Chemical composition of distilled essential oils and hydrosols of four Senegalese citrus and enantiomeric characterization of chiral compounds

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ABSTRACT

Peels of four local Citrus species (*Citrus sinensis* L. Obsbeck, *Citrus reticulata* Blanco, *Citrus maxima* Burm. and *Citrus aurantifolia* christm.) grown in a same locality under the same climatic conditions were subjected to steam distillation. The essential oils and floral waters obtained were analyzed by gas chromatography coupled with a flame ionization detector (CPG-FID) and by gas chromatography coupled to a mass spectrometer (CPG-MS). The essential oils yields were ranged between 0.2 and 0.7%. The qualitative and quantitative analyses show 74 compounds in all oils samples. The oils were largely dominated by hydrocarbon monoterpenes with limonene as major compound (91.5-94.0%; 90.4-93.4%; 77.7-93.7% and 34.8-51.2%) in oils from *Citrus sinensis*, *Citrus reticulata*, *Citrus maxima* and *Citrus aurantifolia*, respectively. In addition to limonene, oils of *Citrus aurantifolia* contained high amounts of β-pinene (6.8-14.4%), p-cymene (5.8-12.2%), γ-terpinene (0.3 - 7.4%), neral (1.5-9.4%), geraniol (1.9-12.7%). Although presenting the same major compound (limonene), the oils had compositions that were qualitatively and quantitatively different. The enantiomeric analyses showed that the chiral major compounds were (R) - (+) - limonene, (S) - (-) – limonene, (1S) - (-) - β-pinene, (1R)-(+)-β-pinene and (S) - (+) - carvone. The hydrosols analyzed were composed of oxygenated compounds and did not have the same major compound. A qualitative and quantitative difference in chemical composition was noted between the Hydrosols.

Keywords: Citrus, Distilled essential oils, Hydrosols, Enantiomeric analyses

INTRODUCTION

The fruit-bearing production of Senegal, primarily for a national consumption, is concentrated in Casamance and Niayes areas. This production consists mainly of mangos, citrus fruits and bananas. In recent years, there has been a notable increase in citrus fruits plantations in

Niayes, near Dakar (Rufisque, Sebikhotane, Pout, Mbour etc…). In 1020 ha of fruit cultivation in Niayes, the 820 ha are occupied by citrus fruits. In addition to this national production, Senegal also imports citrus to supplement its fruit needs. After cola and bananas, citrus fruits are the most-imported fruits. Although the citrus fruits are widely consumed and distributed in Senegal, an exploitation of the peels by the valorization of their essential oils has yet to occur in Senegal.

The genus citrus from the Rutaceae family, which accounts for approximately 16 species in the citrus family, include fruits such as mandarin oranges, lemons and grapefruits, which are very interesting sources of essential oils [1]. Citrus essential oils are used, in the food industry as a spice and perfume [2]. They are also used in medicine and as an antifungal, antibacterial, antiviral or antiparasitics agent [3]. Essential oils activities depend exclusively on their chemical compositions. Several studies on the chemical composition of citrus essential oils report limonene as a major compound. According to Dugo et al. [4] the *Citrus sinensis* essential oil contained more than 90% of limonene. Singh et al. [5] reported in *citrus sinensis* and *C. maxima* essential oils a composition dominated by limonene with respective percentages of 90.7 and 31.8%. Besides limonene, several derived oxygenated monoterpenes and sesquiterpenes, such as aldehydes (citral), ketones, acids, alcohol (linalool) and esters, are often recorded in citrus oil composition [6].

In perfumery, sensory properties of volatile compounds containing asymmetric carbons differ from one isomer to another. In addition to the sensory difference, there can be also a significant difference in biological activity [7]. The majority of citrus essential oils are rich in chiral molecules such as limonene β-pinene, α-pinene, carvone etc. A complete analysis of the various isomers of chiral major compounds contained in essential oils can be very interesting before valorization.

Hydrosols, also called floral waters or aqueous distillates, are a sub-product of the distillation of essential oils. Several studies of floral waters have shown that their compositions are largely dominated by oxygenated molecules. Although less common than essential oils, floral waters are beginning to gain popularity as a natural additive for food and cosmetics. The hydrosol of *C. sinensis* analyzed by Labadie et al.[8] showed a chemical composition composed of 44.1% of linalool and 23.7% of α-terpineol and 5.7% of cis-linalool oxide.

The present study reports an investigation focused on yield, and chemical composition of essential oils and their corresponding hydrosols extracted from *citrus sinensis*, *citrus reticulata*, *citrus maxima* and *citrus aurantifolia* growing in the same condition in Senegal. The drying influence on yields and chemical compositions of oils has also been taken into account. Optical isomers of major volatiles components were determined. This is the first study carried out on essential oils and floral waters of citrus grown in Senegal.

MATERIALS AND METHODS

Plant materials

The fruit samples of *Citrus reticulata*, *Citrus sinensis*, *Citrus maxima* and *Citrus aurantifolia* were collected at the same farm in Pout (14 ° 46 '26 "North, 17 ° 03'37" West) in the region of Thiès. The culture conditions of the four species are the same. After harvesting, the fruits are cleanly washed with tap water before being peeled and drying the zest in the shade (25 ± 5 °C).

Extraction of essential oils

For each sample from the three, 100 g of peel were submitted to steam distillation for 90 min (with 1.5 L water) using a Clevenger-type apparatus. Oil yields have been calculated relative to the fresh matter and the presented results are the mean ± standard deviation of triplicates.

Extraction of the volatile constituents from hydrosols

A liquid-liquid extraction method was undertaken to isolate components soluble in hexane of aqueous distillates which were recovered after essential oil hydrodistillation (after 7 days of drying). In a separatory funnel, 20 mL of aqueous hydrosols and 4 mL n-hexane were mixed. After decantation, the extracts have been dried over anhydrous sodium sulphate and analyzed.

Gas chromatography

Oils and aqueous distillates have been analyzed by gas chromatography fitted with a flame ionization detector (GC-FID) and gas chromatography coupled with a mass spectrometer (GC-MS).

