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Supercritical Carbon Dioxide (SC-CO_2) Extraction of Grapefruit Flavedo

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ABSTRACT: Grapefruit flavedo (*Citrus paradisi* Macf.) was extracted by different methods: hydrodistillation; and solvent extraction using pentane, ethanol and supercritical carbon dioxide (SC-CO_2) at two fluid densities. The composition of the distillates and oleoresins were compared. Monoterpene hydrocarbons decrease in SC-CO_2 extracts at 87–90% with respect to their quantity in pentane extracts (95%) and in hydrodistillates (97%); these levels in monoterpene hydrocarbons were related to the limonene content, the most representative compound in grapefruit essence. Sesquiterpenes, aldehydes, alcohols and esters increased their GC area percentage in SC-CO_2 extract at a high density of the solvent, with respect to the hydrodistillate and the pentane extract. Very interesting was the high increase in nootkatone concentration in the SC-CO_2 extracts; this grapefruit essence component was 4.72% in the extract at 8 MPa, and it was 5.19% in that at 25 MPa; the ketone was very low in the hydrodistillates (0.22–0.26%). The monoterpene hydrocarbon concentrations, expressed as g of component in 100 g of extract, showed a decrease in SC-CO_2 oleoresins. Oxygenated, sesquiterpenes and particularly nootkatone increase their amount in SC-CO_2 extracts. © 1998 John Wiley & Sons, Ltd.

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Introduction

Fruits of the *Citrus genus* are important agricultural products thanks to their nutritional and industrial use. The genus *Citrus* consists of many species, all of which produce characteristic distinct flavours used in foods, perfumery and cosmetics. Grapefruit (*Citrus paradisi* Macf.), which is recognised as a natural hybrid of the pommelo (*Citrus grandis* Osbeck), grown mainly in America, is cultivated principally to obtain the juice. The world production of grapefruit essential oil is about 200 tons[1] and Brazil is the most important producer.

The glands, which contain the essential oil, are located in the flavedo portion of the fruit peel and different methods can be employed to extract them: distillation, solvent extraction and cold pressing. The various technologies give differences in yield and in the quality of the extract. By distillation it is possible to obtain a yield higher than 1%, but with a Pipkin press machine the yield is lower than 0.08%,[2] this is explained by the absorption of the oil into the peel, and even high pressures will not squeeze it out from the epicarp. However, the temperatures used in the distillation process could give hydrolysis and thermal degradation of some components and in this way the smell of the essential oil could change. The use of solvent extraction has recently been questioned because of the toxicity of some solvents.

The importance of supercritical fluid extraction (SFE) and separation processes has increased in the food industry in recent years. Supercritical carbon dioxide (SC-CO_2) offers unusual possibilities for the selective extraction, fractionation and purification of volatile oils, thanks to the possibility of adjusting the composition of the extract by varying the solvent density. These features are related to the critical state of the fluid; at temperatures and pressures above 31°C and 7.3 MPa the compressed gas (CO_2) is called a supercritical fluid, having characteristics of both gases and liquids. It has the density of a liquid and solubilizes solids like a liquid solvent, but has a diffusion power similar to a gas and permeates through solid materials very easily. The power of solubilization increases with the density of the fluid; high densities of a supercritical fluid are possible at high pressures and allow it to dissolve large quantities of organic compounds. The dissolved compounds can be recovered from the fluid by reduction of its density, made possible by decreasing the

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pressure or increasing the temperature. This low temperature separation process prevents the degradation of the chemical compounds of the extract due to heat, as in steam distillation.

