

Multidimensional Capillary GC-GC for the Analysis of Real Complex Samples

Part IV. Enantiomeric Distribution of Monoterpene Hydrocarbons and Monoterpene Alcohols of Lemon Oils

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Summary

This paper describes a fully automated, multidimensional, double-oven GC-GC system, developed in our laboratory. The system is based on the use of mechanical valves which allow the multitransfer of different fractions during the same GC analysis and the use of the two GC independently when the multitransfer options is not used. Pneumatic and electronic circuits permit maintenance of constant retention times in the pre-column, even for the components eluted after numerous transfers. The system has been used for the determination of the enantiomeric distribution of β -pinene, sabinene, limonene, linalol, terpinen-4-ol, and α -terpineol in lemon oils. The results obtained allowed the characterization of cold-pressed lemon oils.

1 Introduction

Recently we developed in our laboratory a multidimensional gas chromatographic system based on the use of mechanical valves [1–3]. The system, which consists of two Shimadzu (Milan, Italy) Model 17 gas chromatographs, a hot transfer line, and two Shimadzu CR 3A integrators, allowed automatic multiple transfers from the pre-column to the main column, and the analysis of all the transferred fractions during the same gas chromatographic run. A system of pneumatic valves permitted variations in the pressure to maintain constant retention times in the pre-column even for the components eluted after numerous transfers. Moreover, when the system was not used in the multidimensional configuration, the two gas chromatographs could be used at the same time independently without any change in the hardware. This system has been used for the determination of the enantiomeric distribution of monoterpene hydrocarbons and monoterpene alcohols in lime [2] and mandarin [3] essential oils. In this paper some changes made in the pneumatic and electronic circuits to simplify the use of the instrumentation and improve his reliability are described.

The enantiomeric distribution of β -pinene, sabinene, limonene, linalol, terpinen-4-ol, and α -terpineol in lemon essential oils has been determined with the new version of the instrument. Determination of the enantiomeric distribution of the components of lemon oil has been the object of numerous studies carried out by gas chromatography with chiral capillary columns coated with cyclodextrins [4–21]. Some studies have been carried out by direct GC analysis of the whole oil [8, 9, 12, 21], and others performed after pre-separation of the components by preparative

gas chromatography [13] or by LC on-line coupled with gas chromatography [17]. Most of the work has been carried out by multidimensional gas chromatography [4–7, 10, 14–16, 18–20]. Some papers report results for monoterpene hydrocarbons [4–9, 14, 15], while others report data on monoterpene alcohols [11–13, 16, 17], and three papers are on both monoterpene hydrocarbons and monoterpene alcohols [18–20]. Another paper reports results of the enantiomeric distribution of citronellal, methyl jasmonate, and methyl epi-jasmonate in a concentrated lemon oil [10].

2 Experimental

2.1 Samples Analyzed

The studies were carried out on 148 genuine cold-pressed lemon oils, produced during the 1996/97 season with the most commonly used technologies in Citrus processing (Pelatrice, Sfumatrice, Torchi, FMC) (See **Table 1**); 6 samples of commercial lemon oils; 2 samples of distilled lemon oils.

Table 1. Cold-pressed lemon oils analyzed.

Period of production	Technology of extraction and no. of samples				All
	Pelatrice	Sfumatrice	Torchi	FMC	
October 1996	1	–	–	14	15
November 1996	3	8	7	10	28
December 1996	2	12	13	3	30
January 1997	4	4	4	3	15
February 1997	3	2	3	2	10
March 1997	3	3	3	3	10
April 1997	3	3	3	3	12
May 1997	3	2	3	3	11
June 1997	–	–	–	3	3
July 1997	–	–	–	2	2
August 1997	1	–	–	3	4
September 1997	3	–	–	3	6
All	26	34	36	52	148