GC-FID

The gas chromatograph fitted with a flame ionization detector (THERMO-TRACE, Interscience, Belgium) was equipped with an OPTIMA-5-MS Accent capillary column from Agilent (Belgium) (30m long, 0.25mm diameter and 0.50 µm film thickness). Helium (He) was used as carrier gas at a flow rate of 1.1ml/min. The oven temperature ranges from 40 to 250°C according to the following program: 40 °C for 3 minutes and then a programmation at 5° C / min until 250°C with a final hold of 5 minutes at this temperature. The injector used in splitless mode was set at 280° C. The detector temperature was 280°C; air and hydrogen flows were of 350 mL/min and 35 mL/min respectively. A makeup gas (N_2) was used with a flow rate of 30 mL/min.

GC-MS

The gas chromatograph (AGILENT 6890- USA) equipped with MS (AGILENT 5973 NETWORK mass selective detector) in the electron impact mode (70 eV) source and quadrupole temperatures were of 280°C and 150°C respectively. The scanned mass range was fixed at 35 to 350 amu. The column was the same than GC-FID. The oven temperature was programmed as follows: isotherm of 5 min at 40 °C then a progression of 8°C/min up to 280°C with a final hold of 5 minutes at 280°C. The injector, used in splitless mode, was at 240 °C. The carrier gas was Helium (He) with a constant flow rate of 1.1 mL/min.

The identification of the compounds was made using data of computer library (Wiley 275L) connected to the GC-MS and retention indices of components calculated using retention times of n-alkanes compared with those of the literature [9-10]. Whenever possible, the identifications were confirmed by comparison of the recorded retention data with those of pure standard compounds injected in the same conditions.

CPG-FID equipped with a chiral column

The gas chromatograph (K0733B) is equipped with a silica-type chiral capillary column (Beta Dex TM 110), 30m Long 0.25mm diameter and 0.25µm film thickness. The oven temperature was programmed as follows: initial oven temperature was held at 40°C for 2 min, then increases from 2 °C/min to 220 °C (4 min). Helium was used as the carrier gas at a constant flow rate of 1.1 ml/min. Injector (splitless mode) and flame ionization detector temperatures were set at 220°C and 230°C, respectively. The flow rate of the hydrogen is 35 ml / mm and that of the air 350 ml / min. A series of n-alkanes (C_7-C_{30}) is injected for the calculation of the retention indices. The identification of the compounds is made by referring to the retention indices of standard compounds injected in the same conditions and by superposing the chromatograms of standards compounds and of the essential oils (Figures: 2 and 3).

The standard compounds used, racemic limonene, (1S)-(-)-β-pinene (99%) (S)- (+)-carvone (98.5%) were purchased from Sigma-Aldrish (Boornem, Belgium).

RESULTS AND DISCUSSION

Results

Essential oil yields

The essential oils yields from the *C. sinensis*, *C. reticulata*, *C. maxima*, and *C. aurantifolia* peels based on the fresh weight are presented in Table 1.

The yields were between 0.2 and 0.7%. Although all species provide very similar yields, *C. sinensis* was the species most rich in oil with a maximum of 0.7% obtained in fresh peels. Results show that the best yields were obtained from fresh peel for all species. The variation of yields according to the drying time can be explained by some losses of more volatile compounds.

Chromatographic analyzes

The results of qualitative and quantitative analyzes of essential oils were shown in Table 2. A total of 74 components, listed according to their linear retention indices on the column, have been identified in all oils constituting 97.4-99.7% of oils. The compounds were grouped into four different classes: hydrocarbon monoterpenes, oxygenated monoterpenes, hydrocarbon sesquiterpenes and oxygenated sesquiterpenes.

Analysis revealed that, all oils were rich in hydrocarbon monoterpenes with 93.9-96.9% in *C. sinensis* oils; 94.5-96.3% in *C. reticulata* oils; 83.6-97.0% in *C. maxima* oils and 58.5-81.9% in *C. aurantifolia* oils. The oxygenated monoterpenes proportion was 2.1-4.2% in *C. sinensis* oils; 2.6-4.3% in *C. reticulata*; 1.9-11.5% in *C. maxima* and 11.8-33.4% in *C. aurantifolia*. All oils had a low percentage of sesquiterpenes. Limonene was the major compound of all oils with: 91.5-94.0% in *C. sinensis* oils; 90.4-93.4% in *C. reticulata*; 77.7-93.7% in *C. maxima* and 34.8-51.2% in *C. aurantifolia*. In *C. sinensis* oils, behind limonene, myrcene and linalool had proportion higher than 1%, with (1.5-1.8%) and (0.9-1.9%), respectively. In *C. reticulata*, only myrcene (1.1-1.7%) had a percentage higher than 1%. The oils of *C. maxima* show myrcene (0.7-1.7%), n-octanal (0.6-2.6%), linalool (0.4-1.9%), n-decanal, 4-1.3%), trans-carveol (0.1-1.3%) and carvone (0.1-2.0%) as major compounds behind limonene. β-pinene

(6.8-14.4), p-cymene (5.8-12.2%), γ-terpinene (0.3-7.4%), neral (1.5-9,4%) and geraniol (1.9-12.7%) were present at high proportion in *C. aurantifolia* oils.

Several compounds such as α-thujene, cis-pinocanphone, p-cymen-8-ol, trans-p-mentha-1- (7) -8-dien-2ol, nerol, tymol, carvacrol, cis- Bergamotene, trans-α-bergamotene, β-santalene, α-selinene, β-bisabolene, isospathulenol and α-bisabolol were found only in *C. aurantifolia* oils. On the other hand, compounds such as δ-3-carene, perillaalcohol, E,E,-α-farnesene were present only in *C. sinensis* oils.

Limonene proportion increased with drying in *C. maxima* and *C. aurantifolia* oils. No differences in limonene content were observed in *C. sinensis* and *C. reticulata* oils following drying. The proportion of β-pinene and myrcene increased also with drying in all oils (Table 2). The increase of limonene, β-pinene and myrcene content was promoted by evaporation of the more volatile compound during drying.

The results of chiral analysis were shown in Table 3. The table listed isomers of major compounds found in oils and theirs entiomeric excess percentage.

Result showed that (R)-(+)-limonene was the major enantiomer of limonene found in all oils. (1S)- (-)-β-pinene, (S)-(+) – carvone were the isomers found in *C. aurantifolia* oils (Table 4).

Analyzed aqueous distillates showed a chemical profile composed mainly by oxygenated compounds (Table 4).

