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Research Article

Volatile Composition and Enantioselective Analysis of Chiral Terpenoids of Nine Fruit and Vegetable Fibres Resulting from Juice Industry By-Products

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Fruit and vegetable fibres resulting as by-products of the fruit juice industry have won popularity because they can be valorised as food ingredients. In this regard, bioactive compounds have already been studied but little attention has been paid to their remaining volatiles. Considering all the samples, 57 volatiles were identified. Composition greatly differed between citrus and noncitrus fibres. The former presented over 90% of terpenoids, with limonene being the most abundant and ranging from 52.7% in lemon to 94.0% in tangerine flesh. Noncitrus fibres showed more variable compositions, with the predominant classes being aldehydes in apple (57.5%) and peach (69.7%), esters (54.0%) in pear, and terpenoids (35.3%) in carrot fibres. In addition, enantioselective analysis of some of the chiral terpenoids present in the fibre revealed that the enantiomeric ratio for selected compounds was similar to the corresponding volatile composition of raw fruits and vegetables and some derivatives, with the exception of terpinen-4-ol and α-terpineol, which showed variation, probably due to the drying process. The processing to which fruit residues were submitted produced fibres with low volatile content for noncitrus products. Otherwise, citrus fibres analysed still presented a high volatile composition when compared with noncitrus ones.

1. Introduction

The recovery, recycling, and upgrading of waste material are particularly relevant in the food and food processing industry, in which waste, effluents, residues, and by-products can be reclaimed and often turned into useful higher-value-added products [1]. The food industry can take advantage of the physicochemical properties of these products to improve the viscosity, texture, sensory characteristics, and shelf life of final products. Hence, fibre-rich by-products can serve as inexpensive, noncaloric bulking agents for the partial replacement of flour, fat, or sugar. They can also be used to enhance water and oil retention and to improve emulsion or the oxidative stability of food products [2, 3]. Due to the increasing importance of these products in the food industry, several studies have addressed their characterisation, either of physicochemical properties [4, 5] or of composition in bioactive compounds [6, 7]. Although aroma is a key sensory attribute to consider when using a product in the food industry, to the best of our knowledge, only one study has been devoted to the volatile composition of one by-product, namely, apple [8].

Gas chromatography-mass spectrometry (GC-MS) is the ideal analysis technique to analyse the composition of the volatile fraction of fibres derived from the juice industry since GC offers high separation power and MS useful spectra for compound identification and quantification. On the other hand, solid-phase microextraction (SPME), introduced by Arthur and Pawliszyn [9] and extended to headspace (HS) sampling by Zhang and Pawliszyn [10], is a reliable routine technique to sample the volatile fraction of complex matrices because of its simplicity, sensitivity, possibility of automation,

and lack of solvent use. Enantioselective-gas chromatography (Es-GC) analysis using cyclodextrins as chiral selectors has been applied in the quality control of several fruits and beverages to detect adulteration with synthetic flavours [11, 12] and to monitor the possible effects of orange juice thermal processing on the enantiomeric ratio of several terpenic components [13]. Therefore, the study of the enantiomeric ratio of diagnostic chiral volatile compounds present in fibre samples can offer further useful information for their comparison.

The aim of this work was to characterize the volatile fraction of several fruit and vegetable matrices which play an important role in juice producing industries and are expected to be further applied as food ingredients resulting in the valorisation of what initially was considered as a residue. The fibres analysed included apple, pear, peach, carrot, lemon flesh, orange flesh, orange peel, tangerine flesh, and tangerine peel. These fibres were obtained from several batches of processed industrial raw material from a currently operative juice production line. Moreover, the composition of these fruit-derived by-products has been compared to the results of several existing studies reporting the volatile composition of raw fruits and juices to assess the differences between fruits and related fibres resulting from processing. In addition, an enantioselective analysis of some of the chiral terpenes present in the fruit fibre samples was performed and their enantiomeric ratios were compared to those reported in the literature, in order to determine possible variations caused by the processing to which the fruit was subjected in the juice industry.

2. Materials and Methods

2.1. Samples. A local juice company (Indulleida S.A., Alguaire (Lleida), Spain) provided fibre samples from apple (6), pear (5), peach (5), carrot (1), lemon flesh (5), orange flesh (6), orange peel (1), tangerine flesh (1), and tangerine peel (1). All samples were industrially processed according to the scheme shown in Figure 1. This procedure involved washing with potable water followed by wet milling. Next, samples were submitted to a drying step and milled again. Finally, fibres were sieved to achieve a homogenous texture and sacked.

2.2. Headspace Solid-Phase Microextraction (HS-SPME). Between 100 mg and 1 g, depending on the sample, of fruit fibre was homogenised in 10 mL of H_2O saturated with NaCl and placed in a 20 mL headspace vial.

HS-SPME of the volatile fraction was carried out with a 2 cm SPME fibre CAR/PDMS/DVB (carboxen/polydimethylsiloxane/divinylbenzene; 50/30 μm) from Supelco (Bellefonte, PA, USA) at 50°C for 45 min using agitation of 250 rpm.

