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Bigarade Peel Oil Fractionation by Supercritical Carbon Dioxide Desorption

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Desorption of bigarade peel oil from a polar adsorbent was performed by supercritical CO_2 to improve the oil quality by selectively eliminating hydrocarbon terpenes and coumarins. The oil fractions obtained at 40 °C, at pressures between 77 and 120 bar, and at different desorption times were analyzed by GC−MS. Three fractions were characterized: terpenic fraction, deterpenated fraction, and residue. The content of oxygenated compounds in the deterpenated fraction was 6.6 times higher than in the crude oil. Coumarins, psoralens, polymethoxyflavones, and waxes contained in the starting material were recovered and identified in the residue fraction.

INTRODUCTION

Citrus peel oils are traditionally produced by mechanical expression of the whole citrus fruit. They are mainly constituted of hydrocarbon terpenes (from 60 to 98%), oxygenated terpenes (from 2 to 38%), and nonvolatile compounds such as waxes, coumarins, psoralens, and flavones (McHale and Sheridan, 1988; Lawrence, 1992; Di Giacomo and Mincione, 1994).

Only oxygen-containing constituents contribute to citrus peel oil fragrance. Hydrocarbon terpenes are relatively unstable and tend to decompose, impairing the quality of the products and shortening the shelf life of the flavored preparation. For example, the easy autoxidation of limonene to carvone and carveol has been suggested as being responsible for terpene-like off-note formation (Ziegler et al., 1991). Coumarins and waxes can partly precipitate, giving turbidity to oil. Moreover, some psoralens contained in peel oils have a well-established allergenic and phototoxic action on the human skin (Naganuma et al., 1985). Therefore, it would be advisable to reduce the hydrocarbon terpene content and to eliminate the nonvolatile fraction from the citrus peel oils.

Liquid and supercritical CO_2 extraction (SFE) have been widely used to obtain aromas from vegetable matter (Stahl and Gerard, 1985; Reverchon, 1992; Reverchon and Senatore, 1992; Moyler, 1993; Reverchon et al., 1994). In many cases oils with an aroma profile that better resembled that of the vegetable matrix were obtained, compared to steam-distilled products (Reverchon and Senatore, 1994; Reverchon et al., 1995). SFE of citrus peel oils has also been attempted by some authors (Poiana et al., 1994).

Stahl et al. (1988) indicated the feasibility of a continuous countercurrent separation by supercritical CO_2 in a high-pressure column with an axial temperature gradient. Their operation conditions were deduced from vapor-equilibrium data of pure oil compounds. Recently, Sato and Goto (1994) used a supercritical CO_2 extraction tower in both semibatch and continuous operation to fractionate a model mixture of citrus oil constituted by two components (limonene and linalool).

Yamauchi and Saito (1990) proposed the desorption of lemon peel oil from a column packed with silica gel, using a semipreparative supercritical chromatographic system. They obtained four different fractions that were characterized by GLC. Cully et al. (1990) proposed the peel oil desorption from several adsorbents by supercritical CO_2, using temperatures from 50 to 70 °C and pressures from 70 to 90 bar. The use of the supercritical CO_2 desorption technique has been suggested to deterpenate the lemon (Barth et al., 1994), bergamot (Chouchi et al., 1995), and mandarin (Della Porta et al., 1995) peel oils. These authors also eliminated coumarins and psoralens from the cited oils. They operated the fractional desorption by increasing CO_2 density in successive steps. Vega-Bancel and Subra (1995) examined the desorption breakthrough curves from silica gel of a model mixture constituted by six hydrocarbon terpenes and six oxygenated terpenes. They showed that at CO_2 densities around 0.75 g/cm³ (37 °C, 130 bar) all breakthrough curves overlapped; thus, no selectivity was obtainable at those conditions. At CO_2 densities of 0.50 g/cm³ (47 °C, 100 bar) two different curve families were obtained for hydrocarbon and oxygenated terpenes. Better selectivities should be obtained at lower CO_2 densities. Dugo et al. (1995) used an ISCO 2.5 cm³ internal volume apparatus to deterpenate sweet orange and lemon oils. These authors characterized the performance of different adsorbents and concluded that

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silica gel is the most indicated for supercritical desorption of citrus peel oils. They also compared products obtained by supercritical desorption to the ones obtained by vacuum distillation.