C sinensis had linalool (34.8 %), α-terpineol (9.5 %), limonene-10-ol (9.5%) and citronellol (8.4%) as major compounds. The dominated compounds in *C reticulata* hydrosol were linalool (17.5%), α-terpineol (10.1%), trans-carveol (12.2 %) and citronellol (16.4%). As it concerns *C. maxima*, hydrosol was composed by trans-linalooloxide (furanoid) (21.3%) as major compound followed by α-terpineol (13.0%), cis-linalooloxide (furanoid) (10.3%), linalool (9.8%), geraniol (6.8%) and of neral (5.9%). In floral water of *Citrus aurantifolia* the seven major compounds were geranial (18.3%), nerol (15.8%), neral (15.3%), geraniol (13.1%), α-terpineol (14.6%), terpinene-4-ol (5.8 %) and linalool (3.6%).

DISCUSSION

C. sinensis, C. reticulata, C. maxima and *C. aurantifolia* peels which were the subject of this study, provided average yields of essential oils but comparable to those of Kamal et al. [11] whose oils were extracted from the fresh zest of *C. reticulata* and *C. sinensis*, with yields of 0.3% and 0.5% respectively. The highest yields were obtained from the fresh peels and after 3 days of drying. The drying duration had no positive effects on yield so it was not necessary to dry the peels for more than three days to avoid oil losses by evaporation.

The qualitative and quantitative analyses showed that essential oils were very rich in monoterpenes including limonene who is the major constituent of all oils. The results were in agreement with those of Michaelakis et al. [12] who proved that limonene was the major compound of *C. sinensis* and *C. limon* with 96.2% and 74.3% respectively. Singh et al. [5] study showed also limonene (90.7%) as major component of *C. sinensis* oil. Japanese *C. reticulata* oil obtained by pressing showed a limonene proportion lower than those reported in our study [13]. This showed the importance of local citrus species studied for a valorization. Our study showed a qualitative and quantitative difference of oils composition (Table 2). Indeed, the limonene percentage noted in *C. sinensis*, *C. reticulata*, and *C. maxima* had no significant difference. In contrast to *C. aurantifolia* who showed proportion of limonene significantly lower than those of other species (Table 2). These differences noted in oils composition confirm the results of Ahmad et al. [14] conducted on *C. sinensis*, *C. paradisi*, and *C. limon* from Pakistan and those of Bourgou et al. [15] who showed a lower percentage of limonene (37.6-69.7%) in *C. limon* oil compared to 3 others species oil from Tunisia. According to Ahmad et al. [14], the qualitative and quantitative difference in composition could be related to genetic factors. Our oils of *C. aurantifolia* showed behind limonene a high proportion of β-pinene, γ-terpinene and p-cymene, similarly to Campolo et al. [16] results. Our oils from *C. sinensis*, *C. reticulata* and *C. maxima* present a composition sufficiently similar to the pressed oils[17]. The low content of limonene of our *C. aurantifolia* oils may be related to the extraction method. Dugo et al.[17] reported limonene content lower to the hydrodistillation oil then in those of cold pressed commercial oils.

Drying had a good effect on *C. maxima* and *C. aurantifolia* limonene's content. This result corroborates those of kamal et al. [11] conducted on *C. paradissi*. They found that limonene levels increased significantly during drying.

(R) - (+) - limonene was the major enantiomer found in all oils of four citrus species from Senegal with enatiomeric ratios greater than 94% (Table 3). Padrayuttaw et al. [7], found (R) - (+) limonene as major compound of *C. sinensis*, *C. reticulata*, *C. maxima* and *C. aurantifolia* essential oils with more than 90% of enantiomer ratios. The determination of enantiomer ratios or excesses is of high importance in the essential oil field. Chiral analysis allows particular attention to be devoted to the enantiomeric distribution trends during the production season, to define useful parameters for quality assessment[18]. According to Karlberg et al. [19], (R)-(+)-limonene can be used for flavoring, as perfume in household products and as additive in cleaning products.

The hydrosols showed chemical profiles composed mainly by oxygenated molecules. These results confirm previous work on citrus floral waters [8]. Contrary to essential oils, floral waters did not have the same major compound, but some oxygenated monoterpenes compounds such as linalool, α-terpineol, nerol, néral and carvone found in oils were present in hydrosols with higher percentages. This suggests that during extraction a high proportion of oxygenated molecules pass into the hydrosols [20].

CONCLUSION

In this work, a quantitative and qualitative analysis of essential oils and their corresponding hydrosols from four citrus species was carried out. Although oils had the same major compound (limonene), a qualitative and quantitative difference in composition is noted between species. The number of compounds identified in the oils of *C. aurantifolia* peels was higher than those obtained with the other oils. It was also noted that the percentages of some major compounds vary with drying. The difference in yield and chemical composition noted according to species may likely be related to genetic or biotic factors. Essential oils and hydrosols compositions established in this study are important in term of quality control for an effective future valorization of citrus peels native to the country. This study is the first carried out on the essential oils and floral waters of citrus grown in Senegal.

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Table1: Essential oil yields from peels of *C. sinensis*, *C. reticulata*, *C. maxima*, and *C. aurantifolia*

Drying times species	Fresh peels	3 days	7 days	14 days	21 days
C. sinensis	0.7 **±0.1**	0.5 **±0.0**	0.3 **±0.1**	0.3 **±0.1**	0.3 **±0.0**
C. reticulata	0.4 **±0.0**	0.4 **±01**	0.2 **±0.0**	0.2 **±0.0**	0.3 **±0.01**
C. maxima	0.3 **±0.1**	0.3 **±0.1**	0.2 **±0.1**	0.2 **±0.0**	0.3 **±0.0**
C. aurantifolia	0.5**±0.2**	0.3 **±0.1**	0.3 **±0.1**	0.2 **±0.0**	0.3 **±0.1**

Table 2: Chemical composition of oils from *Citrus sinensis*, *Citrus reticulata*, *Citrus maxima*, and *Citrus aurantifolia*