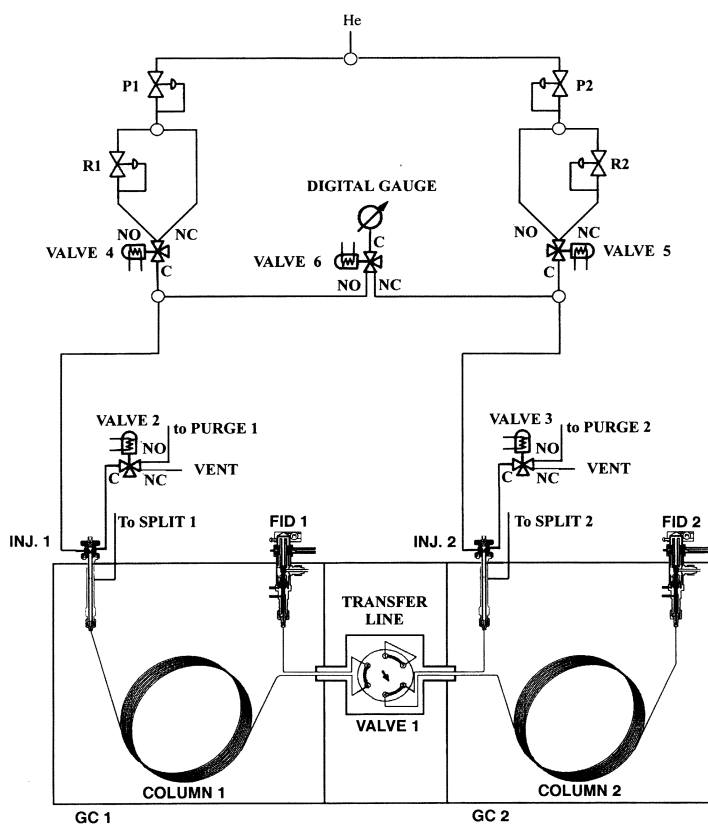


Figure 1. Pneumatic and electronic scheme of the GC-GC system, in the stand-by position.

2.2 Multidimensional GC

All the samples were analyzed by multidimensional GC injecting 1 μ L of 1:5 (V/V) solution of essential oil in pentane with a split ratio of 1:15. The multidimensional system used in this study was an improved model of a developmental instrument formerly described in detail [1–3]. The instrumental set-up and the experimental conditions used are described below and in **Figure 1**.

2.2.1 GC1

Injector (Inj. 1): Split/splitless injector at 250°C; split ratio 1:15.

Column (Column 1): SE-52 capillary column 30 m, 0.32 mm i. d., 0.40–0.45 μ m film thickness (Mega, Legnano, Italy).

Temperature program: 45°C for 6 min then to 240°C at 2.0°/min.

Carrier: He, 90 kPa (Stand-by position), 170 kPa (Cut position).

Detector (FID 1): Flame Ionization Detector at 280°C connected to CLASS-VP Chromatography Data System (channel 1) (Shimadzu, Milan, Italy).

Valve 2: Three-way solenoid valve (SIRAI, Milan, Italy) connected to CLASS-VP Chromatography Data System (Event 1) (Shimadzu, Milan, Italy).

A micro-switch assembled on the injector allows auto start of the analysis by syringe inserting.

2.2.2 GC2

Injector (Inj. 2): Split/splitless injector at 250°C; split ratio 1:15.

Column (Column 2): Diethyl-*tert*-butyl- β -cyclodextrin capillary column 25 m, 0.25 mm i. d., 0.25 μ m film thickness (Mega, Legnano, Italy).

Temperature program: 45°C for 6 min then to 90°C (10 min) at 2.0°/min then to 230°C at 2.0°/min.

Carrier: He, 110 kPa (Stand-by position), 5 kPa (Cut position).

Detector (FID 2): Flame Ionization Detector at 280°C connected to CLASS-VP Chromatography Data System (channel 2) (Shimadzu, Milan, Italy).

Valve 3: Three-way solenoid valve (SIRAI, Milan, Italy) connected to CLASS-VP Chromatography Data System (Event 1) (Shimadzu, Milan, Italy).

The analysis starts by programming of the event 2 on CLASS-VP Chromatography Data System (Shimadzu, Milan, Italy).

2.2.3 Multidimensional Interface

Transfer line: aluminum thermoregulated block (200 °C) equipped with a heater, a PT sensor, and a thermocouple (Shimadzu, Milan, Italy) connected to the AUX 1 exit on gas chromatograph 1.

Valve 1: 6-port (1/16") two-position W type valve (A3C6WT) (Valco Europe, Schenkton, Switzerland) equipped with a heated valve enclosure (HVEA-220) (Valco Europe, Schenkton, Switzerland) connected to CLASS-VP Chromatography Data System (Event 1) (Shimadzu, Milan, Italy).

