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Research Note

The characterisation of oat lipids produced by supercritical fluid technologies

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Among cereals, oats are unique because of their high oil content, typically 2–12% (Zhou et al., 1999). Oat lipids are regarded as nutritionally important because they are highly unsaturated and contain several essential fatty acids (Youngs, 1986) and show a very high level of antioxidants (Peterson, 2001). Oats are important sources of glycolipids providing a large proportion of digalactosyl diacylglycerol (DGDG) (Andersson et al., 1997; Forssell et al., 1992). Traditionally oat lipids are divided into free and covalently bound forms according to their solubility properties. The polar lipids (PL, mainly covalently bound lipids) include glycolipids and phospholipids (Alkio et al., 1991), which are typically extracted from oat flakes by polar organic solvents.

Supercritical carbon dioxide (SC-CO_2) is the most common medium for the extraction of natural compounds. SC-CO_2 is produced by compressing CO_2 and heating it above its critical pressure and temperature. So far there are only a few reports of extraction of cereal lipids with SC-CO_2 (Hubbard et al., 2004; Rohrer et al., 2004) although extraction of oat lipids with SC-CO_2 was reported by Fors and Eriksson (1990). Alkio et al. (1991) removed the non-polar lipids from oat oil using SC-CO_2, and Forssell et al. (1992) compared methods for removing polar lipids from oat oil. Andersson et al. (1997) described a process for the production of DGDG from oat oil involving SC-CO_2.

The product obtained in a typical supercritical fluid extraction (SFE) process is an oil containing neutral lipids and volatile compounds. To isolate more polar lipids, e.g. glyco- and phospholipids, co-solvents are added to the fluid. Suitable co-solvents for cereals are ethanol and water (Dunford and Zhang, 2003; Fors and Eriksson, 1990). The micronisation of pharmaceutical compounds is a typical application of the supercritical antisolvent process (Harjo et al., 2005). In this study, we used SC-CO_2 with and without ethanol as co-solvent to isolate polar lipid fractions from oat flakes. In addition, a supercritical fluid technique resembling the antisolvent process (Reverchon, 1999) was used to precipitate the polar lipids from the ethanolic solution. The oils obtained were analysed for fatty acids and for glyco- and phospholipids.

Oat seeds were either groated with an homogenizer (Ultra Turrax, IKA, Germany) or dehulled and mechanically flattened to flakes in a local flour mill (Riihikosken Vehnämylly, Pöytyä, Finland). Both materials were kept at +4 °C until used.

The chemical composition of the flakes and their fractions were determined by the following methods: Moisture content was determined by weighing the samples. Samples were weighed before and after holding them at 105 °C for 16 h. Protein content was determined by multiplying Kjeldahl nitrogen (determined with the Kjeltec Auto 1030 Analyzer, Tecator, Sweden) by the factor 6.25. The crude fat content was determined by the Twisselman method (AOAC, 1980). Ash content was determined by weighing the samples before and after burning at 500 °C overnight.

Abbreviations: DGDG, Digalactosyl diacylglycerol; PC, Phosphatidyl choline; PL, Polar lipids (from oat); SC-CO_2, Supercritical carbon dioxide; SC-CO_2 -EtOH, Supercritical carbon dioxide with co-solvent ethanol; SF, Supercritical fluid; SFE, Supercritical fluid extraction

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The content of total carbohydrates was calculated using the formula:

Total carbohydrates (%/FW) = 100 − moisture (%) − protein content (%/FW) − crude fat (%/FW) − ash(%/FW) = total carbohydrates (g/100 *g* FW) (FW = fresh weight of the sample).

Fatty acids were analysed as their methyl esters using a Hewlett-Packard 5890 capillary gas chromatograph equipped with a DB-23 column (60 m × 0.25 mm id, film thickness 0.25 μm) and a mass-selective detector. A mixture of standard fatty acids (C4:0–C24:1) purchased from Nu-Check-Prep Inc. (Minnesota, USA) was used as a standard to identify the peaks. Lipid classes were analysed by liquid chromatograhy as described by Kivini et al. (2004). The quantitative yield of phosphatidylcholine (PC) and digalactosyl diglyceride (DGDG) is given as mg/g of precipitated lipids or g/l of ethanolic solution. All the other lipid classes were identified tentatively and determined only qualitatively.