2.3. Gas Chromatography-Mass Spectrometry (GC-MS) Analysis. GC-MS analyses were performed with an MPS-2 multipurpose sampler (Gerstel, Mülheim an der Ruhr, Germany) assembled on an Agilent 6890 (Palo Alto, CA, USA) gas chromatograph coupled to an Agilent 5973N Quadrupole Mass Selective Detector (MSD). The SPME fibre was desorbed into the injection port at 250°C in split mode (ratio 1 : 5) for 5 min. Compounds were separated with a MEGA5 column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) from Mega (Legnano, MI, Italy) using helium as carrier gas (1 mL·min^{-1}). The oven was temperature-programmed from 50°C (held for 1 min) to 160°C at 3°C·min^{-1} and then to 250°C at 20°C·min^{-1} (held for 2 min). Mass spectra were recorded in electron impact (EI) mode at 70 eV within the mass range 35–350 m/z. The transfer line, the ionization source, and the quadrupole were thermostated at 280, 230, and 150°C, respectively. Acquisition was done using MSD ChemStation software (Agilent Technologies, Palo Alto, CA, USA). All analyses were performed in duplicate.

Volatile compound identification was based on the comparison of experimental spectra with those of the Wiley 7 and Essential Oils mass spectral libraries (Wiley, New York, NY, USA) and was further confirmed by linear retention indices (LRI) calculated using an *n*-alkane mixture (C9 : C30) [14], which were compared to those reported in Adams database [15] and Nist WebBook [16].

Peak areas calculated from total ion current (TIC) for each compound were normalised by in-fibre internal standardisation [17] as follows: 5 μL of 50 ppm solution of tridecane in dibutyl phthalate was sampled for 15 min at 50°C and the relative abundance data (percentage on total volatile composition) were then calculated. This procedure was adopted to normalise the analytical deviation produced by variations in the performance of fibre and instrumentation [17].

2.4. Enantioselective-Gas Chromatography (Es-GC) Analysis. Fruit fibres were manually sampled using the same conditions as described in Section 2.2. The analyses were carried out on a Shimadzu GC-2010 system coupled to a FID detector and controlled with Shimadzu GC Solution 2.30.00 software (Shimadzu, MI, Italy).

The SPME fibre was desorbed into the injection port at 220°C in split mode (ratio 1 : 5) for 5 min. Analyses were carried out on columns coated with 30% 2,3-di-*O*-ethyl-6-*O*-*tert*-butyldimethylsilyl-β-cyclodextrin (diEt-CD) diluted in PS-086 and 30% 2,6-dimethyl-3-*O*-pentyl-β-cyclodextrin (Pentyl-CD) diluted in PS-086, both from Mega (Legnano, MI, Italy), using hydrogen as carrier gas (1.25 mL·min^{-1}). The oven was temperature-programmed from 50°C to 127°C at 1.87°C·min^{-1} and then to 220°C at 15°C·min^{-1} (held for 1 min). The chromatographic conditions were selected on the basis of the conditions used for the construction of the dedicated chiral library [18] and translated using the GC Method Translator Software (Agilent). LRI were calculated using a mixture of *n*-alkanes (C9 : C30). The elution order of each enantiomer was assigned using a dedicated chiral library of racemic standards available in the laboratory [18].

3. Results and Discussion

3.1. Analysis of the Volatile Fraction of Fruit Fibres. The HS-SPME-GC-MS method described above was used to analyse the volatile fraction of nine fruit fibres derived from processed industrial raw materials obtained from a juice

