °C and 60 bar, 65.3 wt% at 55 °C and 40 bar, 57.8 wt% at 55 °C and 60 bar and at the central point of the experimental, 45 °C and 50 bar a value of 54.9 ± 1.1 wt% (triplicate runs). Thus, the yield obtained (defined as the weight percentage of the oil extracted with respect to the initial charge of the raw material in the extractor) using cold pressing was 58.9 wt%

and from ~53 to 65.3 wt% using pressurized *n*-butane, being the maximum yield recorded at the highest temperature (55 °C) and lower pressure (40 bar), whereas the lowest yield was noticed at the lowest temperature and pressure. These results were expected, as *n*-butane behaves like a piston, hydraulic, fluid with almost invariant solvent density at such conditions of temperature and pressure and hence higher temperatures will favor the extraction due to the greater oil vapor pressure oil components. As an example, Fig. 1 (supplementary material) shows the kinetics of pecan nut oil extraction at 35 °C and 40 bar using *n*-butane and the results clearly showed that 2 h was far enough to provide complete extraction, and no additional processing time for this and all other experimental conditions was required. The analysis of variance shown in Table 1 (supplementary material), showed that temperature variable had a significant influence on the extraction yield of pecan nut oil with pressurized *n*-butane (95% confidence level).

Table 2 (supplementary material) shows the fatty acid composition of pecan nut oil obtained by cold pressing, extraction with pressurized *n*-butane and commercial samples. The oleic acid was present in higher concentration in sample obtained by cold pressing (78.1%), which also presented the lower concentration of linoleic acid (13.6%). In samples obtained with pressurized *n*-butane and in commercial samples the values determined for oleic acid were lower (from 53 to 65.3 and from 60.1 to 73.9%, respectively). The concentration of linolenic acids in those samples were higher (between 26.2 e 24.8%, and 18.1 e 30.3%, respectively) 66.18–63.74% when compared with the samples obtained by cold pressing. The saturated fatty acid (Palmitic acid) present in higher concentration between 5.5 and 6.5% in the studied samples. Larger amounts of saturated fatty acids, (stearic and palmitic acid) were obtained at the highest pressure of 60 bar, independent of the system temperature, probably due to the better solvation of these apolar constituents by the surrounding solvent molecules. The results showed that the different conditions used for the extraction with pressurized had slight effect on the fatty acid composition of the samples. Overall, the chemical composition of pecan nut oil obtained by pressurized *n*-butane extraction was similar to that found by Villarreal-Lozoya et al. (2007) for several different pecan nut cultivars, on an average 6, 2, 67, 23, 1% for palmitic, stearic, oleic, linolenic, and linolenic fatty acids, respectively.

Conclusion

Extraction yields using pressurized *n*-butane, up to 65.3 wt%, was higher than that obtained from cold pressing, 58.9 wt%. In general, fatty acid composition was not affected for pressure and temperature conditions tested in *n*-butane extraction. Different contents were verified among samples most with regard to oleic and linolenic fatty acids. Extraction with *n*-butane showed to be efficient and interesting from a practical point view since mild temperatures and pressure may be used to afford good extraction yields.

Acknowledgements The authors are grateful to Divinut Ind. de Nozes Ltda (Cachoeira do Sul—RS), CNPq, CAPES, FAPERGS/RS, FAPESC/SC and MCTI-FINEP for financial support and scholarships.

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