P1, P2, R1, R2: pressure regulators (Shimadzu, Milan, Italy) connected to CLASS-VP Chromatography Data System (Event 1) (Shimadzu, Milan, Italy).

Valve 4,5,6: three-way solenoid valve (SIRAI, Milan, Italy) connected to CLASS-VP Chromatography Data System (Event 1) (Shimadzu, Milan, Italy).

Digital gauge: a digital gauge 0–400 kPa (Generalcontrol, Milan, Italy) reading the inlet pressures of the two injectors both in stand-by and cut positions.

3 Results and Discussion

Figure 1 shows a scheme of the multidimensional system in the stand-by position, used in this study. When the 6-port valve is in stand-by position, flow paths are: injector 1 to column 1 through the hot transfer line to FID 1, and injector 2 through the hot transfer line to column 2 and FID 2. In the cut position flow paths are: injector 1 to column 1 through the hot transfer line to column 2 and FID 2, and injector 2 through the hot transfer line to FID 1. In the stand-by position valve 4 is normally opened (NO) and the pressure regulator P1 is followed by the pressure regulator R1 that acts as a restrictor, thus reducing the pressure at the inlet of injector 1 to the same level which occurs when the system is working in the cut position when the restrictor 1 is replaced by the column 2 and valve 4 is in the position of normally closed (NC). On the other side, valve 5 is normally opened (NO) and the pressure in the inlet of column 2 is dictated by the pressure regulator P2. When the system is in cut position valve 5 is switched in the normally closed (NC) position and the pressure regulator P2 is followed by the pressure regulator R2 that acts as a restrictor with a backpressure equal of that of column 1. Moreover, as can be seen from Figure 1, another two solenoid valves have been added to the system to overcome the following drawbacks. Valves 2 and 3 are in the normally opened position (NO) when the system is in stand-by position (purge flow). When the system is in cut position valve 3 is diverted to vent position for a fraction of second, to allow the gas accumulated in the injector 2 to escape rather than blowing out the flame of FID 1, after removing column 2. On the other side, when the system is switched again to the stand-by position valve 2 is diverted to vent position for a fraction of second to allow the gas accumulated in the injector 1, column 1, after removing column 2 to escape rather than displacing the compounds in column 1 faster than when the system is in stand-by position. As result, the retention times of all the compounds eluted from column 1, even those eluted after the compounds that are transferred to the second GC column, are consistent with the retention times of the same compounds when the mixture is injected into the system in stand-by position. The time at which the valves should be

Table 2. Percentage composition of the transferred components in cold-pressed lemon oils and transfer windows.

	Min	Max	Transfer windows
Sabinene	1.596	2.507	} 15.96–16.20
β-Pinene	11.700	18.389	
Limonene	52.194	67.322	20.10–20.35
Linalol	0.051	0.170	25.50–25.90
Terpinen-4-ol	0.019	0.117	31.17–31.62
α-Terpineol	0.057	0.279	32.25–32.70

switched to begin the cuts can be determined from a preliminary analysis on the first column. After this, a fully-automated analysis is possible by adding the retention windows in the external events table of the CLASS-VP Chromatography Data System.

A lemon essential oil was first analyzed with the SE-52 column to determine the retention times of the components of interest, maintaining the multidimensional system in the stand-by position. Depending on the retention times and the concentration of each component in the lemon oil different transfer windows were chosen and automatically programmed. The composition, based on relative percentage of peak areas, of the transferred components in cold-pressed lemon oils and the transfer windows are shown in **Table 2**.

Figure 2 reports the chromatogram of a cold-pressed lemon oil obtained with the SE-52 column and the system in the stand-by position, the chromatogram of the same oil obtained with the SE-52 column and the system in the cut position (on this chromatogram the cuts are shown), and the chromatogram obtained with the chiral column for the fractions transferred from the SE-52 column.

To obtain, on the chiral column, well-resolved peaks both for the compounds present in large amounts and for the minor components, limonene and β-pinene + sabinene were only partially transferred because of their high concentration, while the other components analyzed were quantitatively transferred since they were present in lower amounts.

3.1 Cold-Pressed Oils

The oils analyzed are listed according to production month and, for each month, according to the extraction technology. For every group, the average value of the enantiomeric distribution has been determined. **Table 3** reports the monthly average values of the enantiomeric distribution, while **Figure 3** shows values of the enantiomeric excess, in accordance to the month of production of the oils.