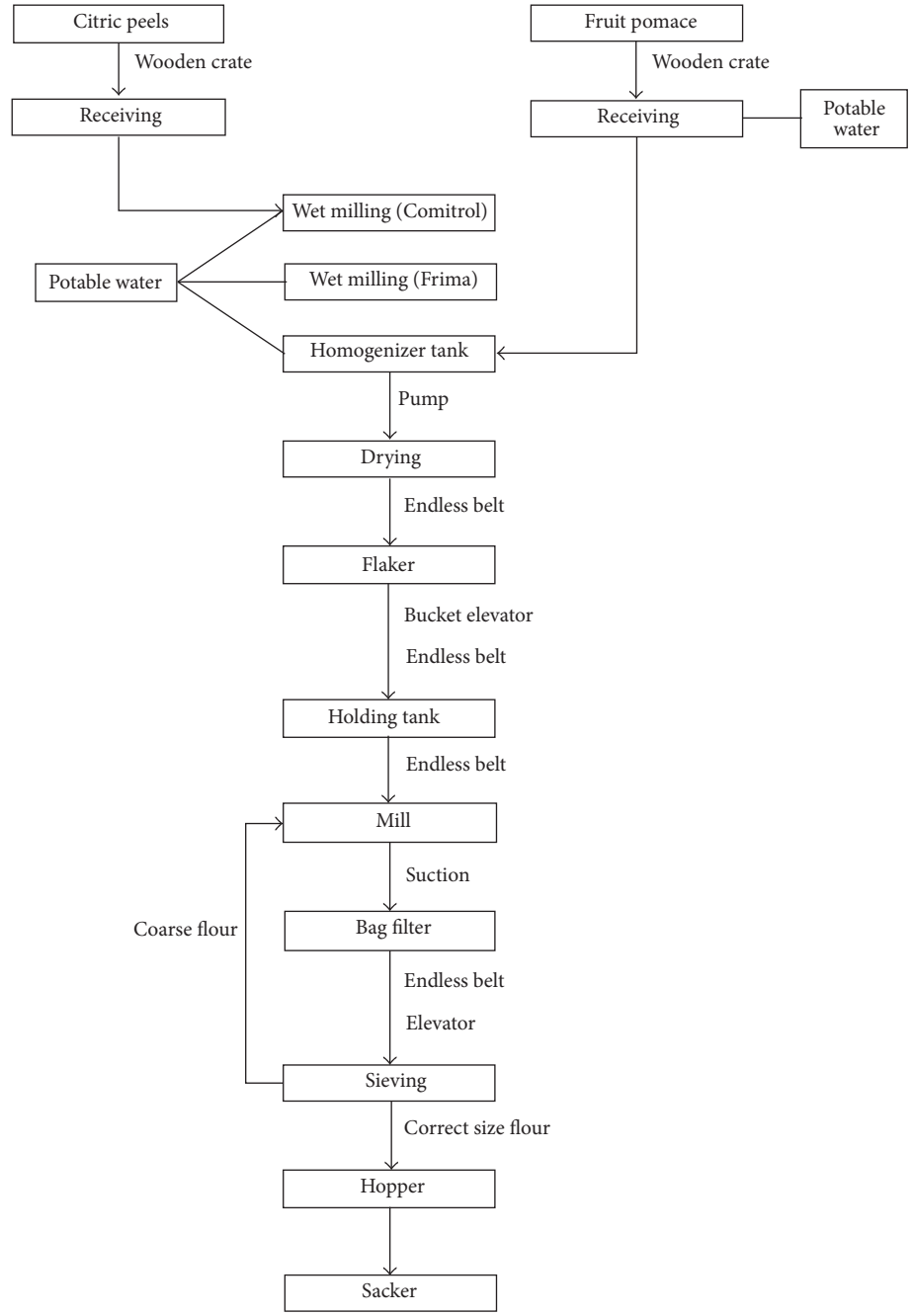

Figure 1: Schematics of the production process to obtain the analysed fruit fibres from residues of the juice industry.

production line. Volatiles were identified through their LRI and mass spectral data. As expected, the profile of the chromatograms revealed a high similarity between the citrus samples, namely, orange, orange peel, tangerine, tangerine peel, and lemon. On the other hand, the volatile fraction of apple, pear, peach, and carrot samples was relatively poor. Figure 2 shows the HS-SPME-GC-MS profile corresponding to lemon fibre. Peach and lemon fibres were used to evaluate the repeatability of the method. Five replicates were analysed for each fibre on various days, resulting in a satisfactory % RSD < 11% for both fibres.

3.2. Volatile Composition of Citrus Fibres. The volatile composition of citrus fibres (Table 1) consisted mainly of terpenoids, especially limonene, which accounted for about 52.7% of the total volatile fraction in lemon and over 90% in orange and tangerine fibres. Although limonene was the predominant volatile compound, all samples showed relatively high percentages of a large number of other terpenoids. For instance, lemon fibre contained, among others, 13.7% *p*-cymene, 7.4% γ-terpinene, 5.1% α-terpinolene, 4.7% α-terpineol, and several other compounds at lower percentages.

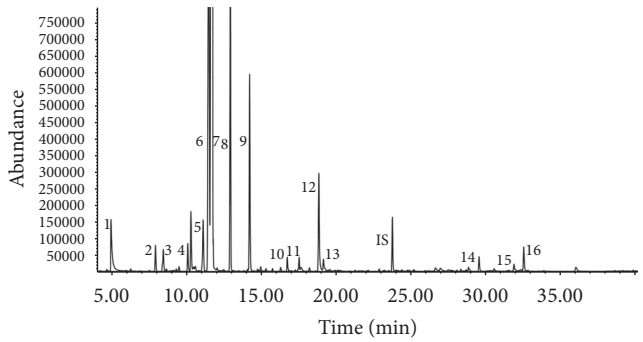

Figure 2: HS-SPME-GC-MS profile of a lemon flesh sample. Peak identification: (1) furfural, (2) α-pinene, (3) α-fenchene + camphene, (4) myrcene, (5) α-terpinene, (6) *p*-cymene, (7) limonene, (8) γ-terpinene, (9) α-terpinolene, (10) *cis*-β-terpineol, (11) terpinen-4-ol, (12) α-terpineol, (13) γ-terpineol, (14) *trans*-α-bergamotene, (15) valencene, and (16) β-bisabolene.

Aldehydes accounted for 8.5% of the total volatile composition in lemon fibre, the most abundant of them being furfural, which probably derived from the decomposition of sugars on the fibre. Other aldehydes found in lemon samples were heptanal, hexanal, (*E*)-2-heptenal, benzaldehyde, and nonanal. Ketones, esters, and alcohols were also found in the samples but at low concentrations (in all cases below 1%). Of note, the composition of the volatile fraction of citrus fibre is qualitatively comparable to those of raw fruits, essential oils [20], and juices [21–23].