Some researchers studied the supercritical extraction of *Citrus* products. Di Giacomo *et al.*[3] measured the solubility of limonene and citral in SC-CO_2 and observed that at the same temperature and pressure the solubility of citral is lower than that of limonene. Temelli *et al.*[4] extracted citrus oils and showed the high solubility of the volatile components in SC-CO_2; critical- and liquid-phase samples at 8.3 MPa and 70°C were analysed by GC, and these chromatograms showed that the terpene hydrocarbons were solubilized by CO_2 to a greater extent. Terpenes, which are not polar, have smaller molecular weight and are more soluble, but these differences are possible in a supercritical system at conditions near the critical point — at a low density of the solvent. Calame and Steiner[5] reported a higher content of alcohols in a lemon extract by CO_2 at 30 MPa of pressure and 40°C than in a cold pressed lemon oil. The possibility of obtaining psoralene-free extracts from bergamot peel by SC-CO_2 extraction was also studied.[6] By using CO_2 at 8 MPa and 45–50°C a six-fold reduction of bergaptene content in the extract was obtained.

The aim of this study is to evaluate the application of SC–CO_2 to extract grapefruit peel and to compare this technology with other traditional extraction methods.

Experimental

Material

Grapefruit at maturity were harvested from a tree in Reggio Calabria. The flavedo was separated from the endocarp and chopped up using a mincer. The flavedo portion was about 23.5% of the whole fruit.

Standard compounds were purchased from Aldrich, Extrasynthese, and Carlo Erba.

Drying Process

The drying process was carried out at 40°C for 6 h, so the flavedo water content decreased from about 70–72% to 40–42%.

Hydrodistillation of the Essential Oil

An oil separator trap equipped with a tightly fitted condenser and connected to a 1 dm^3 flask was used for the determination of the oil in the minced peels of grapefruit according to an AOAC method.[7]

The essential oil obtained was about 1.40% (v/w) from the fresh flavedo portion, and 2.56% (v/w) from the dried starting material. The yield related to the dry matter was 4.88% (v/w) from the fresh peels and 4.35% (v/w) from the dried.

Extraction

The solvent extractions of the dried peels were carried out with a Soxhlet apparatus using pentane and ethanol as solvents. After a 5 h extraction the solvent was removed in a rotary evaporator; the extract was 4.2% w/w of the starting material. The oleoresins obtained were then analysed by GC.

The supercritical carbon dioxide extractions were performed in an extraction plant (Mueller GmbH) equipped with a 0.6 dm^3 internal volume extractor. CO_2 was pressurized by a membrane pump of a maximum flow rate of 3.6 kg/h. After the dynamic solubilization process the SC-solution was expanded to a pressure of 4.5–5.0 MPa at a temperature of 20–25°C in a separating vessel, where the solute precipitated. The CO_2 pressure of the extraction vessel containing the minced grapefruit flavedo was set by a manual valve. The extraction temperature was achieved with water baths. After expansion the fluid was recondensed and recycled into the extraction step. Extraction temperature and pressure were checked by an electronic apparatus. The starting extraction time was settled when the working pressure was reached. The dynamic extraction runs were carried out at this pressure for 4 h and at two conditions:

A. Pressure 8 MPa at 40°C with a CO_2 density of 281 g/dm^3.
B. Pressure 25 MPa at 40°C with a CO_2 density of 875 g/dm^3.

The extracts, manually recovered from the separation vessel, were separated from coextracted water and then analysed by GC. The extraction yields were calculated by differences between the essential oil contained in the starting material and the oil contained in the extracted flavedo. The quantitative evaluation of the essential oil was performed by hydrodistillation as described above. More than 95% of the oil contained in the starting material was extracted by SC-CO_2 in all extraction conditions.

Gas Chromatography

The gas chromatographic analyses were performed by a Perkin-Elmer 8600 gas chromatograph, equipped with a flame ionisation detector. A fused-silica column (30 m × 0.25 mm i.d., film thickness 0.25 μm) coated

with a DB 5 (J & W Scientific) stationary phase was used. Helium was the carrier gas at a flow rate of 1.1 ml/min. The column temperature programme was: initial, 70°C (8 min), rate of rise 3°C/min up to 180°C, rate of 5°C/min up to 290°C, then isothermal for 30 min. The injector and FID were at 250°C and 300°C respectively. Samples (1 μl), previously dissolved in hexane, were injected in the split mode with a split ratio of 25. Recording and integration were carried out by the apparatus itself.

