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Extraction of Citrus Oil from Peel Slurry of Japanese Citrus Fruits with Supercritical Carbon Dioxide

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Abstract: Peel slurry of some Japanese citrus fruits, such as lemon, shikuwasa and daidai, was used as an alternative source of citrus oil and the extraction was conducted by using supercritical carbon dioxide at 333 K and 20 MPa in order to compare the compositions and the extraction efficiency of oils extracted from these slurries. The peel slurry of citrus fruits containing oil, water and solid cellulose materials was used as a feed material of this study. Extraction was carried out at 333 K and 20 MPa while the extraction efficiency over 80% was obtained for lemon and shikuwasa but it was about 60% for daidai peel slurry. The extracted oils were analyzed by GC-FID and GC-MS to compare the compositions of oils among these peel slurries. The compositions of extracted oils differed qualitatively and quantitatively from each other of feed materials in such a way that the monoterpenes ($C_{10}H_{16}$) content varied 89.23 to 93.20% with the type of peel slurry, while limonene as a major compound. Oxygenated compounds in these oils represented 8.84, 5.5 and 4.49% in lemon, daidai and shikuwasa peel slurry, respectively. The obtained product with the composition was almost the similar with the other citrus oils extracted from fresh fruit peels.

Key words: Supercritical carbon dioxide, peel slurry, citrus oil compositions, oxygenated compounds, extraction efficiency

INTRODUCTION

Peel slurry of the citrus fruits is produced as an industrial waste after extraction of juice in various citrus fruits processing industries that contains citrus oils, water and solid cellulose materials. The citrus oils are widely used in the food, beverage, pharmaceutical, perfume and cosmetic industries. It is usually extracted from citrus fruits by cold-pressing or steam distillation. Citrus oils from Colombian lemon and orange have been extracted by steam distillation and/or cold pressing and the compositions also have been compared at different stages of maturity of the fruits[1]. The conventional production methods of oils such as steam distillation or solvent extraction can lead to degradation of heat sensible compounds and partial hydrolysis of water sensible compounds. Supercritical fluid extraction is an alternative process to the conventional methods.

Supercritical fluid extraction has received increasing attention in a variety of fields due to the following factors: (I) supercritical fluids provide solubility and mass transfer rates; (ii) operation can be manipulated by changing the pressure or temperature[2,3]. Carbon dioxide is mostly used as supercritical fluid for the extraction of citrus oils from natural materials because of its low critical temperature that prevents the thermal degradation of volatile components of the citrus oils, no residual problem, odorless and colorless properties. It is also non-toxic and is generally accepted as a harmless ingredient of foods and beverages and easily available. The physical properties of carbon dioxide that make it widely used in extraction processes are low surface tension and viscosity and high diffusivity[4]. The diffusivity of supercritical fluid is one to two orders of magnitude than those of other liquids, which permits rapid mass transfer, resulting in a larger extraction rate than that obtained by conventional methods.

The extraction of the flavoring materials from fruit juice[5] and many other natural products[6,7] with supercritical carbon dioxide has been carried out. This method shows great potential in replacing conventional methods such as liquid solvent extraction and steam distillation[8].

Citrus oil is an essential oil composed of two main components of which are the terpene hydrocarbons (the major component) and oxygenated terpinoids[9]. The citrus oil generally contains over 90% monoterpenes, about 5% oxygenated compounds and less than 1% non

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volatiles such as wax and pigments[10]. Limonene is a principal (about 70%) compound of monoterpenes but do not contribute much to the flavor or fragrance of the oil but a good solvent for polystyrol in chemical recycling process[11]. Furthermore, non volatiles such as wax and pigments are high viscous and show phototoxic activity that produce the turbidity in the oil. The characteristics flavor of citrus oil is provided by the oxygenated terpenes that mainly consist of alcohols, aldehydes and ester such as linalool, citral (neral and geranial) and linalyl acetate. Considering these properties of terpenes of citrus oil, there were so many works have been done by a group of researchers, for the separation of terpenes from citrus oil that was extracted from different kind of citrus fruits[12,13]. But there is no little attention to the slurry of citrus fruit peel as a source of citrus oils.