RI	Compounds	Fresh				3 days				7 days				14 days				21 days			
		C. sine	**C. retic**	**C. max**	**C. aur**	**C. sine**	**C. retic**	**C. max**	**C. aur**	**C. sine**	**C. retic**	**C. maxi**	**C. aur**	***C. sine***	***C. retic***	***C. maxi***	***C. aur***	***C. sine***	**C. retic**	***C. maxi***	***C. aur***
925	α-thujene	-	-	-	0.2 **±0.1**	-	-	-	0.4 **±0.1**	-	-	-	0.5 **±0.1**	-	-	-	0.5 **±0.1**	-	-	-	0.4 **±0.1**
934	α-pinene	0.2 **±0.1**	0.4 **±0.1**	0.2 **±0.1**	0.6 **±0.1**	0.3 **±0.0**	0.4 **±0.1**	0.4 **±0.1**	1.5 **±0.1**	0.4 ±0.2	0.4 ± **0.0**	0.2 **±0.1**	2.9 **±1.4**	0.4 **±0.1**	0.6 **±0.1**	0.4 **±0.1**	1.8 **±0.3**	0.4 **±0.0**	0.7 **±0.3**	0.4 **±0.0**	1.8 **±0.2**
973	sabinene	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	1.0 **±0.1**	0.2 **±0.0**	0.3 **±0.1**	0.2 **±0.0**	1.2 **±0.1**	0.2 **±0.1**	0.2 ± **0.0**	0.1 ± **0.0**	0.9 ± **0.4**	0.2 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	1.3 **±0.1**	0.2 **±0.0**	0.2 **±0.1**	0.2 **±0.0**	1.2 **±0.3**
980	β-pinene	0.1 **±0.1**	0.1 **±0.0**	0.2 **±0.0**	6.8 **±1.2**	0.1 **±0.0**	0.2 **±0.0**	0.3 **±0.1**	10.4 **±0.6**	0.1 **±0.0**	0.5 **±0.0**	0.2 **±0.0**	14.4 **±2.9**	0.1 **±0.0**	0.3 **±0.1**	0.1 **±0.1**	11.4 **±1.3**	0.1 **±0.0**	0.7 ± **0.2**	0.1 **±0.0**	11.7 **±0.3**
986	myrcene	1.5 **±0.1**	1.7 **±0.1**	0.7 **±0.1**	1.0 **±0.1**	1.6 **±0.1**	1.1 **±0.5**	1.3 **±0.1**	0.9 **±0.1**	1.6 **±0.0**	1.4 **±0.1**	1.4 **±0.1**	1.8 **±0.8**	1.8 **±0.1**	1.5 **±0.2**	1.7 **±0.1**	1.1 **±0.1**	1.7 **±0.1**	1.6 **±0.0**	1.6 **±0.1**	1.0 **±0.3**
999	n-octanal	0.2 **±0.0**	0.2 **±0.0**	2.0 **±0.3**	0.1 **±0.0**	0.3 **±0.0**	0.2 **±0.1**	2.6 **±0.2**	0.1 **±0.0**	0.2 **±0.0**	0.3 **±0.0**	1.4 **±0.1**	0.2 **±0.1**	0.1 **±0.0**	0.2 **±0.0**	0.9 **±0.1**	tr	0.1 **±0.0**	0.1 **±0.0**	0.6 **±0.1**	tr
1003	2-carene	-	-	-	-	-	0.1 **±0.0**	-	-	-	-	-	-	-	0.1 **±0.0**	-	-	-	-	-	-
1006	α-phellandrene	tr	tr	0.2 **±0.0**	tr	tr	-	tr	-	tr	-	Tr	0.1 **±0.0**	tr	Tr	tr	tr	tr	0.2 **±0.0**	tr	tr
1009	δ-3-carene	tr	-	-	-	tr	-	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	tr	-	-	-
1017	α-terpinene	tr	-	-	0.1 **±0.0**	tr	0.1 **±0.0**	-	0.1 **±0.0**	tr	-	-	0.1 **±0.0**	tr	-	-	0.1 **±0.1**	tr	tr	-	0.1 **±0.0**

1025	p-cymene	0.1 **±0.1**	0.1 **±0.0**	0.3 **±0.1**	5.8 **±0.4**	0.1 **±0.0**	0.8 **±0.1**	0.2 **±0.0**	9.1 **±0.3**	0.1 **±0.0**	0.4 **±0.1**	0.1 **±0.0**	10.5 **±3.9**	0.1 **±0.0**	0.3 **±0.1**	0.1 **±0.0**	12.2 **±2.2**	0.1 **±0.1**	0.6 **±0.0**	0.1 **±0.0**	10.0 **±0.7**
1032	limonene	91.5 **±1.1**	93.4 **±0.7**	77.7 **±1.3**	34.8 **±1.2**	91.7 **±1.2**	90.9 **±3.1**	82.1 **±1.8**	38.6 **±1.6**	91.8 **±0.1**	90.4 **±1.7**	86.3 **±1.0**	45.9 **±1.0**	93.2 **±1.1**	90.9 **±1.1**	91.2 **±1.1**	47.2 **±1.0**	94.0 **±0.1**	90.7 **±3.4**	93.7 **±1.2**	51.2 **±1.5**
1034	1,8-cineole	0.1 **±0.0**	0.1 **±0.0**	-	0.5 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	-	0.3 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	-	0.3 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	-	0.2 **±0.0**	0.1 **±0.0**	0.7 **±0.1**	-	0.3 **±0.1**
1044	E-β-ocimene	0.1 **±0.0**	0.1±0. **0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.1**
1058	γ-terpinene	-	tr	0.1 **±0.0**	7.4 **±1.7**	tr	0.1 **±0.0**	0.1 **±0.0**	5.0 **±0.0**	0.1 **±0.0**	-	Tr	4.1 **±0.0**	tr	0.1 **±0.0**	tr	4.2 **±0.5**	tr	0.1 **±0.0**	tr	0.3 **±0.2**
1066	n-octanol	0.1 **±0.0**	tr	0.4 **±0.1**	-	0.2 **±0.0**	0.1 **±0.0**	0.6 **±0.0**	-	0.1 **±0.1**	0.1 **±0.0**	0.3 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	-	0.1 **±0.0**	tr	tr	
1086	p-cymenene	tr		0.4 **±0.0**	0.5 **±0.1**	tr	0.1 **±0.0**	0.4 **±0.1**	0.3 **±0.0**	0.1 **±0.0**	-	0.2 **±0.0**	0.3 **±0.2**	tr	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.1**	tr	tr	0.1 **±0.0**	0.3 **±0.1**
1096	linalool	1.8 **±0.2**	0.6 **±0.1**	1.4 **±0.2**	1.5 **±0.2**	1.9 **±0.0**	0.6 **±0.3**	1.9 **±0.1**	1.2 **±0.0**	1.7 **±0.1**	0.7 **±0.1**	1.4 **±0.2**	1.6 **±0.3**	1.2 **±0.1**	0.6 **±0.1**	0.6 **±0.0**	0.7 **±0.0**	0.9 **±0.3**	0.5 **±0.0**	0.4 **±0.0**	0.8 **±0.1**
1101	nonanal	0.1 **±0.0**	-	0.4 **±0.0**	-	0.1 **±0.0**	-	0.4 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	Tr	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	tr	tr	0.1 **±0.0**	0.1 **±0.0**	tr
1123	mentha-1,3,8-triene	0.1 **±0.0**	0.1 **±0.0**	0.5 **±0.0**	tr	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	tr	tr	0.1 **±0.1**	0.1 **±0.0**	Tr	0.1 **±0.0**	0.2 **±0.0**	tr	0.1 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**
1135	trans-p-2,8-menthadien-1-ol	tr	tr	1.0 **±0.7**	-	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	-	tr	-	0.2 **±0.1**	Tr	0.1 **±0.0**	Tr	0.1 **±0.0**	0.2 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**
1139	neo allo-ocimene	0.1 **±0.0**	0.1 **±0.0**	1.6 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.3 **±0.1**	0.1 **±0.1**	0.2 **±0.1**	0.1 **±0.1**	0.2 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.3 **±0.2**	0.2 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.2 **±0.1**
1140	trans-limonene oxide	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	-	-	-	-	0.1 **±0.1**	-	-	-	0.1 **±0.1**
1149	citronellal	0.2 **±0.0**	0.1 **±0.0**	0.10 **±0.1**	0.2 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	tr	0.1 **±0.0**
1157	isoborneol	-	-	0.3 **±0.0**	0.1 **±0.0**	-	-	0.1 **±0.0**	0.1 **±0.0**	-	-	Tr	Tr	-	-	tr	tr	-	-	-	tr