Orange and tangerine flesh samples presented almost the same volatile composition, again showing a profile clearly dominated by terpenes (99.4 and 98.9% of total volatiles with a high predominance of limonene 92.3 and 94.0%, resp.). The same behaviour was observed for orange and tangerine peel fibres, which showed the same individual volatiles and similar percentages of the same. Moreover, the orange and tangerine peel samples presented a greater variety of compounds, including some terpenic acetates (e.g., α-terpinyl, citronellyl, and neryl acetate) and sesquiterpenoids, such as β-cubebene, alloaromadendrene, α-caryophyllene, and the cyclic monoterpene α-(*E*)-ionone, which were not detected in the flesh samples.

On the basis of the total area, the residual amount of volatile fraction in tangerine and orange peel was higher than that in the corresponding flesh, the latter being much higher than the amount found in lemon. This finding is in agreement with previous studies that report a major content of volatile compounds, especially of limonene, in orange peel compared to orange flesh [24, 25].

3.3. Volatile Composition of Noncitrus Fruit and Carrot. Unlike citrus fibre, apple, pear, peach, and carrot fibres showed a volatile composition with a lower percent of terpenoids (Table 2). In this case, the analyses revealed that the most abundant group of compounds in apple fibre was that of aldehydes (57.5%), the main ones being hexanal (19.7%), benzaldehyde (15.6%), and (*E*)-2-heptenal (14.9%). Esters accounted for 16.3% of the volatile fraction, with butyl isobutyrate (12.1%) as the major component. Also, ketones were present in a considerable amount (11.6%), while terpenoids accounted for 11.4%.

The volatile fraction composition of apple fibre was severely affected during fibre production if compared to that of raw fruit described in several publications [26, 27]. This observation could be attributed to the thermal treatment used during the juicing process. Former studies report ethyl esters, higher alcohols, and α-farnesene as the main components rather than aldehydes.

Pear fibre contained esters as the main constituents (54.0%), with hexyl acetate being the most abundant (49.1%). Volatile aldehydes accounted for a substantial fraction of these samples (32.8%), the most abundant being furfural (15.2%), followed by hexanal, (*E*)-2-heptenal, benzaldehyde, octanal, and heptanal. Other groups of compounds, such as alcohols, ketones, ethers, and terpenoids, were present in minor percentage. In this case, the volatile fraction of pear fibre is qualitatively comparable to that of raw fruits reported in previous studies [28], where esters were found to be the main fraction. Riu-Aumatell et al. [29] reported hexyl acetate as one of the compounds consistently found in 11 commercial samples of pear juice.

Peach fibre also showed a high proportion of aldehydes (69.7%), where furfural (43.2%) and hexanal (17.4%) prevailed, together with heptanal, benzaldehyde, (*E*)-2-heptenal, and nonanal in percentages ranging on average between 1.4 and 2.6%. For these samples, terpenoids accounted for 22.4% of the volatile fraction. The main terpenoids found in peach fibre were mainly α-terpineol, limonene, and α-phellandrene. Ketones and ethers were present in lower percentages, 6.1 and 1.6%, respectively. The volatile fraction of the peach fibres contained several terpenoids at a percentage comparable to that of raw fruits [29], while lactones, key markers of peach aroma [30, 31], were not detected.

The volatile fraction of carrot fibre contained terpenoids as the main group of compounds (35.3%). Other studies have reported that these compounds account for 97% of the total volatile fraction of fresh carrot samples [32]; the lower percent found in the analysed sample could be explained by the loss of volatiles during the washing and drying treatment applied during industrial fibre processing. The most abundant components of carrot fibre were α- and β-ionone, at 8.1 and 9.8%, respectively. The correlation between carotenoid degradation caused by processing and the production of degradative terpenes such as ionones has been described by Kanasawud and Crouzet [33]. Aldehydes accounted for 32.8% of total volatile composition of this fibre, with hexanal at 20.3% and ketones at 16.1%. These included 1-octen-3-one, 6-methyl-5-hepten-2-one, 2-methyl-3-octanone, 2,2,6-trimethylcyclohexanone, and 2,3,4-trimethylcyclohexen-1-one, all present at between 1.9 and 6.5%. Esters, ethers, and alcohols were present at 5.1, 1.8, and 1.3%, respectively. On the basis of the total area, the volatile fraction of noncitrus fibre was about 10-fold lower than citrus flesh fibre and almost 100-fold lower than citrus peel fibre, that is, the matrices containing the highest amount of volatile compounds.

Table 1: Average relative percentage of volatile contents and their distribution ranges in different production batches (in parenthesis) of citrus fibres, as determined by HS-SPME-GC-MS analysis.