In this study we used a pilot-scale multi-use SFE plant (Chematur Ecoplanning, Rauma, Finland). General information and technical details on the SFE plant are given in Adami et al. (2003). In the SFE step, the extraction chamber was filled either with groated oat or oat flakes. The mass of the material was 1.0 kg. Extraction was performed using pure CO_2 under supercritical conditions (70 °C, 450 bar, flow-rate 0.4 l/min measured as liquid). The total extraction time was 5 h. The quantity of extract (constituting mostly triacylglycerols and moisture) was measured every 30 min. In the second step, ethanol was added as a steady flow to the stream of CO_2 prior to the heating unit. SC-CO_2 modified with ethanol (96%, v/v) was allowed to flow through the partly de-oiled oat materials. The mass relation between ethanol and SC-CO_2 was approximately 10:90 and the corresponding extraction time was six hours. SC-CO_2–EtOH extraction was performed at 70 °C, 400 bar, flow-rate 0.25 l/min (measured as liquid), with 10 l of ethanol. Three batches of the ethanol solution (total volume 30 l) containing the slightly polar oat lipids were collected and reduced to 1/50 of the original volume using a rotary evaporator (Heidolph Laborata 20, Heidolph, Germany). In the antiosolvent procedure, the pressure of the system was set at 230 bar, temperature at 70 °C and SC-CO_2 flow-rate at 0.25 l/min. The ethanol solution was pumped (liquid flow 7.1 ml/min) with a high-pressure liquid pump to a second extractor acting as an antisolvent precipitation chamber. The polar lipids were precipitated on the walls of the chamber, and the ethanol was removed with the SC-CO_2 flow. The precipitates were weighed and stored at −18 °C.

The SC-CO_2 extraction curves for two different oat samples are shown in Fig. 1. The pale yellowish mixture of oily lipids, containing 62% of lipid, 32% water and 6% carbohydrate, was collected from the separator after SC-CO_2 extraction. The carbohydrate content was calculated by difference and

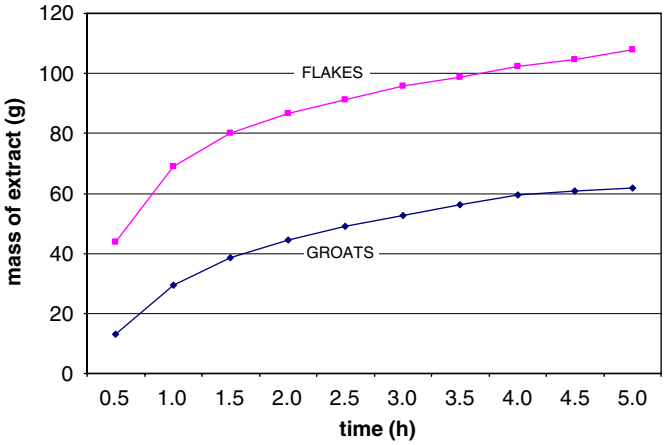

Fig. 1. SC-CO_2 extraction curves in 1 kg of oat flakes and 1 kg of oat groats (70 °C, 450 bar, flow rate 0.41 min measured as liquid).

Table 1
Basic compositions of oat flakes before and after the SF extractions

	Oat flakes	Oat flakes after SFE	Oat flakes after SFE-EtOH
Protein	12.20*	11.4	13.6
Carbohydrates	69.40	76.8	76.1
Lipids	5.27	1.36	0.73
Water	10.60	8.39	7.7
Ash	2.51	2.01	1.91

*% of fresh weight.

includes any components not found by the other analytical methods used to determine the basic chemical composition. The HPLC analysis showed that the extract contained neutral lipids (triacylglycerols, sterols, carotenoids) and free fatty acids. During storage at +4 °C, a clear water phase separated at the bottom of the storage bottles. With oat flakes the extraction efficiency was 1.7 times more effective than with groated oats. Oat flakes were therefore selected as the material for further SC-CO_2 processes.

The compositions of the oat flake samples before and after the SC-CO_2 processes are given in Table 1. About 87% of the original crude fat was removed in the two extraction steps (SC-CO_2 extraction and SC-CO_2–EtOH extraction). Based on the data in Table 1, about 53 g of neutral lipids and 106 g of water would be extractable from 1.0 kg of starting materials using SC-CO_2. As shown in Fig. 1, the yield of extract from oat flakes was about 108 g. After storage at +4 °C, the oil phase was typically 50–60% of the total volume, which agrees well with the values in Table 1. Andersson et al. (1997) used acetone for the extraction of lipids and reported a lipid value of 52 g/kg.

The SC-CO_2–EtOH process yielded a pale yellow ethanol solution in the separator. This solution was further processed using an antisolvent-type process. The volume of the feed was 600 ml. The precipitation of the SFE–EtOH–PLs in the antisolvent process produced a greyish-green, grease-like fraction. The precipitate weighed 15 g on