The aim of this study was to pay attention to the peel slurry of citrus fruits, such as lemon, shikuwasa and daidai as an alternative source of citrus oil. Oil was extracted from peel slurry by using supercritical carbon dioxide at 333 K and 20 MPa in order to compare the compositions of oils extracted from these slurries.

MATERIALS AND METHODS

Citrus fruits peel slurry was supplied by Maruboshi Vinegar Co. Ltd. after extraction of juice. This slurry was packaged in a polyethylene bag and stored in a freezer at a temperature of 253 K to avoid the degradation and used as a feed material to extract the citrus oils.

A schematic diagram of the experimental apparatus is shown in Fig. 1. Liquid carbon dioxide from a cylinder with a siphon attachment is passed by a pump through a chiller at a temperature about 263 K and compressed to the operating pressure by Back Pressure Regulator (BPR)-1. Compressed carbon dioxide flows through the heat exchanger into the extraction column (21x5 cm inside diameter) placed in a thermostat bath where the experimental temperature is maintained. The bottom end of the extractor is fixed with a filter and the upper end can be closed or open by a movable filter. The exit fluid from the extractor is expanded at separator to the pressure of 4 MPa and to the temperature of 277 K. The pressure of the separator is controlled by the back pressure regulator-3. The back pressure regulator-2 controls the pressure at the exit of the extractor. Dry gas meter measures the exit flow rate of carbon dioxide. There are four Pressure Gauges (PG) indicate the pressure at the concerning places.

Slurry was squeezed by hand to exude the containing water as much as possible and without any other treatment about ¾ th part of the extractor was filled with a known amount of slurry to avoid the extrusion of the remaining water of the sample while the pressure increased in the column. The empty space of the column was filled with some glass wool and the column was placed vertically in the thermostat bath. Oil was extracted with supercritical carbon dioxide in a semi-continuous-flow extractor. After reaching the chiller temperature of 263 K and the experimental temperature at the thermostat bath, pump was started to flow the carbon dioxide while the pressure was gradually increased at the entrance of the column by BPR-1 to experimental pressure that was indicated on PG-2, the port valve was turned on so that carbon dioxide was began to enter into the column. The same experimental pressure was maintained at the exit point of the column by BPR-2 that was also monitored on PG-3 while the carbon dioxide was passed through the column to start the extraction and the exit fluid (carbon dioxide with citrus oils) was expanded at the separator where oil was collected and the gas was vented through

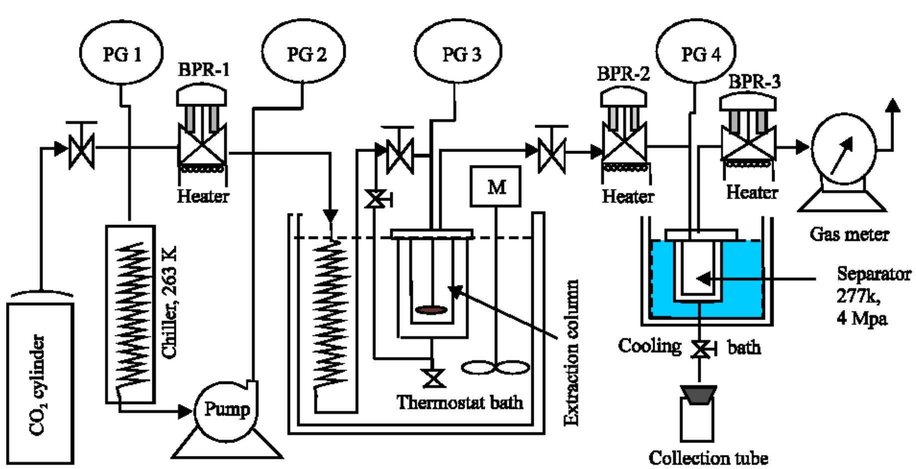

Fig. 1: Scheme of experimental set-up

the dry gas meter. The pressure of the separator was controlled by BPR-3. The extracted oil was so small that was collected by washing out with ethanol. The extraction was carried out for about 6 h at the experimental temperatures and pressures.