	LRI (exp.)	LRI (ref.)	Lemon fibre	Orange flesh fibre	Tangerine flesh fibre	Orange peel fibre	Tangerine peel fibre
			Mean (n = 5)	Mean (n = 6)	Mean (n = 1)	Mean (n = 1)	Mean (n = 1)
Aldehydes							
Hexanal			0.2 (0.1–0.4)	0.1 (traces–0.2)	0.4	Traces	Traces
Furfural			7.7 (4.6–13.0)	Traces	0.1		
Heptanal	902	905	Traces	Traces	0.1		
(*E*)-2-Heptenal	959	957	0.2 (0.1–0.4)	0.1 (traces–0.1)	Traces	Traces	Traces
Benzaldehyde	963	961	0.1 (0.1-0.1)	0.1 (traces–0.2)	0.3		
Nonanal	1106	1103	0.3 (0.2–0.4)	0.1 (traces–0.1)	0.2	Traces	Traces
Decanal	1207	1205		0.1 (traces–0.2)	0.1	0.2	Traces
Subtotal			8.5	0.5	1.2	0.2	0.1
Ketones							
6-Methyl-5-hepten-2-one	989	985	0.1 (0.1-0.1)				
Subtotal			0.1	0.0	0.0	0.0	0.0
Esters							
Butyl isobutyrate	956	954	0.3 (0.1–0.5)	0.1 (traces–0.1)	0.1		
Hexyl butanoate	1194	1190				Traces	Traces
Octyl acetate	1216	1215		Traces	0.1	0.1	0.1
Butyl benzoate	1378	1376	0.3 (0.2–0.4)				
Subtotal			0.6	0.1	0.2	0.1	
Alcohols							
1-Heptanol	973	970	0.1 (traces–0.2)				
Subtotal			0.1	0.0	0.0	0.1	0.1
Terpenoids							
α-Thujene	930	931				0.1	0.1
α-Pinene	937	939	0.7 (0.4–1.2)	0.4 (0.2–0.7)	0.4	0.7	0.9
α-Fenchene[1]	950	951	0.8 (0.6–1.3)				
β-Pinene[2]	978	980	0.1 (traces–0.2)	0.1 (traces–0.1)	Traces	0.5	0.2
Myrcene	996	991	0.6 (0.4–1.4)	2.0 (1.4–3.4)	1.8	3.6	3.6
α-Phellandrene	1005	1005	0.2 (0.1–0.4)				
δ-3-Carene	1011	1011		0.2 (0.1–0.3)	0.1	0.2	Traces
α-Terpinene	1017	1016	1.2 (0.5–3.6)	0.1 (0.1–0.2)	0.1	Traces	Traces
p-Cymene	1018	1018	13.7 (8.9–21.7)	0.6 (0.3–1.7)	Traces	0.2	0.1
Limonene	1027	1026	52.7 (28.3–61.3)	92.3 (88.8–93.6)	94.0	92.2	90.4
β-Ocimene	1031	1031		0.1 (traces–0.2)	0.1	0.2	0.3
γ-Terpinene	1053	1050	7.4 (4.0–15.1)	0.5 (0.3–1.0)	0.4	0.4	2.6
α-Terpinolene	1062	1062	5.1 (3.7–9.3)	0.2 (0.2–0.3)	0.3	0.3	0.3
Linalool	1100	1098	0.1 (0.1-0.1)	0.1 (traces–0.1)	Traces	Traces	Traces
1,3,8-p-Menthatriene	1113	1111		Traces (traces–0.1)	Traces	Traces	Traces
endo-Fenchol	1114	1112	0.2 (0.1–0.2)				
Unknown (MW = 172)	1124		0.1 (0.1–0.2)	Traces	Traces	Traces	Traces
Terpinen-1-ol	1137	1134	0.1 (0.1–0.3)	Traces	0.2	Traces	Traces

Table 1: Continued.

	LRI (exp.)	LRI (ref.)	Lemon fibre	Orange flesh fibre	Tangerine flesh fibre	Orange peel fibre	Tangerine peel fibre
			Mean (n = 5)	Mean (n = 6)	Mean (n = 1)	Mean (n = 1)	Mean (n = 1)
cis-β-Terpineol	1147	1144	0.5 (0.4–0.8)	Traces	Traces		
Borneol	1163	1165	0.5 (0.4–0.6)				
4-Terpineol	1178	1177	0.2 (0.1–0.2)	0.1 (0.1–0.3)	Traces	0.1	0.1
α-Terpineol	1191	1189	4.7 (3.2–6.6)	0.3 (0.1–0.5)	0.2	Traces	Traces
γ-Terpineol	1196	1192	0.4 (0.2–0.9)				
Safranal	1199	1201		Traces	0.1	Traces	Traces
Carvone	1250	1245		Traces	0.1	Traces	Traces
α-Terpinyl acetate	1356	1350				0.1	Traces
Citronellyl acetate	1361	1360				Traces	0.1
Neryl acetate	1371	1368				Traces	0.1
α-Copaene	1379	1376		0.2 (0.1–0.3)	0.3	0.1	0.1
β-Elemene	1393	1391				0.1	0.1
(*E*)-β-Caryophyllene	1420	1418		0.1 (traces–0.1)	Traces		
α-(*E*)-Ionone	1428	1426				0.1	Traces
β-Cubebene	1430	1434				Traces	Traces
trans-α-Bergamotene	1437	1438	0.4 (0.2–0.8)				
Alloaromadendrene	1452	1455				Traces	Traces
α-Caryophyllene	1453	1455				Traces	Traces
β-Farnesene	1459	1458		0.2 (0.1–0.4)		Traces	Traces
β-Ionone	1488	1485					
Valencene	1493	1491	0.5 (0.2–0.7)	1.6 (0.1–4.1)	0.1	0.8	0.7
β-Bisabolene	1510	1509		0.1 (traces–0.4)	0.5	Traces	0.1
α-Farnesene	1511	1508			0.1		
7-epi-α-Selinene	1516	1517		0.1 (traces–0.2)	Traces	Traces	Traces
δ-Cadinene	1525	1524		0.1 (traces–0.1)	0.1	0.1	0.1
γ-Bisabolene	1534	1533	0.6 (0.3–1.4)				
Total (%)			91.0	99.4	98.9	99.8	99.9
Total normalised area			30.6 ± 9.7	68.1 ± 42.7	65.1	408.7	353.3