1172	cis-pinocamphone	-	-	-	0.33 **±0.1**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**
1180	n-nonanol	-	-	0.1 **±0.1**	tr	-	-	tr	0.1 **±0.0**	-		tr	0.1 **±0.0**	-	-	tr	0.1 **±0.0**	-	-	tr	0.2 **±0.0**
1184	terpinene-4ol	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	1.0 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.1**	1.0 **±0.2**	0.2 **±0.1**	0.3 **±0.1**	0.1 **±0.0**	0.9 **±0.2**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.7 **±0.2**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.8 **±0.0**
1187	P-cymene-8ol	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	0.1 **±0.1**	-	-	-	0.19 **±0.12**
1193	trans-p-mentha-1-(7)-8-dien-2ol	-	-	-	-	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	0.1 **±0.0**
1197	α-terpineol	0.2 **±0.1**	0.2 **±0.1**	0.6 **±0.0**	1.9 **±0.0**	0.2 **±0.0**	0.2 **±0.1**	1.0 **±0.1**	1.9 **±0.2**	0.3 **±0.1**	0.3 **±0.0**	0.8 **±0.1**	1.7 **±0.6**	0.2 **±0.0**	0.2 **±0.0**	0.3 **±0.0**	1.3 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.0**	1.5 **±0.1**
1200	trans-dihydrocarvone	0.1 **±0.0**	-	0.4 **±0.2**	-	0.1 **±0.0**	-	0.1 **±0.0**	-	0.1 **±0.0**	-	tr	-	0.1 **±0.0**	-	tr	-	tr	-	tr	-
1202	n-decanal	-	0.2 **±0.1**	1.3 **±0.0**	0.2 **±0.1**	-	0.3 **±0.1**	0.6 **±0.1**	0.2 **±0.0**	-	0.3 **±0.0**	0.7 **±0.0**	0.4 **±0.2**	-	0.3 **±0.1**	0.4 **±0.0**	0.2 **±0.1**	-	0.3 **±0.0**	0.4 **±0.0**	0.1 **±0.1**
1214	octanol acetate	-	-	0.1 **±0.0**	tr	-	-	0.1 **±0.0**	tr	-	-	Tr	-	-	-	tr	0.2 **±0.1**	-	-	-	0.1 **±0.0**
1220	trans-carveol	0.1 **±0.0**	0.1 **±0.0**	1.3 **±0.1**	-	0.1 **±0.0**	0.3 **±0.1**	0.1 **±0.0**	-	0.1 **±0.0**	0.4 **±0.0**	0.1 **±0.0**	-	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	-	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	-
1222	citronellol	0.3 **±0.0**	0.4 **±0.1**	0.2 **±0.0**	1.7 **±0.6**	0.3 **±0.0**	0.3 **±0.1**	0.3 **±0.1**	2.5 **±0.4**	0.2 **±0.1**	0.4 **±0.2**	0.1 **±0.0**	0.9 **±0.1**	0.1 **±0.0**	0.5 **±0.1**	tr	1.3 **±0.4**	0.2 **±0.1**	0.3 **±0.0**	tr	1.4 **±0.1**
1225	cis-carveol	-	-	0.1 **±0.0**	tr	tr	0.1 **±0.0**	0.1 **±0.0**	-	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	tr	tr	tr	0.1 **±0.0**	tr	0.1 **±0.1**
1229	nerol	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.1**	-	-	-	Tr	-	-	-	0.3 **±0.1**	-	-	-	0.1 **±0.1**
1242	neral	0.1 **±0.0**	0.1 **±0.0**	0.7 **±0.2**	9.4 **±3.0**	0.1 **±0.0**	0.1 **±0.0**	0.8 **±0.1**	5.2 **±0.3**	tr	0.18 **±0.04**	0.5 **±0.0**	1.5 **±0.2**	tr	0.1 **±0.0**	0.2 **±0.0**	1.7 **±0.8**	tr	0.05 **±0.00**	0.1 **±0.0**	1.9 **±0.2**
1246	carvone	0.1	0.1	1.0	1.2	0.1	0.1	0.4	1.7	0.1	0.2	0.2	0.6	0.1	0.1	0.1	1.0	0.1	0.1	0.1	1.0