The quantitative results, expressed in w/w, were recalculated on the basis of detector response factors obtained with authentic compounds and using octan-2-ol as internal standard. The GC analyses were performed in duplicate on every sample.

Gas Chromatography–Mass Spectrometry

A Hewlett-Packard 5971A mass selective detector connected with a 5890 Hewlett-Packard gas chromatograph was used. The separation was achieved by a HP-5 fused-silica column (25 m × 0.2 mm i.d., film thickness 0.33 μm; Hewlett-Packard). The column temperature was programmed from 70°C (8 min) to 290°C (20 min) at 3°C/min. Flow rate of helium carrier gas was 1.1 ml/min, samples dissolved in hexane were injected in splitless mode. The MS conditions were: ionization voltage, 70 eV; ion source temperature, 180–190°C. The sample components were identified by matching their mass spectra with those of the Wiley library and confirmed by their GC retention times.

Results and Discussion

The flavedo of grapefruit was extracted by different methods and gave extracts which appeared quite different in colour and state.

The hydrodistillates obtained from the fresh and the dried peels were colourless oils. The pentane extract was an orange-coloured oil; during a storage at 2°C an orange-coloured material precipitated. Both of these essences presented the characteristic smell of the fruit. The ethanol extract was a brown-red oleoresin; at 4–5°C it became a solid material, and had little grapefruit flavour. The SC-CO_2 extracts were orange solid oleoresins at 4–5°C, with an intense smell of fruit. The solvent extractions were performed on the dried peels because the high water content of the fresh flavedo could give problems to the process. The differences in the essence quality between the fresh and the dried peels were tested by GC analysis of the hydrodistilled oils from both the starting materials.

Table 1 shows the components and their peak area ratios, detected in the different extracts and the hydrodistillates obtained from grapefruit flavedo. The sequence of the compounds was according to their gas chromatographic retention times revealed on a DB-5 capillary column. The distribution of the components within various chemical classes is given in Table 2.

A total of 55 components was separated, 50 of which were identified. The five peaks that were not identified from the mass fragmentation were probably sesquiterpenes hydrocarbons and oxygenated derivatives like sinensal.

The drying process produced a 10% reduction of the essential oil content of the flavedo. Both the hydrodistillates yielded the same main compounds, but some differences of the oil composition due to the drying process were observed in the minor components. In particular sabinene, linalol, terpinen-4-ol, α-terpineol, nerol, carveol and octanol decreased to about half of their area percentage content in the oil obtained from the dried flavedo. Neryl acetate and α-copaene showed even higher losses. In contrast, the levels of myrcene, (*Z*)- and (*E*)-(β)-ocimene, citronellal, decanal, β-caryophyllene and germacrene-D increased. In Table 2 the decrease of the total alcohols and esters owing to the drying of starting material is summarized. The alcohols were 0.59% of the oil from the fresh material but only 0.27% in that obtained after drying of the peels; this reduction to a half is particularly due to loss of linalol, the most represented oxygenated terpene in the hydrodistillates: 0.16% and 0.07% respectively. The total acetates fell from 0.24% to 0.15% and it is noteworthy that neryl acetate decreases in the oil distilled from dried flavedo to 0.02%. Nootkatone excepted, the compounds with high GC retention time — sesquiterpenes and unidentified (probably sesquiterpenes too) — increased in the hydrodistillate of the dried material.

Drying of grapefruit peels under the conditions used caused only small changes of the content of some monoterpenes and sesquiterpenes in the essential oil obtained. This fact allowed us to carry out the solvent extractions on dried material excluding the possibility of obtaining a different oleoresin composition related to the different conditioning of starting material.