[1]In lemon fibre, area includes camphene as a result of coelution.

[2]In orange and tangerine peel fibres, area includes sabinene as a result of coelution.

The term "traces" indicates area percentage < 0.05%.

3.4. Es-GC Analysis of Chiral Markers in Fruit Fibre Samples. Here, we sought to study some of the chiral markers present in the fruit fibre samples in order to assess whether the processing (which includes thermal treatment) affects the enantiomeric ratio (ER), that is, with an increase of racemisation of some chiral compounds. HS sampling by SPME was therefore applied in the same optimised conditions as previously described in Section 3.1, in combination with Es-GC with cyclodextrin derivatives as chiral selectors. The ER of the selected chiral markers was compared to those previously reported in the literature for samples of the same fruit origin, namely, fresh fruits, juices, or essential oils, when available.

Only five chiral markers could be selected (α-pinene, β-pinene, limonene, α-terpineol, and α-ionone) for noncitrus fibres due to the low abundance of volatile compounds, as reported in Section 3.3. On the other hand, for citrus samples, chiral marker selection was limited by the presence of coelution. diEt-β-CD and Pentyl-β-CD columns were used to achieve reliable separation of a higher number of compounds. Moreover, pure standard mixtures of racemic terpenes were injected under the same Es-GC conditions to facilitate enantiomer identification.

3.5. Es-GC Analysis of Selected Chiral Markers in Noncitrus Fruit and Carrot Fibres. Very few chiral compounds were analysed in noncitrus fibres. However, the ER variability of chiral compounds among samples of each fruit was low (Table 3). A high ER was measured for the *R*-limonene enantiomer (>99%). α-Pinene and α-ionone in carrot fibre were present with a higher ER in favour of the *S*-enantiomer, while β-pinene in pear was present in a racemic form. α-Terpineol was found in all samples, with a higher abundance

Table 2: Average relative percentage of volatile compounds present and their distribution ranges in different production batches (in parenthesis) of apple, pear, peach, and carrot fibres, as determined by HS-SPME-GC-MS analysis.

	LRI (exp.)	LRI (ref.)	Apple fibre Mean (n = 6)	Pear fibre Mean (n = 5)	Peach fibre Mean (n = 5)	Carrot fibre Mean (n = 1)
Hydrocarbons						
2,4-Dimethyl-1-heptene			2.1 (0.9–4.4)	0.1 (traces–0.3)		
4-Methyl octane			0.5 (traces–1.3)			3.0
Subtotal			2.6	0.1	0.0	3.0
Aldehydes						
Hexanal			19.7 (9.2–27.7)	7.4 (5.2–9.0)	17.4 (10.6–21.3)	20.3
Furfural			2.6 (1.8–3.4)	15.2 (9.0–21.1)	43.2 (38.8–43.3)	1.6
Heptanal	902	905	1.3 (1.0–1.7)	0.7 (0.5–0.9)	1.4 (0.5–1.7)	2.6
(*E*)-2-heptenal	959	957	14.9 (12.1–20.2)	3.9 (1.5–6.4)	2.6 (1.8–4.1)	3.6
Benzaldehyde	963	961	15.6 (11.6–22.4)	3.6 (0.9–6.3)	2.5 (traces–3.6)	1.3
Pentylfuran	993	996	Traces			
Octanal	1004	1001	1.7 (1.0–3.3)	2.0 (1.34–2.41)		
Nonanal	1106	1103	1.7 (1.2–2.2)		2.6 (traces–4.1)	3.0
Decanal	1207	1205				0.4
Subtotal			57.5	32.8	69.7	32.8
Ketones						
1-Octen-3-one	980	980	6.3 (3.9–9.2)	3.1 (0.9–4.4)	1.7 (1.0–3.0)	4.7
2-Methyl-3-octanone	986	985			0.7 (traces–1.8)	
6-Methyl-5-hepten-2-one	989	985	5.3 (2.7–7.7)	2.7 (1.9–3.7)	3.7 (2.50–4.8)	3.0
2,2,6-Trimethylcyclohexanone	1037	1036				6.5
3,4,4-Trimethylcyclohexen-1-one	1082					1.9
Subtotal			11.6	5.8	6.1	16.1
Ethers						
Butyl ether			0.7 (0.4–1.0)	1.0 (0.4–1.4)	1.6 (traces–2.2)	1.8
Esters						
Butyl acetate				3.8 (2.9–6.0)		
Pentyl acetate	917	916		1.1 (0.9–1.2)		
Butyl isobutyrate	956	954	12.1 (9.5–16.6)			0.9
Hexyl acetate	1017	1016	1.5 (0.5–2.7)	49.1 (40.4–61.2)		
Hexyl 2-methylbutanoate	1244	1239	0.6 (0.2–1.1)			
Butyl benzoate	1378	1376	1.3 (1.1–2.0)			4.2
Hexyl hexanoate	1391	1386	0.8 (0.3–2.7)			
Subtotal			16.3	54.0	Traces	5.1
Alcohols						
1-Hexanol				1.2 (0.8–1.7)		
(*E*)-2-Cyclohexen-1-ol	1097	1097				0.9
2,6-Dimethyl cyclohexanol	1110	1114				0.4
Subtotal			Traces	1.2	Traces	1.3
Terpenoids						
α-Pinene	937	939	0.2 (traces–0.5)		0.2 (traces–0.6)	1.2
β-Pinene	978	980		1.2 (0.6–2.3)		
Myrcene	996	991				0.6
α-Phellandrene	1005	1005			3.2 (1.8–6.1)	
p-Cymene	1027	1026			1.1 (0.3–2.0)	2.7
Limonene	1031	1031	3.1 (0.9–3.2)		6.1 (1.9–17.8)	