		±0.0	**±0.0**	**±0.3**	**±0.3**	**±0.0**	**±0.0**	**±0.0**	**±0.3**	**±0.0**	**±0.0**	**±0.1**	**±0.3**	**±0.0**	**±0.0**	**±0.0**	**±0.1**	**±0.0**	**±0.0**	**±0.0**	**±0.0**
1265	geraniol	0.1 **±0.0**	0.1 **±0.0**	0.3 **±0.0**	12.7 **±4.1**	0.1 **±0.0**	0.1 **±0.0**	0.4 **±0.1**	6.8 **±0.4**	0.1 **±0.0**	0.1 **±0.0**	0.6 **±0.1**	1.9 **±0.6**	tr	0.1 **±0.1**	0.2 **±0.0**	2.3 **±0.9**	tr	0.1 **±0.0**	0.1 **±0.0**	2.6 **±0.3**
1280	perillaaldehyde	0.3 **±0.1**	0.1 **±0.0**	0.2 **±0.1**	0.1 **±0.0**	0.3 **±0.0**	0.2 **±0.1**	0.2 **±0.0**	0.2 **±0.0**	0.2 **±0.1**	0.2 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	tr	0.2 **±0.1**
1291	limonene-10-ol	tr	-	-	-	tr	-	-	-	tr	-	-	-	tr	-	-	-	tr	-	-	-
1293	tymol	-	-	-	-	-	-	-	0.1 **±0.0**	-	-	-	-	-	-	-	tr	-	-	-	0.1 **±0.0**
1295	carvacrol	-	-	-	-	-	-	-	0.1 **±0.0**	-	-	-	-	-	-	-	tr	-	-	-	tr
1303	undecanal	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	tr	-	-	-	tr	-	-	-	tr	-
1310	perillaalcohol	0.1 **±0.0**	-	-	-	tr	tr	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	tr	tr	-	-
1339	E-patchenol	-	-	0.1 **±0.0**	0.2 **±0.1**	-	0.1 **±0.0**	0.1 **±0.0**	0.3 **±0.0**	-	-	tr	0.2 **±0.1**	-	-	tr	0.2 **±0.1**	-	tr	tr	0.2 **±0.1**
1343	citronellylacetate	-	0.1 **±0.0**	-	0.1 **±0.0**	-	0.2 **±0.0**	-	0.1 **±0.0**	-	0.3 **±0.1**	-	0.1 **±0.1**	-	0.1 **±0.1**	-	0.1 **±0.0**	-	0.1 **±0.0**	-	0.1 **±0.0**
1352	nerylacetate	-	0.1 **±0.0**	0.3 **±0.0**	2.0 **±0.4**	-	0.2 **±0.0**	0.1 **±0.0**	1.5 **±0.1**		0.1 **±0.0**	0.1 **±0.0**	0.8 **±0.1**	-	0.2 **±0.1**	tr	1.4 **±0.1**	-	0.1 **±0.0**	-	1.8 **±0.5**
1371	α-copaene	-	-	0.3 **±0.1**	1.0 **±0.2**	-	-	0.2 **±0.0**	0.6 **±0.0**	-	-	0.1 **±0.0**	0.8 **±0.3**	-	-	0.1 **±0.0**	0.6 **±0.0**	-	-	tr	0.7 **±0.2**
1382	geranylacetate	tr	0.1 **±0.0**	0.4 **±0.0**	-	tr	0.1 **±0.0**	0.2 **±0.0**	-	0.1 **±0.0**	0.1 **±0.1**	0.2 **±0.0**	-	tr	0.1 **±0.0**	0.1 **±0.0**	-	tr	tr	0.1 **±0.0**	-
1393	β-elemene	0.1 **±0.0**	0.1 **±0.0**	0.4 **±0.0**	0.2 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.0**	0.1 **±0.0**	tr	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**
1405	dodecanal	0.1 **±0.0**	Tr	0.1 **±0.0**	-	0.1 **±0.0**	0.1 **±0.0**	Tr	tr	0.1 **±0.0**	0.1 **±0.0**	tr	0.1 **±0.1**	tr	0.1 **±0.0**	tr	tr	tr	tr	tr	tr
1416	cis-α-bergamotene	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**