The aim of this work was the supercritical CO_2 fractional desorption of bigarade (bitter orange) peel oil to reduce its content of hydrocarbon terpenes. Elimination of the high molecular weight compounds (nonvolatile fraction) was also attempted. GC−MS analysis of the various desorbed fractions was performed to obtain the optimal process conditions and to identify the bigarade peel oil compounds.

EXPERIMENTAL APPARATUS, MATERIALS, AND METHODS

Apparatus and Methods. The desorption unit was equipped with a membrane pump (Milton Roy, Pont Saint Pierre, France; Model Milroyal D) for supercritical solvent delivery, capable of CO_2 flow rates up to 3.6 dm^3 h^{-1} at a maximum pressure of 250 bar. The desorption column had an internal volume of 0.18 dm^3. A thermostated jacket controlled the temperature inside the column. The desorber was manually filled with 100 g of the adsorbent (silica gel, Merck, Darmstadt, Germany). Peel oil was charged into the desorption column with a piston pump (Milton Roy, Model Instrument Minipump A). CO_2 flow rate was measured at the outlet of the apparatus by a calibrated rotameter.

The desorbed fractions were precipitated in two high-performance thermostated cyclonic separators operated in series at 30 bar, 40 °C and at 20 bar, 15 °C, respectively. It was possible to discharge the product continuously from the bottom of each separator. By using this technique, it was possible to analyze the various fractions produced during the desorption process. Some desorption tests were also performed by changing the operating pressure around the optimum conditions obtained in previous works (Barth et al., 1994; Chouchi et al., 1995).

A typical desorption test started with charging the citrus peel oil (20 g) into the desorber by the liquid pump and waiting for 12 h for its adsorption on the silica gel, filled in the high-pressure column. The column was then heated to 40 °C. The desorption test took place when the CO_2 started to flow.

The oil fractions at the beginning of the desorption process were collected every 5 min. Then we waited for longer times when, due to the progressive exhaustion of the charge, smaller quantities of oil were collected. The oil fractions were analyzed by GC−MS to establish the progress of desorption. At the end of the desorption process the column was regenerated with ethanol to remove the most strongly adsorbed compounds. More details on the desorption apparatus and on the experimental procedures were given in previous papers (Barth et al., 1994; Chouchi et al., 1995).

Materials. Bigarade (*Citrus aurantium* L.) peel oil was kindly supplied by IFF (Longvic, France). Oil was produced by cold pressing and was postprocessed by "chilling". This procedure consists of suddenly freezing the oil, allowing the precipitation of part of the high molecular weight compounds (waxes and coumarins). This procedure is widely used to improve peel oil quality (Hendrix et al., 1992).

Industrial CO_2 (99% purity) was supplied by Carboxyque Francaise (Hauconcourt, France).

Analytical Methods. The GC−MS apparatus was a Varian (San Fernando, CA) capillary GC connected to an ion trap detector (Finnigan MAT, San Jose, CA; Model ITS 40 Magnum). Separation was achieved by a fused-silica capillary column (Model DB-5, J&W, Folsom, CA), 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness. GC conditions were as follows: oven temperature of 40 °C for 5 min and then programmed heating from 40 to 250 °C at 2 °C min^{-1} and subsequent holding at 250 °C for 60 min. The injector was maintained at 280 °C (splitless 20 cm^3 min^{-1}), and helium was used as the carrier gas (1 cm^3 min^{-1}). Samples were run in dichloromethane with dilution of 0.05% by weight.

The area percentage of compounds desorbed was calculated from the chromatogram. The area percentages were converted to absolute values using ion trap relative response factors estimated from the ion trap responses of pure standard compounds having the same molecular weight of the compound families that constitute the bigarade oil. The compounds were identified by matching their mass spectra and retention times with those of pure compounds whenever possible. NIST (U.S. National Institute of Standards and Technologies), and WILEY5 mass spectra libraries were also used as references.

RESULTS AND DISCUSSION

The process was monitored by considering bigarade peel oil as constituted by two key pseudocompounds: hydrocarbon terpenes and oxygenates terpenes.