Table 2: Continued.

	LRI (exp.)	LRI (ref.)	Apple fibre Mean ($n = 6$)	Pear fibre Mean ($n = 5$)	Peach fibre Mean ($n = 5$)	Carrot fibre Mean ($n = 1$)
γ-Terpinene	1062	1062	5.6 (4.0–8.9)		2.2 (0.4–3.4)	
α-Terpinolene	1086	1088				1.3
Linalool	1100	1098			0.9 (0.5–2.0)	
cis-β-Terpineol	1147	1144	0.2 (0.1–0.3)			
4-Terpineol	1178	1177			0.4 (traces–1.3)	
α-Terpineol	1191	1189	1.5 (0.8–2.0)	1.5 (1.0–1.9)	6.6 (4.1–9.5)	1.0
β-Cyclocitral	1223	1222				3.5
Neryl acetate	1371	1368			1.1 (0.6–1.5)	
(*E*)-β-Caryophyllene	1420	1418				1.9
α-Ionone	1428	1426				8.1
Geranyl acetone	1454	1455				2.5
β-Ionone	1488	1485				9.8
Valencene	1493	1491	0.4 (0.1–0.5)		0.2 (traces–0.5)	
α-Farnesene	1511	1508	0.4 (0.2–0.8)	0.2 (0.2–0.3)		
7-epi-α-Selinene	1516	1517			0.4 (traces–2.1)	
γ-Bisabolene	1534	1533				2.7
Total (%)			11.4	2.9	22.4	35.3
Total normalised area			7.7 ± 2.4	5.0 ± 1.5	4.1 ± 2.3	5.6

The term "traces" indicates area percentage < 0.05%.

Table 3: Chiral markers, calculated LRI, and corresponding enantiomeric ratio for noncitrus fruit fibre.

Chiral marker	Configuration	LRI	Apple ($n = 6$)	Pear ($n = 5$)	Peach ($n = 5$)	Carrot ($n = 1$)
α-Pinene	S	923				69.7
	R	925				30.3
β-Pinene	R	946		47.5–51.9		
	S	956		52.5–48.1		
Limonene	S	1056	Traces		Traces	
	R	1072	>99.9		>99.9	
α-Terpineol	R	1296	39.5–46.6	40.6–41.3	35.3–42.0	25.2
	S	1309	60.5–63.4	59.4–58.7	64.3–58.0	74.8
α-Ionone	R	1414				12.6
	S	1424				87.4

of the *S*-enantiomer, ranging from 58.0 to 74.8%, in all noncitrus samples.

3.6. Es-GC Analysis of Selected Chiral Markers in Citrus Fruit Fibre. ERs were calculated for eight chiral markers in lemon fibre (Table 4). The results are, in general, in good agreement with those reported for the enantiomeric composition of essential oils. An ER was observed for all the chiral markers except for linalool, which was almost in a racemic form. This result is in agreement with the literature reporting that the enantiomeric composition of linalool in lemon essential oils is highly variable depending on the cultivar and harvest period [34]. The monoterpenes α-pinene, β-pinene, borneol, and α-terpineol presented a higher ratio of the *S*-enantiomer while camphene and limonene gave higher ratios of the *R*-enantiomer. The ERs calculated for these compounds show in all cases the same predominance of one of the enantiomers as reported in the literature [19]. However, the ER of terpinen-4-ol tended to vary as a consequence of the high temperatures applied during processing: the pretreatment of the lemon fibres at high temperatures might explain a lower ER of the *R*-enantiomer in these fibres when compared with essential oils and juices [35].