1430	trans-β-caryophyllene	0.2 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.5 **±0.2**	0.2 **±0.0**	0.1 **±0.0**	0.4 **±0.0**	0.3 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	0.6 **±0.0**	0.4 **±0.0**	0.1 **±0.0**	0.1 **±0.1**	0.3 **±0.0**	0.2 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.2 **±0.0**	0.2 **±0.1**
1436	trans-α-bergamotene	-	-	-	1.1 **±0.1**	-	-	-	1.0 **±0.1**	-	-	-	0.8 **±0.1**	-	-	-	0.8 **±0.0**	-	-	-	0.9 **±0.2**
1463	β-santalene	-	-	-	tr	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**
1466	α-humulene	-	tr	0.1 **±0.0**	-	tr	0.1 **±0.0**	0.1 **±0.0**	-	tr	-	0.1 **±0.0**	0.1 **±0.0**	tr	-	0.1 **±0.0**	-	tr	-	tr	-
1488	α-selinene	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**
1490	germacrene D	-	-	-	-	-	-	tr	-	-	-	tr	-	-	-	tr	-	-	-	tr	-
1500	valencene	0.6 **±0.1**	0.1 **±0.1**	0.1 **±0.0**	0.4 **±0.1**	0.4 **±0.1**	0.1 **±0.0**	0.1 **±0.0**	0.4 **±0.0**	0.3 **±0.1**	0.2 **±0.0**	tr	0.4 **±0.1**	0.2 **±0.0**	0.2 **±0.0**	-	0.2 **±0.1**	0.2 **±0.1**	0.1 **±0.0**	-	0.2 **±0.1**
1508	β-bisabolene	-	-	-	2.2 **±0.0**	-	-	-	2.3 **±0.1**	-	-	-	1.9 **±0.2**	-	-	-	1.5 **±0.0**	-	-	-	1.7 **±0.3**
1521	E,E-α-farnesene	0.1 **±0.1**	-	-	-	0.1 **±0.0**	-	-	-	0.2 **±0.0**	-	-	-	tr	-	-	-	-	-	-	-
1523	δ-cadinene	-	0.1 **±0.0**	0.1 **±0.0**	-	-	0.1 **±0.0**	0.3 **±0.0**	-	0.1 **±0.1**	0.1 **±0.0**	0.4 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	0.1 **±0.1**	0.1 **±0.0**	-	0.1 **±0.0**	0.1 **±0.0**	0.1 **±0.0**	-
1549	α-calacorene	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	tr	tr	0.1 **±0.0**	-	tr	0.1 **±0.0**	tr	-	tr	tr	-	-
1553	elemol	0.1 **±0.0**	tr	0.1 **±0.0**	-	tr	0.1 **±0.0**	0.2 **±0.0**	-	tr	0.1 **±0.0**	0.1 **±0.1**	-	tr	0.1 **±0.0**	0.1 **±0.0**	-	tr	tr	tr	-
1569	nerolidol	-	tr	tr	-	-	0.1 **±0.0**	0.1 **±0.0**	-	-	0.1 **±0.1**	0.1 **±0.0**	-	-	0.2 **±0.0**	tr	-	-	0.1 **±0.0**	-	-
1595	caryophylleneoxide	0.1 **±0.0**	-	1.3 **±0.1**	0.2 **±0.1**	0.1 **±0.0**	-	0.1 **±0.0**	0.3 **±0.0**	0.1 **±0.0**	tr	0.1 **±0.0**	0.2 **±0.0**	tr	0.1 **±0.0**	tr	0.3 **±0.1**	tr	tr	tr	0.4 **±0.2**
1623	tetradecanal	-	-	0.1 **±0.0**	0.1 **±0.0**	-	-	0.1 **±0.0**	0.2 **±0.0**	-	-	tr	0.1 **±0.0**	-	-	tr	0.1 **±0.0**	-	-	-	0.1 **±0.0**
1641	γ-eudesmol	-	-	-	-	-	-	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-

											±0.0										
1652	α-cadinol	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	0.1 **±0.0**	-	-	-	tr	-	-	-	-	-
1668	α-eudesmol	-	-	-	0.1 **±0.0**	-	-	-	0.3 **±0.0**	-	-		0.1 **±0.0**				0.1 **±0.0**				0.2 **±0.1**
1690	α-bisabolol	-	-		0.2 **±0.1**				0.4 **±0.1**				Tr				0.2 **±0.0**				0.2 **±0.1**
Hydrocarbon monoterpenes		**93,9**	**96.3**	**83.6**	**58.5**	**94.6**	**94.7**	**87.7**	**67.9**	**94.9**	**93.9**	**90.1**	**81.9**	**96.2**	**94.5**	**95.0**	**80.4**	**96.9**	**95.2**	**97.0**	**78.3**
Oxygenated monoterpenes		**4,0**	**2.6**	**11.5**	**33.4**	**4.2**	**3.7**	**8.1**	**24.1**	**3.8**	**4.3**	**5.9**	**11.8**	**2.8**	**3.6**	**2.6**	**12.6**	**2.1**	**3.3**	**1.9**	**14.1**
Hydrocarbon sesquiterpenes		**1,0**	**0.4**	**1.2**	**5.6**	**0.8**	**0.5**	**1.4**	**5.0**	**0.8**	**0.6**	**1.5**	**4.9**	**0.4**	**0.6**	**0.7**	**3.7**	**0.5**	**0.4**	**0.4**	**4.1**
Oxygenated sesquiterpenes		**0.2**	**0.0**	**1.6**	**0.6**	**0.1**	**0.2**	**0.6**	**1.2**	**0.1**	**0.3**	**0.4**	**0.4**	**0.0**	**0.4**	**0.1**	**0.7**	**0.0**	**0.1**	**0.0**	**0.9**

RT= Retention times, IR= Retention Index, C. sine = *Citrus sinensis*, C. retic= *Citrus reticulata*, C. max= *Citrus maxima*, C. aur= *Citrus aurantifolia* tr= trace (< 0.1%)

Table 3. Chiral major compounds found in oils

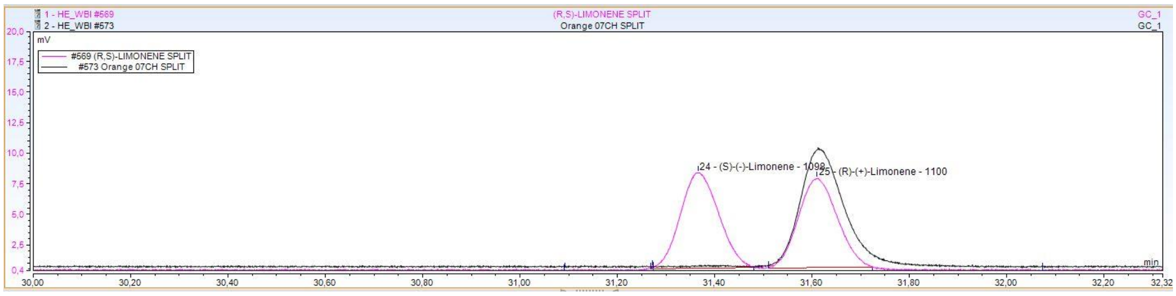
Oils	Major compounds	Area %	Enantiomeric excess (%)
Citrus sinensis	(R)-(+)-limonene	99.5	99.0
	(S)-(-)-limonene	0.5	
Citrus reticulata	(R)-(+)-limonene	99.7	99.4
	(S)-(-)-limonene	0.3	
Citrus maxima	(R)-(+)-limonene	100	100
	(S)-(-)-limonene	0.0	
Citrus aurantifolia	(R)-(+)-limonene	97. 8	94.6
	(S)-(-)-limonene	3.2	
	(S)-(+)-carvone	100	100
	(R)-(+)-carvone	0.0	
	(1S)-(-)-β-pinene	99.7	99.4
	(1R)-(+)-β-pinene	0.3	

Table 4. Chemical composition of aqueous distillates from *C. sinensis*, *C. reticulata*, *C. maxima* and *C. aurantifolia* after 7 days of drying.