As can be observed from Table 3 and Figure 3, limonene shows values of the enantiomeric distribution practically constant all around the year. These values are consistent with most of the results reported in the literature [4–9, 13, 18] and differ only from those reported by Casabianca *et al.* [15]; these authors report a ratio of (-)/(+)-limonene that ranges between 0.5/99.5 and 5/95. The lowest values of the ratio (-)/(+)-limonene reported by Casabianca could be due to the presence of sweet orange oil in the lemon oils analyzed [20] while the highest values could be due to the presence of reconstituted oils [9]. The

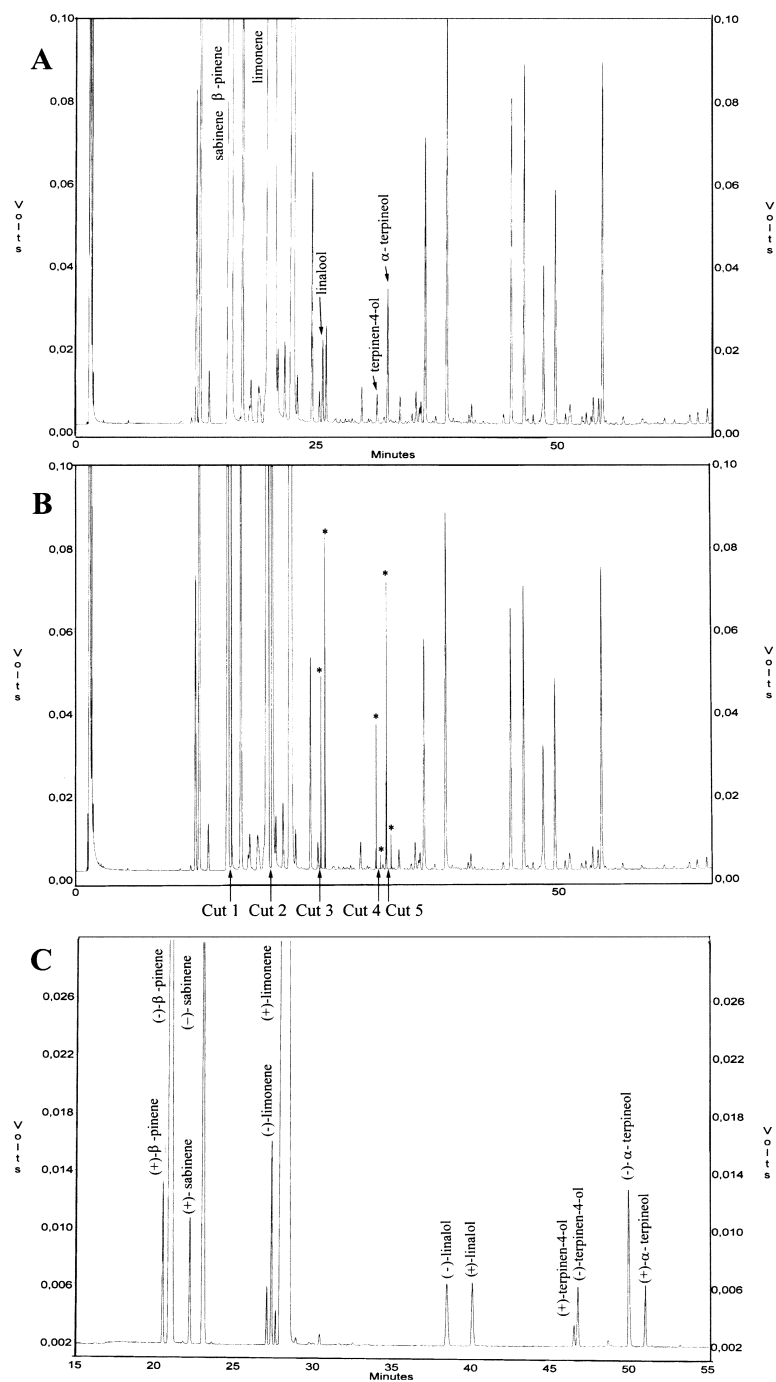
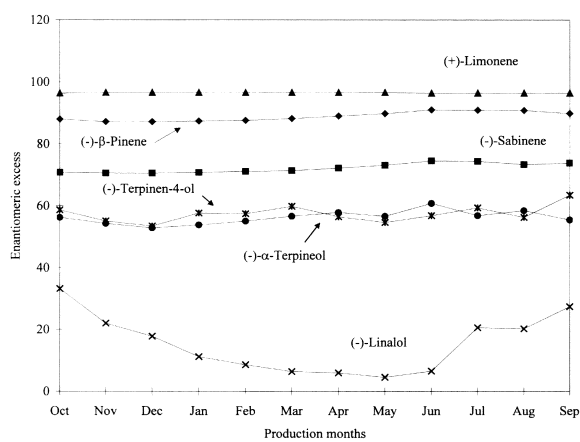