The extracted oils were analyzed with capillary gas chromatography-flame ionization detector (GC-FID) and Gas Chromatography-mass Spectrometry (GC-MS) methods. The GC-FID analysis was performed with a Shimadzu GC-14A instrument (Shimadzu Inc., Tokyo, Japan) equipped with a J and W DB5-fused silica capillary column (15x0.25 mm I. d.x0.25 μm film and FID. The operation conditions of the GC were: oven temperature 343 K for 1 min. then programmed from this temperature to 434 K at 3 K min^{-1}. and subsequently isothermal at 434 K for 2 min. Injector and detector temperature were 523 K and 573 K, respectively.

The GC-MS analysis was carried out at the same conditions as in the GC-FID analysis by using Hewlett Packard-5890 series II gas chromatograph equipped with a mass selective detector (HP 5972). The column used was a HP-5 (30 m x 0.25 mm id., film thickness 0.25 mm). The identification of compounds was based on the comparison of the retention times of some pure compounds and of mass spectra libraries.

RESULTS AND DISCUSSION

Citrus oils were extracted from the slurry of fruit peels of lemon, shikuwasa and daidai with supercritical carbon dioxide at 20 MPa and temperature of 333 K. The total amount of extractable citrus oils was determined on the basis of GC-FID analysis after extraction with hexane for about 72 h to compare the amount of extracted oils in supercritical carbon dioxide extraction. The extraction efficiency in supercritical carbon dioxide extraction was calculated by comparing the yield obtained in this process with the amount of extractable oils that was above 80% for lemon and shikuwasa peel slurry but it was 65% for daidai. This may be due to the more sticky property of daidai peel slurry.

Composition analysis: The extracted citrus oils at experimental condition were analyzed by using GC-FID and GC-MS. The typical gas chromatograms of the extracted oils are shown in Fig. 2. The compounds were identified by comparison of the retention times of some pure compounds and of mass spectra libraries in GC-MS and also with the literature[1]. The GC-FID peak ratios of extracted oil compounds with external standard compound were converted to mole ratios for quantitative analysis by comparing with the calibration curve, Fig. 3 that was computed on the FID response (peak ratios) of two pure standard compounds, such as limonene and linalool as major compounds of citrus oils and an external standard compound (n-pentane) versus the respective mole ratios of these compounds.

About total 20 compounds were detected in these extracted oils in which 12 for lemon, 16 for shikuwasa and 12 for daidai while the compositions differed considerably both quantitatively and qualitatively (Table 1). Limonene was the main compound of the extracted oils from all feed materials, with a mass ratio that varies in the ranges 62-89%.

Figure 4 shows comparative chemical compositions of extracted oils from different feed materials, based on the compound group classification. Daidai peel slurry possessed highest content (92%) of monoterpenes ($C_{10}H_{16}$) while lemon and shikuwasa peel slurry contained 89 and 90%, respectively. The amount of oxygenated compounds in oil extracted from lemon peel slurry was about 8.8% that was 1.5 and 2 times greater than those extracted from daidai and shikuwasa peel slurry, respectively.

Figure 5 shows the comparative chemical compositions of oxygenated compounds found in extracted citrus oils analyzed. Acetate compounds were 1.6 and 5 times more abundant in daidai peel slurry oil (3%) than in lemon and shikuwasa peel slurry oils but aldehyde compounds were mostly abundant in lemon peel slurry (5.5%) that was negligible amount in both other two feed materials in comparison of this amount. Shikuwasa peel slurry oil contained more alcohol compounds than those of daidai and lemon peel slurry oils.

Table 1: Chemical compositions (wt. %) of citrus oils extracted from peel slurry of lemon, shikuwasa and daidai at 20 MPa and 333 K

Compounds	Lemon (wt. %)	Shikuwasa (wt. %)	Daidai (wt. %)
α-Phellandrene	0.20	0.41	---
α-Pinene	1.12	2.14	0.20
β-Pinene	6.82	2.45	0.70
β-myrcene	0.92	1.58	1.50
Limonene	69.74	62.65	89.00
3-Carene	10.42	22.73	1.6
β-Phellandrene	----	----	0.20
Linalyl propanoate	0.67	0.52	----
Unknown-al	----	0.92	0.40
Linalool	1.55	3.05	2.10
Neral	2.37	----	----
Geranial	3.15	----	----
Linalyl acetate	1.10	----	3.00
Caryophyllene	1.23	0.68	0.40
Camphene	----	0.23	0.60
Copaene	----	0.22	----
Elemene	----	0.24	----
Germacrene D	---	0.72	----
Germacrene B	----	0.78	0.30
Unknown	0.70	0.58	----