Different extract compositions could be obtained by different extraction methods applied to natural products. Hydrodistillation selects the distilled compounds by their volatility; extractions with non-polar solvents extract all the non-polar molecules except those with high molecular weight. In many cases separation of extract from solvent will result in a loss of the more volatile compounds. The use of pentane as solvent reduces volatiles losses because of its low boiling point. CO_2 can be separated from solutes without loss of volatiles because of its extreme volatility. The solvent power of SC-CO_2 is strictly related to its density. To obtain an extract containing more volatiles the fluid has to be used at very low solvent power, otherwise a 'total

Table 1. Volatile components of grapefruit flavedo hydrodistillates and extracts

No.	Component	Reliability of identification[a]	Retention indices	Peak area (%)				
				Hydrodistilled		Pentane extract	$SC\text{-}CO_2$ Extracts	
				Fresh	Dried		8 MPa	25 MPa
1	α-Thujene	b	934	tr	tr	tr	0.02	0.02
2	α-Pinene	a	940	0.50	0.49	0.38	0.32	0.21
3	Camphene	a	954	0.01	tr	tr	0.02	0.02
4	Sabinene	b	975	0.24	0.17	0.21	0.17	0.17
5	β-Pinene	a	976	0.02	0.01	0.01	0.08	0.06
6	Myrcene	a	990	1.65	1.86	1.75	1.48	1.40
7/8	Octanal and β-phellandrene	b	1000	0.03	0.03	0.27	0.47	0.47
9	α-Terpinene	a	1011	0.03	0.03	0.02	0.05	0.03
10/11	Limonene and *p*-cymene	a	1032	94.98	94.88	92.45	86.12	84.06
12	*Z*-(β)-Ocimene	b	1039	tr	0.03	0.03	0.10	0.09
13	*E*-(β)-Ocimene	b	1050	0.13	0.18	0.27	0.32	0.28
14	γ-Terpinene	a	1060	0.01	0.01	0.05	1.80	0.74
15	*trans*-Sabinene hydrate	b	1067	tr	tr	tr	0.01	0.01
16	Octanol	a	1073	0.16	0.10	tr	0.11	0.11
17	Terpinolene	a	1088	0.04	0.05	tr	0.11	0.06
18	Linalol	a	1100	0.16	0.08	0.21	0.36	0.43
19	Nonanal	b	1102	0.03	0.04	0.03	0.05	0.05
20	Citronellal	b	1155	0.03	0.05	0.08	0.10	0.12
21	Terpinen-4-ol	b	1178	0.05	0.03	0.03	0.07	0.07
22	α-Terpineol	a	1191	0.07	0.03	0.12	0.24	0.32
23	Decanal	b	1205	0.19	0.26	0.30	0.49	0.63
24	Octyl acetate	b	1213	0.03	0.03	0.05	0.06	0.09
25	Carveol	a	1220	0.05	tr	tr	tr	0.03
26	Nerol	b	1230	0.04	tr	0.01	0.04	0.05
27	Neral	b	1242	0.05	0.04	0.05	0.12	0.15
28	Geraniol	a	1258	0.02	tr	tr	0.04	0.18
29	Geranial	b	1271	0.04	0.03	0.16	0.21	0.15
30	Perillaldehyde	b	1274	0.03	0.01	tr	0.03	0.05
31	Undecanal	b	1306	0.10	0.09	tr	0.03	0.09
32	α-Terpenyl acetate	b	1352	tr	0.02	tr	0.01	0.02
33	Citronellyl acetate	b	1355	0.01	0.01	0.04	0.03	0.04
34	Neryl acetate	a	1366	0.12	0.02	tr	0.04	0.05
35	α-Copaene	b	1379	0.13	0.04	0.10	0.14	0.34
36	Geranyl acetate	b	1384	0.08	0.07	0.08	0.20	0.34
37	β-Cubebene	b	1392	0.04	0.05	0.09	0.15	0.36
38	Dodecanal	b	1408	0.03	0.04	0.05	0.02	0.03
39	β-Caryophyllene	a	1424	0.13	0.19	0.37	0.65	1.42
40	α-Bergamotene	b	1440	0.01	0.03	tr	0.04	0.07
41	α-Humulene	a	1458	0.03	0.05	0.14	0.15	0.31
42	β-Farnesene	a	1484	0.02	0.04	0.08	0.14	0.40
43	Unidentified 1	–	1496	0.05	0.05	tr	0.02	0.05
44	Germacrene-D	b	1501	tr	0.03	0.10	0.04	0.11
45	α-Farnesene	c	1508	tr	0.01	tr	0.06	0.09
46	δ-Cadinene	b	1529	0.02	0.05	0.19	0.19	0.52
47	Unidentified 2	–	1539	0.01	0.01	tr	0.03	0.04
48	Elemol	c	1557	0.01	0.01	tr	0.06	0.11
49	E-Nerolidol	b	1571	0.02	0.02	0.13	0.09	0.15
50	Unidentified 3	–	1595	0.04	0.01	tr	0.03	0.08
51	β-Sinensal	d	1669	0.04	0.05	0.14	0.20	0.31
52	*cis*-Farnesol	b	1700	0.01	0.01	tr	0.04	0.08
53	Unidentified 4	–	1748	0.01	0.05	tr	0.08	0.11
54	Unidentified 5	–	1798	0.01	0.02	0.04	0.13	0.12
55	Nootkatone	b	1823	0.26	0.22	1.28	4.72	5.19