Figure 2. A) GC chromatogram of a cold-pressed lemon oil obtained with the SE-52 column. B) GC chromatogram of a cold-pressed lemon oil obtained with the SE-52 column with the five heart-cuts. C) GC-GC chiral chromatogram of the transferred components. Asterisks in (B) show electric spike coming from the valve switching. In the case of cut 3 (linalol) the electric spike in the end of the cut is higher than the initial spike because under this spike there is the nonanal peak. In the case of cut 1 (sabinene+ β -pinene) and cut 2 (limonene) the electric spikes are not visible because the transfer of these peaks was only partial and these spikes are placed on the signals of those compounds that are not completely transferred.

Table 3. Average values of the enantiomeric distribution of the analyzed components in cold-pressed lemon oils grouped for months of production (in brackets the samples number is reported).

		October (15)	November (28)	December (30)	January (15)	February (10)	March (10)	April (12)
β-Pinene	1 <i>R</i> ,5 <i>R</i> (+)	6.0	6.4	6.4	6.3	6.2	5.9	5.5
	1 <i>S</i> ,5 <i>S</i> (-)	94.0	93.6	93.6	93.7	93.8	94.1	94.5
Sabinene	1 <i>R</i> ,5 <i>R</i> (+)	14.6	14.7	14.7	14.6	14.4	14.3	13.9
	1 <i>S</i> ,5 <i>S</i> (-)	85.4	85.3	85.3	85.4	85.6	85.7	86.1
Limonene	4 <i>S</i> (-)	1.8	1.7	1.7	1.7	1.7	1.7	1.7
	4 <i>R</i> (+)	98.2	98.3	98.3	98.3	98.3	98.3	98.3
Linalol	3 <i>R</i> (-)	66.6	61.0	58.9	55.6	54.3	53.2	53.0
	3 <i>S</i> (+)	33.4	39.0	41.1	44.4	45.7	46.8	47.0
Terpinen-4-ol	4 <i>S</i> (+)	20.7	22.5	23.3	21.2	21.3	20.1	21.8
	4 <i>R</i> (-)	79.3	77.5	76.7	78.8	78.7	79.9	78.2
α-Terpineol	4 <i>S</i> (-)	78.1	77.1	76.4	76.9	77.5	78.3	78.9
	4 <i>R</i> (+)	21.9	22.9	23.6	23.1	22.5	21.7	21.1
		May.	Jun.	Jul.	Aug.	Sept.	All	Max
β-Pinene	1 <i>R</i> ,5 <i>R</i> (+)	5.1	4.5	4.6	4.6	5.1	4.2	7.0
	1 <i>S</i> ,5 <i>S</i> (-)	94.9	95.5	95.5	95.4	94.9	93.0	95.8
Sabinene	1 <i>R</i> ,5 <i>R</i> (+)	13.4	12.7	12.8	13.3	13.1	12.5	15.3
	1 <i>S</i> ,5 <i>S</i> (-)	86.6	87.3	87.2	86.7	86.9	84.7	87.5
Limonene	4 <i>S</i> (-)	1.7	1.8	1.9	1.8	1.8	1.5	2.0
	4 <i>R</i> (+)	98.3	98.2	98.2	98.2	98.2	98.0	98.5
Linalol	3 <i>R</i> (-)	52.3	53.3	60.3	60.1	63.7	56.8	71.5
	3 <i>S</i> (+)	47.7	46.7	39.7	39.9	36.3	28.5	43.2
Terpinen-4-ol	4 <i>S</i> (+)	22.7	21.6	20.4	21.9	18.3	13.7	26.9
	4 <i>R</i> (-)	77.3	78.4	79.7	78.1	81.7	73.1	86.3
α-Terpineol	4 <i>S</i> (-)	78.3	80.4	78.4	79.2	77.7	64.2	82.0
	4 <i>R</i> (+)	21.7	19.6	21.6	20.8	22.3	18.0	35.8