The desorption process was based on the hypothesis that supercritical CO_2 at an opportune density can selectively desorb hydrocarbon terpenes and oxygenated terpenes, leaving the high molecular weight compounds undesorbed. Indeed, good fractionation results were obtained by operating at 40 °C, 77 bar pressure (CO_2 density about 0.25 g cm^{-3}), and a CO_2 flow rate of 1.3 kg h^{-1}. Tests performed at higher densities gave a lower process selectivity. Indeed, a fine tuning of the solvent power is required during supercritical processes to avoid the simultaneous extraction of several families of compounds (Reverchon, 1992; Reverchon and Senatore, 1994; Reverchon et al., 1994).

We observed that hydrocarbon terpenes were rapidly desorbed at the beginning of the desorption process. Therefore, they were collected in high percentages in the initial fractions. Then, the desorption of this family of compounds reached an asymptotic value. All of the fractions recovered at desorption times higher than 30 min contained oxygenated terpenes and minor percentages of hydrocarbon terpenes (around 20%). These fractions were collected together as the deterpenated fraction. Final desorption steps were performed at 40 °C, 100 and 120 bar, to completely desorb the oxygenated compounds. No coumarins were detected in the GC traces of desorbed fractions during any of the desorption process.

The identifications of compounds constituting the crude bigarade peel oil are reported in Table 1. The percentage of hydrocarbon terpenes in the crude oil was 92.45%, with limonene as the major constituent (82.12%).

GC−MS analysis was performed for each fraction collected by discharging the separation vessel. These GC traces can be used to evaluate the shift of the desorbed samples toward compounds with higher retention times, i.e., compounds with a higher polarity and/or molecular weight. The hydrocarbon and oxygenated fractions were extensively analyzed, and their detailed composition is reported in Table 1.

The hydrocarbon fraction of bigarade peel oil was extracted in 30 min at 77 bar and 40 °C. Its composition is reported in Table 1 (column F_1). It was mainly constituted of hydrocarbon terpenes (99.41%), with a limonene content of 88.79%. Small quantities of oxygenated terpenes were also detected (0.58%).

The subsequent fractions show a progressive enrichment in oxygenated compounds. The second fraction reported in Table 1 (column F_2) was collected from 30 to 140 min of the desorption process. It presented an area of oxygenated compounds of 49.87%, with the main contributions coming from linalool (4.70%), linalyl acetate (6.09%), α-terpineol (3.08%), and geranyl acetate (2.75%), that are the characteristic components of this peel oil (Di Giacomo and Mincione, 1994). *cis-* and

Table 1. Compounds Identified and Their Percentages in the Bigarade Peel Oil (Crude Oil) and Its Fractions Produced by Desorption with SC-CO$_2$[a]