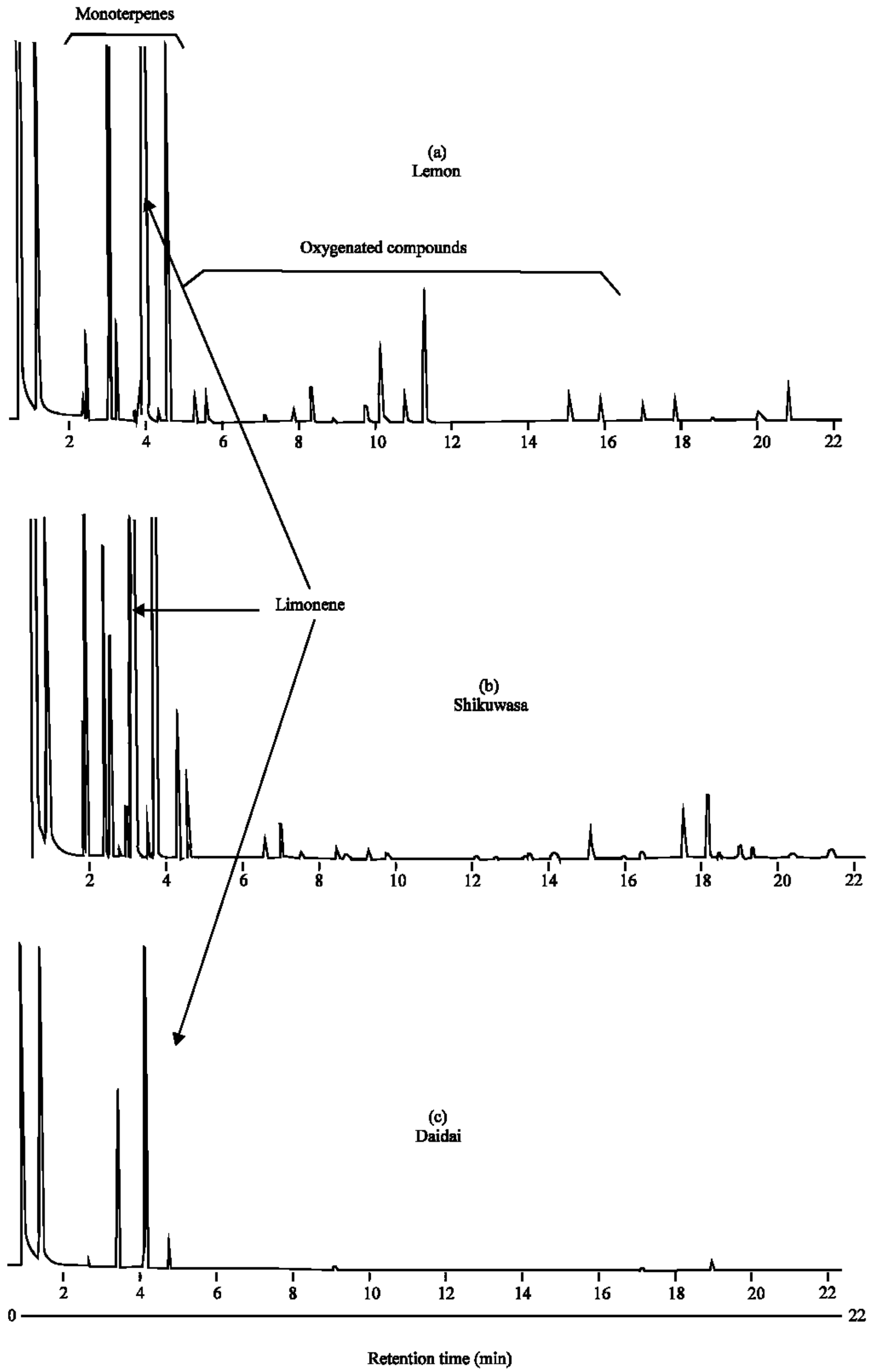

Fig. 2: Typical gas chromatograms of extracted citrus oils from peel slurry of Lemon (a), shikuwasa (b) and daidai ©