**Figure 3.** Variation of the enantiomeric excess of 4*R*(+)-limonene, 1*S*,5*S*(-)-β-pinene, 1*S*,5*S*(-)-sabinene, 4*R*(-)-terpinen-4-ol, 4*S*(-)-α-terpineol and 3*R*(-)-linalol in lemon oils during the productive season.

ratios between (-)- and (+)-β-pinene and (-)- and (+)-sabinene are in a limited range; the average values from October to March are practically constant, while a slow increase can be noted from April onwards. The results obtained for β-pinene generally agree with the values reported in the literature [4–7]. The value of

100% reported for (-)-β-pinene by Casabianca *et al.* [15] for some samples of lemon oil seems inexplicable to us.

With regard to sabinene, the results obtained are consistent with the preliminary results previously obtained for Italian lemon oils [20] and Uruguayan lemon oils [19] in this laboratory. The literature does not report other results for sabinene.

Values of the enantiomeric distribution of terpinen-4-ol and α-terpineol are in rather wide ranges; during the whole production season the enantiomeric excesses of (-)-terpinen-4-ol and (-)-α-terpineol show similar values and trends. Results obtained for terpinen-4-ol and α-terpineol agree with those previously determined in our laboratory [11, 12]. Results reported by Bicchi *et al.* [12] for terpinen-4-ol ((+)/(–)-terpinen-4-ol = 38/62) are probably due to the analytical technique used: in fact, the determination of the enantiomeric distribution by gas chromatographic analysis of the whole oil can give peaks overlap that alter the results, mainly for those components present in small amounts. Values of the enantiomeric distribution of terpinen-4-ol in Uruguayan oils previously analyzed [19] are similar to those found in distilled oils (see **Table 4**). This is probably due to erroneous use of the extraction technology: for example, heating of the centrifuges during the separation of the essential oil can allow a partial racemization of terpinen-4-ol.

Values of the enantiomeric distribution of linalol vary over a wide range. At the beginning of the production season the enantiomeric excess of (-)-linalol is about 33; this value decreases

Table 4. Average values of the enantiomeric distribution of the analyzed components in distilled lemon oils and in commercial lemon oils.

		Distilled oils				Commercial oils				Cold-pressed	
		1	2	1	2	3	4	5	6	Min	Max
β -Pinene	1 <i>R</i> ,5 <i>R</i> (+)	6.4	6.6	7.8	3.5	4.1	6.7	6.1	5.4	4.2	7.0
	1 <i>S</i> ,5 <i>S</i> (-)	93.6	93.4	92.2	96.5	95.9	92.3	93.9	94.6	93.0	95.8
Sabinene	1 <i>R</i> ,5 <i>R</i> (+)	14.6	12.7	58.4	94.0	56.5	50.2	16.9	16.9	12.5	15.3
	1 <i>S</i> ,5 <i>S</i> (-)	85.4	87.3	41.6	6.0	43.5	49.8	83.1	83.1	84.7	87.5
Limonene	4 <i>S</i> (-)	1.7	1.7	13.7	9.6	11.6	14.5	6.9	5.0	1.5	2.0
	4 <i>R</i> (+)	98.3	98.3	86.9	90.4	88.5	85.5	93.1	95.0	98.0	98.5
Linalool	3 <i>R</i> (-)	60.0	53.1	14.8	5.7	10.3	14.6	23.3	20.4	50.8	71.5
	3 <i>S</i> (+)	40.0	46.9	85.2	94.3	89.7	85.4	76.7	79.6	28.5	49.2
Terpinen-4-ol	4 <i>S</i> (+)	28.5	28.4	57.2	75.4	39.9	46.7	33.9	28.9	13.7	26.9
	4 <i>R</i> (-)	71.5	71.6	42.8	24.6	60.1	53.3	66.1	71.1	73.1	86.3
α -Terpineol	4 <i>S</i> (-)	76.4	77.0	39.9	8.8	48.1	34.2	67.1	65.8	64.2	82.0
	4 <i>R</i> (+)	23.6	23.0	60.1	91.2	51.9	65.8	32.9	34.2	18.0	35.8

Table 5. Average values of the enantiomeric distribution of Pelatrice, Sfumatrice, Torchi and FMC oils produced in the period November 1996–January 1997 (the sample numbers are reported in brackets).