ERs were calculated for nine chiral markers in orange and tangerine fibres (Table 5). These results are generally in good agreement with the literature on citrus essential oils [19], often showing a higher ER for one of the enantiomers, as was the case for α-pinene, camphene, limonene, linalool, and carvone. β-Pinene, as previously described, presented a high ER of *S*-enantiomer in orange and tangerine flesh fibres, while it was racemic in both peel fibres [19]. In agreement with the reported data, the drying process applied to the

Table 4: Chiral markers, calculated LRI, and corresponding enantiomeric ratio for lemon fibre.

Chiral marker	Configuration	LRI	Lemon ($n = 5$)	Literature data [19]
α-Pinene[1]	R	923	15.4–22.0	25.5–37.8
	S	925	84.6–78.0	74.5–62.2
Camphene[1]	S	920	72.6–80.7	86.2–92.4
	R	933	27.4–19.3	13.8–7.6
β-Pinene[1]	R	946	15.8–21.3	4.2–7.0
	S	956	84.2–78.7	95.8–93.0
Limonene[1]	S	1056	0.9–4.2	1.0–2.6
	R	1072	99.1–95.8	99.0–97.4
Linalool[2]	R	1212	38.0–49.7	49.5–74.5
	S	1222	62.0–53.3	50.5–25.5
Borneol[2]	S	1307	84.5–91.7	
	R	1317	15.5–8.3	
Terpinen-4-ol[2]	S	1319	30.0–43.0	12.0–32.5
	R	1327	70.0–57.0	88.0–67.5
α-Terpineol[1]	R	1296	11.0–18.5	35.8–18.0
	S	1309	89.0–81.5	64.2–82.0

[1]LRI and enantiomeric ratios calculated using a diEt-CD column.
[2]LRI and enantiomeric ratios calculated using a Pentyl-CD column.

Table 5: Chiral markers, calculated LRI, and corresponding enantiomeric ratios for orange and tangerine fibres.

Chiral marker	Configuration[3]	LRI	Orange flesh ($n = 5$)	Tangerine flesh ($n = 1$)	Orange peel ($n = 1$)	Tangerine peel ($n = 1$)	Literature data [19]
α-Pinene[2]	S	929	7.6–17.8	13.4	11.7	14.5	9.9–0.6
	R	936	92.4–82.2	86.6	88.3	85.5	90.1–99.4
Camphene[2]	S	949			29.2	25.4	
	R	964			70.8	74.6	
β-Pinene[2]	R	975	6.5–12.6	6.1	46.2	49.3	10.6–70.2
	S	978	93.5–87.4	93.9	53.8	50.7	89.4–29.8
Limonene[1]	S	1056	0.6–0.8	0.6	0.5	0.6	0.0–1.1
	R	1072	99.4–99.2	99.4	99.5	99.4	100–98.9
Linalool[1]	R	1175	9.7–20.4	16.4	8.1	11.3	2.2–17.9
	S	1190	90.3–79.6	83.6	91.9	88.7	97.8–82.1
Terpinen-4-ol[2]	S	1319	42.9–51.1	28.9	55.7	57.8	65.3–71.5
	R	1327	57.1–49.9	71.1	44.3	42.1	34.7–28.5
α-Terpineol[1]	R	1296	30.6–42.1	41.5	22.7	48.3	5.1–15.7
	S	1309	69.4–57.9	58.5	77.3	51.7	94.9–84.3
Carvone[2]	R	1346	32.2–41.3	34.9	30.3	26.5	40.7
	S	1352	67.8–58.7	65.1	69.7	73.5	59.3
α-Terpinyl acetate[2]	X	1378			21.0	73.5	
	Y	1381			79.2	26.5	

[1]LRI and enantiomeric ratios calculated using diEt-CD column.
[2]LRI and enantiomeric ratios calculated using Pentyl-CD column.
[3]X and Y were used to indicate that the absolute configuration of the enantiomers could not be determined.

fibres is expected to have modified the ER of terpinen-4-ol and α-terpineol. A similar effect had already been reported for these monoterpene alcohols when citrus essential oils are obtained through distillation instead of cold pressing [19]. Finally, the ERs of α-terpineol in orange and tangerine peel were not coincident and showed distinct behaviour. This difference was also observed in the ER of α-terpinyl acetate. This observation could be explained by the fact that α-terpinyl acetate forms from α-terpineol via acetylation. On the other hand, for tangerine peel, racemisation was observed for α-terpineol, while α-terpinyl acetate probably kept its original configuration.

4. Conclusions

Here, we applied HS-SPME-GC-MS to study the volatile composition of nine types of fruit and vegetable fibres, namely, apple, peach, pear, orange peel and flesh, tangerine peel and flesh, lemon flesh, and carrot, derived from the juice industry. Despite being submitted to processing which involves among others washing and drying, this study shows that the volatiles remaining in the fibres cannot be neglected. In this regard, citrus fibres contained a high amount of volatile compounds, mainly monoterpenoids (limonene). Processing to obtain fruit fibres was shown to produce fibres with low volatile content for noncitrus products. Otherwise, citrus fibres analysed still presented a high volatile composition when compared with noncitrus ones. In addition, the Es-GC analyses of the chiral volatiles present in the samples revealed that, during processing, monoterpene alcohols (terpinen-4-ol and α-terpineol) tend to show a variation in their ER, probably because of the heat applied during drying.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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