These results conform with the literature[1,10] while cold-pressed lemon oil (DA-377, Givaudan-Roure Flav Ltd., produced in Brazil), contained about 96% monoterpenes and 3% oxygenated compound[10] and

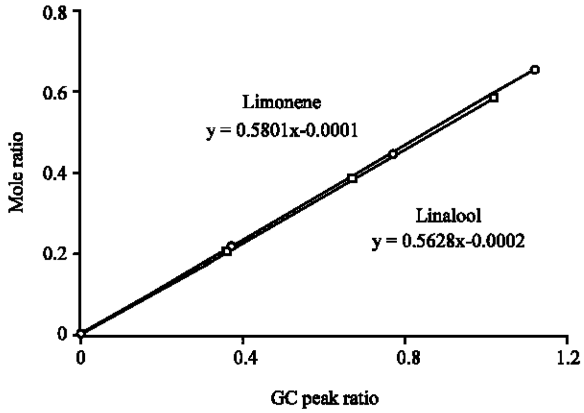

Fig. 3: Calibration curves of lemonene and linalool with n-pentane

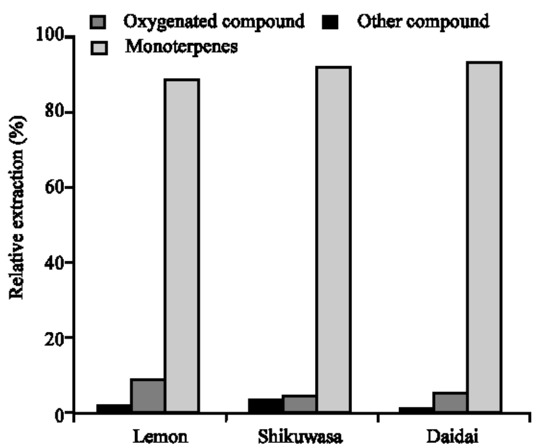

Fig. 4: Comparative chemical compositions of extracted citrus oils with supercritical carbon dioxide

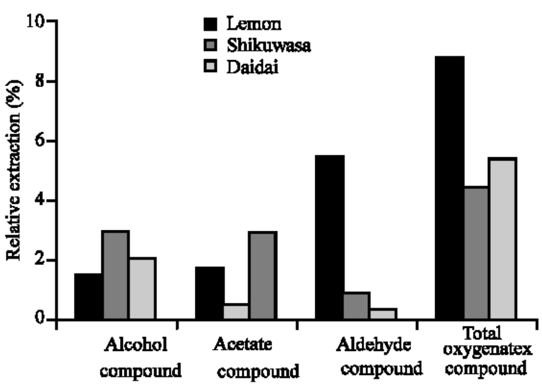

Fig. 5: Comparative chemical compositions of oxygenated compounds in the extracted citrus oils with supercritical carbon dioxide

Colombian lemon, mandarin and orange peel oils contained from 94 to 98% of monoterpenes, lemonene as a major component and from about 1 to 6% of oxygenated compounds[1].

CONCLUSIONS

Citrus oils were extracted from the peel slurry of Japanese citrus fruits such as lemon, shikuwasa and daidai with supercritical carbon dioxide at 20 MPa and 333 K and extracted oils were analyzed by GC-FID and GC-MS. At this condition, the extraction efficiency was about 80% for lemon and shikuwasa but it was about 65% for daidai peel slurry. GC-analysis revealed that the chemical compositions of the extracted oils differed quantitatively and qualitatively from each other of the feed materials. The content of monoterpenes was 89.23, 91.96 and 93.20% and of oxygenated compounds was 8.84, 4.49 and 5.5% in the peel slurry of lemon, shikuwasa and daidai citrus fruits, respectively.

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