compound	RT[b] (min)	crude oil %	F$_1$ %	F$_2$ %	residue %
n-heptanal	10.02	0.08	----	----	0.22
α-thujene	11.19	tr[c]	tr	----	----
α-pinene	11.46	0.75	0.63	----	----
camphene	12.34	0.23	0.28	----	----
benzaldehyde	13.12	0.08	----	----	----
sabinene	14.01	0.05	2.61	0.26	0.05
β-pinene	14.22	2.53	----	0.32	----
5-methylhepten-2-one	15.24	----	----	----	0.04
β-myrcene	15.44	1.59	1.84	2.13	0.49
carene	16.19	tr	tr	----	----
α-phellandrene	16.26	0.27	0.08	3.05	0.85
α-terpinene	16.45	0.13	0.12	0.14	0.06
p-cymene	17.45	2.07	2.83	2.53	0.56
limonene	**18.10**	**82.12**	**88.79**	**32.04**	**1.16**
cis-ocimene	19.02	0.04	----	0.41	0.06
trans-ocimene	19.43	0.06	0.18	0.70	0.13
γ-terpinene	20.15	0.10	0.31	0.17	0.07
acetophenone	20.33	tr	tr	----	----
terpinolene	20.46	tr	----	0.13	----
trans-linalool oxide	21.13	0.02	----	0.08	0.19
n-octanal	21.29	----	----	0.19	----
p-cymenene	22.21	1.36	1.65	3.36	0.62
methyl benzoate	22.38	0.56	----	0.17	----
2-nonanone	22.53	----	----	----	0.11
linalool	**23.22**	**0.52**	**0.10**	**4.70**	**1.40**
n-nonanal	23.41	0.07	0.05	0.14	0.10
1,3,8-*p*-menthatriene	24.00	0.11	0.03	0.26	0.15
cis-sabinene hydrate	24.33	0.66	----	3.09	1.25
cis-limonene oxide	25.28	0.49	0.05	0.16	----
1,3,8-*cis*-menthatriene	25.37	0.33	0.06	2.99	----
trans-limonene oxide	25.49	0.28	0.14	0.32	1.30
pinocarvone	27.23	0.04	----	----	----
trans-β-terpineol	27.49	0.16	----	0.14	----
4-terpineol	28.36	0.15	0.02	1.29	0.40
α-terpineol	29.35	0.11	----	3.08	0.85
methyl salicylate	29.42	0.14	----	tr	----
trans-dihydrocarvone	29.57	0.13	0.02	0.87	0.25
isodihydrocarveol	30.17	0.06	----	1.26	0.75
C$_{10}$H$_{14}$O	30.32	0.06	----	0.06	----
n-decanal	31.00	0.15	----	0.88	----
trans-carveol	31.40	0.62	----	6.92	2.99
cis-carveol	32.29	0.34	----	5.46	2.21
carvone	33.15	1.21	----	2.96	2.24
linalyl acetate	**34.37**	**0.68**	**0.15**	**6.09**	**2.06**
C$_{10}$H$_{14}$	35.07	0.05	----	0.22	----
perillaldehyde	35.17	0.09	----	0.63	----
menthyl acetate	37.17	----	----	tr	0.57
C$_{10}$H$_{16}$O	39.12	----	----	2.44	1.32
C$_{10}$H$_{16}$O	40.09	----	----	----	2.86
perilla alcohol	40.54	----	----	2.61	----
α-terpineyl acetate	41.00	tr	----	tr	1.78
neryl acetate	41.57	----	----	0.33	----
n-undecanol	42.51	----	----	0.09	----
C$_{11}$H$_{20}$O$_2$	42.54	----	----	----	0.44
geranyl acetate	43.14	0.13	----	2.75	1.09
ethyl antranilate	44.15	----	----	0.10	----
cyclic compound MW 194	44.48	----	----	0.30	0.12
caryophyllene	45.02	----	----	0.73	----
n-tetradecane	45.04	----	----	----	0.30
cyclic compound MW 194	46.21	----	----	0.65	0.30
α-humulene	47.11	----	----	0.11	----
cis-β-farnesene	47.53	----	----	0.20	----
γ-muurolene	48.57	----	----	0.13	----
C$_{12}$H$_{24}$O	49.43	----	----	----	0.25
methyl eugenol	50.15	0.76	----	----	----
nerolidol	53.29	----	----	----	0.28
ledol	54.21	----	----	1.39	1.41
spathulenol	54.43	----	----	0.21	0.29
globulol	55.00	----	----	0.56	0.38
santalol	55.41	----	----	0.10	----
cis,cis-farnesol	56.31	----	----	0.06	0.64
oxyg sesquiterp MW 220	57.51	----	----	0.15	0.77
oxyg sesquiterp MW 220	58.53	----	----	----	0.23
oxyg sesquiterp MW 220	59.10	----	----	----	0.26
oxyg sesquiterp MW 220	61.01	----	----	----	0.33
benzyl benzoate	65.16	0.66	----	----	0.83

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Table 1 (Continued)

compound	RT[b] (min)	crude oil %	F$_1$ %	F$_2$ %	residue %
citropten	76.14	----	----	----	0.32
methyl palmitoleate	77.03	----	----	----	0.16
bergapten	**79.38**	----	----	----	**2.16**
isobergapten	80.05	----	----	----	0.09
coumarin MW 266	80.27	----	----	----	0.10
oxyg sesquiterp MW 222	81.30	----	----	----	0.08
suberosin	**83.48**	----	----	----	**5.20**
auraptenol	**86.56**	----	----	----	**2.81**
isomeranzin	**88.35**	----	----	----	**23.47**
n-nonadecenal	89.19	----	----	----	0.70
osthole	**90.11**	----	----	----	**4.24**
5-methoxyisomeranzine	92.27	----	----	----	0.08
8-(3-methyl-2-oxobutyl)-7-methoxycoumarin	93.36	----	----	----	0.22
8-(3-methylbutyl)-7-methoxycoumarin	94.44	----	----	----	0.14
6-(3-methyl-2-oxobutyl)-7-methoxycoumarin	95.23	----	----	----	tr
meranzin hydrate	**96.23**	----	----	----	**6.42**
meranzin	**97.47**	----	----	----	**14.27**
$C_{20}H_{36}O_2$	101.20	----	----	----	0.55
n-heptacosane	107.20	----	----	----	0.02
$C_{20}H_{36}O_2$	111.55	----	----	----	0.07
tangeretin	**130.47**	----	----	----	**2.75**
$C_{22}H_{28}O_5$	136.41	----	----	----	0.18
$C_{22}H_{30}O_4$	142.15	----	----	----	0.46
nobiletin	149.30	----	----	----	0.49