		November (28)				December (30)				January (15)			
		P (3)	S (8)	T (7)	FMC (10)	P (2)	S (12)	T (13)	FMC (3)	P (4)	S (4)	T (4)	FMC (3)
β -Pinene	1 <i>R</i> ,5 <i>R</i> (+)	6.3	6.3	6.3	6.5	6.2	6.3	6.4	6.4	6.4	6.3	6.4	6.2
	1 <i>S</i> ,5 <i>S</i> (-)	93.7	93.7	93.7	93.5	93.8	93.7	93.6	93.6	93.6	93.7	93.6	93.8
Sabinene	1 <i>R</i> ,5 <i>R</i> (+)	14.6	14.6	14.6	14.9	14.6	14.7	14.8	14.6	14.6	14.6	14.7	14.5
	1 <i>S</i> ,5 <i>S</i> (-)	85.4	85.4	85.4	85.1	85.4	85.3	85.2	85.4	85.4	85.4	85.3	85.5
Limonene	4 <i>S</i> (-)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.7	1.7
	4 <i>R</i> (+)	98.3	98.3	98.3	98.3	98.3	98.3	98.3	98.3	98.3	98.2	98.3	98.3
Linalool	3 <i>R</i> (-)	60.2	61.2	61.7	60.6	59.6	58.4	59.3	58.9	54.8	56.0	56.4	55.0
	3 <i>S</i> (+)	39.8	38.8	38.3	39.4	40.4	41.6	40.7	41.1	45.2	44.0	43.6	45.0
Terpinen-4-ol	4 <i>S</i> (+)	16.3	24.5	24.8	21.1	18.3	24.2	23.7	20.6	16.7	23.8	23.7	20.7
	4 <i>R</i> (-)	83.7	75.5	75.2	78.9	81.7	75.8	76.3	79.4	83.3	76.2	76.3	79.3
α -Terpineol	4 <i>S</i> (-)	74.1	78.2	77.0	77.2	78.3	78.2	74.2	78.3	77.6	78.4	73.5	78.6
	4 <i>R</i> (+)	25.9	21.8	23.0	22.8	21.7	21.8	25.8	21.7	22.4	21.6	26.5	21.4

from October to May, and then increases again reaching, in September, values close to those of the beginning of the season. Values reported in the literature for the enantiomeric distribution of linalol in cold-pressed lemon oil [11, 12, 22] are in the ranges found in this work. There are no papers in the literature that report the seasonal variation of the enantiomeric distribution of linalol.

Table 5 compares results obtained for oils extracted by various technologies in November, December, and January. As can be seen from the table, the extraction technology does not seem to influence the enantiomeric distribution of β -pinene, sabinene, limonene, linalol, and α -terpineol. Terpinen-4-ol shows a slight tendency to undergo racemization in the oils extracted with Sfumatrice and with Torchi. In fact, this latter technique allows for a contact of the oil with the liquids coming from the peel and juice residues.

3.2 Distilled Oils and Commercial Oils

Table 4 reports values of the enantiomeric distribution of two lemon oils obtained by distillation of the residues of the cold extraction and of six commercial oils. For the two distilled oils

analyzed, the enantiomeric distribution of all the component analyzed, except for terpinen-4-ol, are in the ranges shown by cold-pressed oils. Terpinen-4-ol has a slight tendency to racemize. This is due to the extraction technology.

For the commercial oils analyzed, only β -pinene shows values of the enantiomeric distribution similar to those of the genuine lemon oils. The other components analyzed show values of the enantiomeric distribution very different from those of genuine oils. The differences are so large that it is impossible to determine the products used in the reconstitution of the oils.

4 Conclusions

The system described, as can be seen from the chromatogram in Figure 2 and from the scheme of the instrument reported in Figure 1, made it possible to carry out fully automated multiple transfers. This was possible because retention times on the pre-column were reproducible even for those compounds eluted after numerous transfers. Moreover, when the multidimensional system was not used, the two GCs can be operated independently without any hardware modification.

The results obtained with this system for the lemon essential oils allowed us to differentiate lemon oils from other citrus essential oils [2, 5, 20, 22] and could be taken as references for the authenticity and quality of the oil.

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