[a] Key for reliability: a = MS and RI identical with those of pure reference compounds; b = MS and RI identical with published data; c = MS identical with published data; d = tentatively identified by MS.

extract' is achieved at high CO_2 solvent power. These different extraction technologies applied to the grapefruit flavedo produced extracts that showed different chemical compositions, as displayed in Tables 1 and 2. The more volatile components show a higher concentration in the hydrodistillate and a lower percentage in the $SC\text{-}CO_2$ extracts, while the pentane extract showed intermediate features. Opposite trends were observed for components with higher boiling points.

Limonene, the main component in grapefruit essence, decreased from 94.9% in the hydrodistillate to 84.1% in the $SC\text{-}CO_2$ extract a high fluid density (B); intermediate values were observed in the limonene concentration of the pentane and $SC\text{-}CO_2$-A extracts. α-Pinene

Table 2. Concentration of various chemical classes of compounds in extracts and hydrodistillates of grapefruit flavedo expressed as peak area (%)

Chemical class	Total no	Hydrodistillate		Pentane extract	SC-CO_2 extracts	
		Fresh	Dried		8 MPa	25 MPa
Hydrocarbons						
Monoterpene	13	97.61	97.71	95.17	90.59	87.14
Sesquiterpene	9	0.38	0.49	1.07	1.56	3.62
Aldehydes[a]	10	0.57	0.64	1.08	1.72	2.05
Alcohols	11	0.59	0.28	0.50	1.06	1.54
Esters	5	0.24	0.15	0.17	0.34	0.54
Ketones	1	0.26	0.22	1.28	4.72	5.19
Unidentified	5	0.12	0.14	0.04	0.29	0.40

[a] β-Phellandrene has a very low percentage in the octanal peak.

and myrcene behave in the same way as limonene, but the opposite trends were seen for the ocimenes, α-terpinene and particularly γ-terpinene. The hydrodistilled oil contained 0.01% of γ-terpinene, whereas it was 0.05% of the volatiles of the pentane extract and reached 1.8% of peak ratio of the SC-CO_2 extract at low fluid density. The highest level of monoterpene hydrocarbons was more than 97% of the hydrodistillates but only 87.1% of the SC-CO_2-B extract (see Table 2); this decrease is particularly due to the limonene, as previously reported, and it is not relatively influenced by the different behaviours of other monoterpene hydrocarbons.