[a] Percentages are expressed without any correction factor. [b] Retention time. [c] Trace, <0.01%.

trans-carveol (12.38%) and carvone (2.96%) were also present; their content is due to the easy autoxidation of limonene and increases during fruit ripening (Boelens and Jimenez, 1989). Hydrocarbon sesquiterpenes (1.82%) and oxygenated sesquiterpenes (2.47%) were also found in low percentage. In comparison, the content of oxygenated compounds in the deterpenated fraction of bigarade oil was approximately 6.6 times higher compared to that in the crude oil. The 80% by weight of the oxygenated compounds (1.21 g) charged into the desorber was recovered in this fraction. Therefore, a good overall performance of the desorption process was obtained.

The nonvolatile material that remained in the column after the desorption process was recovered by washing the adsorbent medium with warm ethanol. The weight of this fraction was 1.11 g. Its analysis is reported in Table 1 (column residue). We adopted this procedure to recover the undesorbed material instead of further increasing the operating pressure. It is simpler and we were not interested in a further fractionation of the charge. The ethanol-extracted product contained hydrocarbon terpenes (5.00%), oxygenated terpenes (23.77%), and oxygenated sesquiterpenes (6.17%). It also contained paraffins and fatty acid methyl esters (1.18%). High percentages of coumarins (59.52%), polymethoxyflavones (3.24%) and other high molecular weight compounds (1.18%) were also detected. Only a few waxes were detectable in the residue since the oil was previously submitted to a winterization process (Hendrix et al., 1992).

The percentage content of terpenes in the residue indicates that longer processing times were perhaps necessary to obtain the complete desorption of the volatile compounds. As indicated by Barth et al. (1994), the content of terpenes in the residue could be attributed to the presence in the column of high molecular weight compounds, which can block some pores of the adsorbent medium and prevent the whole desorption of the oil. However, the most interesting characteristic of residue was the high content of coumarins and psoralens. We identified citropten (0.32%), bergapten (2.16%), isobergapten (0.09%), suberosin (5.20%), auraptenol (2.81%), isomeranzin (23.47%), osthole (4.24%), meranzin hydrate (6.42%), meranzin (14.27%), and some other disubstituted coumarin isomers with a molecular weight between 244 and 260 (see Table 1). The significant amount of coumarin derivatives coming from osthol and meranzin could be due to the hydrolysis of glycosides of these two compounds during the cold-pressing process. For example, meranzin [8-(2′,3′epoxy-3-methylbutyl)-7-methoxycoumarin) and meranzin hydrate [8-(2,3-dihydroxy-3-methylbutyl)-7-methoxycoumarin) were produced by the hydrolysis of 13-*O*-β-D-glucopyranoside of meranzin during the fruit processing (McHale et al., 1987). Isomeranzin, instead, may be an artifact formed from auraptenol (Stanley et al., 1965). These coumarins do not have any demonstrated photosensitizing activity. However, their presence gives an indication of the complexity of the high molecular weight compounds contained in bigarade crude oil.

Some polymethoxyflavones that are specific to this peel oil (Di Giacomo and Mincione, 1994) were also found in the residue. We identified tangeretin (2.75%) and nobiletin (0.49%). They were not detectable in the crude oil because of their very low concentrations in the starting material.

CONCLUSION

The supercritical CO_2 fractional desorption was demonstrated to largely reduce the content of hydrocarbon terpenes in the bigarade peel oil. The "oxygenated enriched fraction" did not show terpene-like off-note formation even after long storage. Moreover, all of the high molecular weight compounds present in the oil were eliminated.

The large number of high molecular weight and cyclic compounds that were identified in the residue suggested that the desorption process could also be a useful analytic method for the study of nonvolatile compounds contained in citrus peel oils.

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