All the sesquiterpene hydrocarbons revealed a tendency to increase in the extracts obtained by SC–CO_2 with respect to the hydrodistillate and pentane extract. Sesquiterpenes are 0.49% in the hydrodistillate compared with the 1.07% in the pentane extract, but even higher quantities were found in the SC-CO_2 oleoresins: 1.56% in the extraction performed at 8 MPa and 3.62% in that at 25 MPa. Caryophyllene is the most abundant sesquiterpene in the grapefruit essence; its content was 0.65% in SC–CO_2 extract at 8 MPa, 1.42% in that carried out at 25 MPa, while in the hydrodistillate this compound was only 0.19%. Analogous increments were observed for α-copaene, 0.04% in hydrodistillate and 0.34% in SC-CO_2 extract; β-cubebene, from 0.05% to 0.36%; α-humulene, 0.05% and 0.31%; β-farnesene, 0.04% and 0.40%, δ-cadinene, 0.05% and 0.52%; all of them presented the higher area percentage in the extract obtained at 25 MPa.

All the other chemical classes showed a higher percentage in the extracts obtained at high CO_2 density. Decanal, the most important aldehyde, was two–three times higher in SC-CO_2 extracts (0.49–0.63%) than in hydrodistillate (0.26%), and geranial was seven times higher in the SC-CO_2 extract at 8 MPa (0.21%) than in distillates 0.03%; in the same way, the tentatively identified β-sinensal increased from 0.05% of the distilled oil to 0.31% in the extract obtained by CO_2 under 'B' conditions. In contrast to decanal, other aliphatic aldehydes were practically at the same level in all the extracts. As reported in Table 2, the aldehyde class was higher than 1.7% in SC-CO_2 extracts, about 0.6% in the hydrodistillates and 1% in the pentane extract.

Octanol was the most abundant alcohol in the distilled oil (0.1%), but linalol was 0.21% in the pentane extract and 0.36–0.43% in SC-CO_2 extracts, when octanol was at lower concentrations. Like linalol, the other terpene alcohols increased their area ratios in the solvent extracts.

The esters, represented by geranyl acetate, contributed 0.54% of the total GC peak area in the oleoresin extracted at 25 MPa and were less in the other extracts and distillates.

An increase of solubility in the SC-CO_2 was observed for nootkatone, a sesquiterpene ketone, low levels were found in hydrodistillate (0.22%), higher levels in the pentane extract (1.28%), and even higher levels in SC-CO_2 extracts: 4.72% at 8 MPa and 5.19% at 25 MPa.

High levels of oxygenated compounds and sesquiterpenes were found in supercritical fluid, extracts of rosemary by Reverchon and Senatore[8] compared with hydrodistilled oils. The data reported by these researchers were in agreement with our results obtained in SC–CO_2 extraction of grapefruit flavedo.

Table 3 shows the quantitative concentration of the most representative compounds expressed as g/100 g of extract. The weight was calculated by comparison of the GC peak areas of every compound with their response factors obtained with pure standards. From these results it is possible to see that great variations appear, according to the different extraction methods. In hydrodistillation a higher concentration of volatiles was obtained; in fact, the value of 84% (w/w) for the limonene is the highest when compared with other extractions. Hydrodistillation of the fresh and the dried peels at 40°C gave the same percentage of each volatile, except for linalol and caryophyllene. The former was 0.16% in the fresh hydrodistillate and less (0.10%) in the dried peels distillate. The latter was 0.22% in the oil from the dried matter and half (0.12%) in the oil from fresh peels. When a solvent was used to extract the grapefruit peels, other compounds like waxes were dissolved and

Table 3. Percentage (weight/weight) of volatile in 100 g of extracts

Compound	Hydrodistillate		Solvent extract		$SC\text{-}CO_2$ extract	
	Fresh peel	Dried	Pentane	Ethanol	80 MPa	250 MPa
α-Pinene	0.45	0.44	0.19	–	0.18	0.06
β-Pinene	0.02	0.01	0.01	–	0.04	0.02
Myrcene	1.85	1.88	1.20	–	0.98	0.48
Limonene	84.64	83.32	55.18	0.07	47.54	23.97
γ-Terpinene	0.01	0.01	–	–	1.01	0.21
Linalol	0.16	0.10	0.12	0.01	0.23	0.15
α-Terpineol	0.08	0.06	0.07	0.01	0.16	0.12
Geraniol	0.04	0.04	–	0.01	0.03	0.06
β-Caryophyllene	0.12	0.22	0.22	0.01	0.38	0.45
α-Humulene	0.03	0.02	0.07	–	0.08	0.09
Nootkatone[a]	0.25	0.22	0.73	0.05	2.82	1.66

[a] Using the same response factor of α-humulene.

collected in the extracts; these molecules, which have a high boiling point, were not present in hydrodistillates. Solvents have different solubility power with respect to waxes and high volatile compounds, so in the pentane extract from grapefruit peels the 11 measured compounds accounted for 57.8% of the extract, while in the hydrodistillate it was 86–88%. In the pentane extract a reduction of low-boiling compounds like hydrocarbon monoterpenes was seen but similar amounts of terpene alcohols and sesquiterpenes were found in the hydrodistillates and in the pentane extract. An increase was observed for nootkatone: 0.73% in the pentane extract but only 0.22–0.25% in the distillates.

The ethanol extract contained a very low quantity of volatile compounds, like monoterpenes and sesquiterpenes. This could be explained by the difficulty of obtaining these oleoresins with a Soxhlet apparatus and by the subsequent distillation of ethanol at a reduced pressure; at these conditions much of the low-boiling point material was lost. By alcohol extraction, compounds like waxes and heterocycles were recovered from the flavedo, and these compounds diluted the volatile components.

The solubility of organic compounds in $SC\text{-}CO_2$ is increased by raising the fluid density. At a 281 g/dm^3 CO_2 density the 11 quantified terpenes were 53.5% (w/w) similar to the amount in the pentane extract, while at 875 g/dm^3 (25 MPa, 40°C) they were 27.3% (w/w). A comparison with other extraction methods showed that hydrocarbon monoterpenes were less in the high pressure $SC\text{-}CO_2$ extract compared to the hydrodistillate, but monoterpene alcohols and sesquiterpene hydrocarbons were present in the greatest amount in the $SC\text{-}CO_2$ extract at 8 MPa. A dilution of volatile compounds was obtained in the 25 MPa extract by the waxes and high boiling components dissolved under these extraction conditions, i.e. when the volatile components were completely solubilized at low CO_2 densities like that obtained at 8 MPa and 40°C (281 g/dm^3). An anomalous amount of 1.01% was observed for the γ-terpinene in the $SC\text{-}CO_2$ extract at 8 MPa; in hydrodistillates and pentane extract this compound was present in a quantity of 0.01%.

The quality of a grapefruit extract is related to the nootkatone level; this compound is the major flavour contribution component of grapefruit essential oils, and it is useful in the taxonomy of *Citrus grandis* (pommelo) and *Citrus paradisi* (grapefruit).[9,10] The nootkatone concentration found, assuming the same response factor as α-humulene, was 0.22–0.25% (w/w) in the hydrodistillate, in concordance with literature data. In the pentane extract nootkatone increased to 0.73% (w/w); a big rise was also observed in the $SC\text{–}CO_2$ extract at 8 MPa where the component was 2.82% of the weight of the oleoresin.

From the reported data we have found that high quality grapefruit extracts were obtained by $SC\text{-}CO_2$ extraction. But at high CO_2 density a lot of high-boiling compounds were co-extracted, therefore the best conditions to obtain a good grapefruit aroma extract are at low CO_2 density.

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