RI	Compounds	*C. sinensis*	*C. reticulata*	*C. maxima*	*C. aurantifolia*
853	E-hexan-3ol	0.4 ± **0.1**	2.1 ± **0.0**	0.7 ± **0.0**	-
981	6-methyl-5-hepten-2-one	0.4 ± **0.0**	0.5 ± **0.0**	0.3 ± **0.1**	0.5 ± **0.0**
986	myrcene	-	0.3 ± **0.0**	0.2 ± **0.0**	-
989	6-methyl-5-hepten-2-ol	-	0.1 ± **0.0**	0.1 ± **0.0**	0.1 ± **0.0**
999	n-octanal	-	-	2.7 ± **0.1**	-
1032	limonene	0.1 ± **0.0**	0.1 ± **0.0**	0.1 ± **0.0**	0.1 ± **0.0**
1034	1,8-cineole	0.1 ± **0.0**	0.1 ± **0.0**	0.1 ± **0.0**	0.6 ± **0.0**
1044	benzeneacetaldehyde	0.1 ± **0.0**	0.1 ± **0.0**	0.4 ± **0.0**	0.2 ± **0.0**
1066	n-octanol	0.2 ± **0.0**	0.1 ± **0.0**	4.3 ± **0.0**	-
1071	trans-linalooloxide(furanoid)	0.2 ± **0.1**	0.2 ± **0.0**	21.3 ± **0.2**	0.2± **0.0**
1086	cis-linalooloxide(furanoid)	0.2 ± **0.0**	0.2 ± **0.0**	10.3 ± **0.1**	0.1 ± **0.0**
1096	linalool	34.8 ± **0.5**	17.5 ± **0.2**	9.8 ± **0.2**	3.6 ± **0.3**
1101	n-nonanal	-	-	0.1 ± **0.0**	0.1 ± **0.0**
1112	cis-thujone	0.1 ± **0.0**	0.4 ± **0.0**	0.1 ± **0.0**	0.2 ± **0.0**
1135	trans-p-mentha-2,8-dien-1-ol	1.8 ± **0.1**	4.6 ± **0.3**	0.9 ± **0.1**	0.4 ± **0.0**
1138	terpinen-1-ol	1.6 ± **0.1**	4.0 ± **0.1**	0.6 ± **0.0**	0.3 ± **0.0**
1144	trans-limoneneoxide	0.1 ± **0.0**	0.1 ± **0.0**	0.1 ± **0.0**	0.3 ± **0.0**
1152	citronellal	1.3 ± **0.0**	0.4 ± **0.1**	0.5 ± **0.0**	0.2 ± **0.0**
1157	isoborneol	0.1 ± **0.1**	-	0.1 ± **0.0**	0.3 ± **0.0**
1177	borneol	-	0.1 ± **0.0**	0.1 ± **0.0**	0.4 ± **0.0**
1181	cis-pinocamphone	0.5 ± **0.0**	0.8 ± **0.0**	0.2 ± **0.0**	0.8 ± **0.0**
1183	terpinene-4ol	1.8 ± **0.2**	2.5 ± **0.1**	1.1 ± **0.0**	5.8 ± **0.5**
1189	trans-p-mentha-1-(7)-8-dien-2ol	0.7 ± **0.0**	0.7 ± **0.0**	0.6 ± **0.0**	0.1 ± **0.0**
1197	α-terpineol	9.5 ± **0.1**	10.1 ± **0.0**	13.0 ± **0.1**	14.6 ±**0.1**
1200	cis-dihydrocarvone	3.1 ± **0.1**	0.1 ± **0.0**	tr	0.3 ± **0.0**
1202	n-decanal	2.2 ± **0.0**	6.5 ± **0.0**	0.8 ± **0.0**	0.1 ± **0.0**
1208	trans-piperitol	2.4 ± **0.1**	0.8 ± **0.0**	0.2 ± **0.0**	-
1214	octanolacetate	0.3 ± **0.0**	0.4 ± **0.0**	0.6 ± **0.0**	-

1220	trans-carveol	1.2 ± 1.1	12.2 ± 0.1	1.9 ± 0.0	0.2 ± 0.0
1222	citronellol	8.4 ± 0.9	16.4 ± 0.0	1.4 ± 0.0	-
1225	cis-carveol	1.1 ± 0.0	0.7 ± 0.0	0.4 ± 0.0	-
1230	nerol	0.4 ± 0.0	1.7 ± 0.0	0.2 ± 0.0	15.8 ±0.3
1237	pulegone	0.2 ± 0.0	0.3 ± 0.0	-	-
1242	neral	0.1 ± 0.1	0.3 ± 0.0	5.9 ± 0.1	15.3 ±0.3
1246	carvone	2.2 ± 0.2	4.0 ± 0.1	4.10 ± 0.1	-
1265	geraniol	0.1 ± 0.0	0.1 ± 0.0	6.8 ± 0.4	13.1 ± 0.6
1268	geranial	-	-	-	18.3 ±0.2
1273	nonanoic acide	0.3 ± 0.0	0.1 ± 0.0	1.7 ± 0.0	1.0 ± 0.1
1280	perillaaldehyde	3.8 ± 0.3	-	1.2 ± 0.0	0.6 ± 0.0
1292	limonene-10-ol	9.5 ± 0.1	2.2 ± 0.1	1.1 ± 0.0	0.2 ± 0.1
1301	undecanal	3.2 ± 0.2	2.6 ± 0.2	0.6 ± 0.1	0.1 ± 0.0
1310	perillaalcohol	2.8 ± 0.3	2.3 ± 0.2	0.9 ± 0.0	0.1 ± 0.0
1339	E-patchenol	0.3 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0
1343	citronellylacetate	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
1352	nerylacetate	-	-	tr	0.1 ± 0.0
1394	cis-jasmone	-	0.1 ± 0.0	-	-
1416	cis-α-bergamotene	-	-	-	0.1 ± 0.0
1553	elemol	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	-
1636	γ-eudesmol	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
1655	T-muurolol	tr	0.1 ± 0.0	0.1 ± 0.0	-
1664	β-eudesmol	-	0.1 ± 0.0	0.1 ± 0.0	-
1667	α-eudesmol	-	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
1690	α-bisabolol	-	-	-	0.1

RT= Retention times, RI= retention Index tr= trace (< 0.1%)



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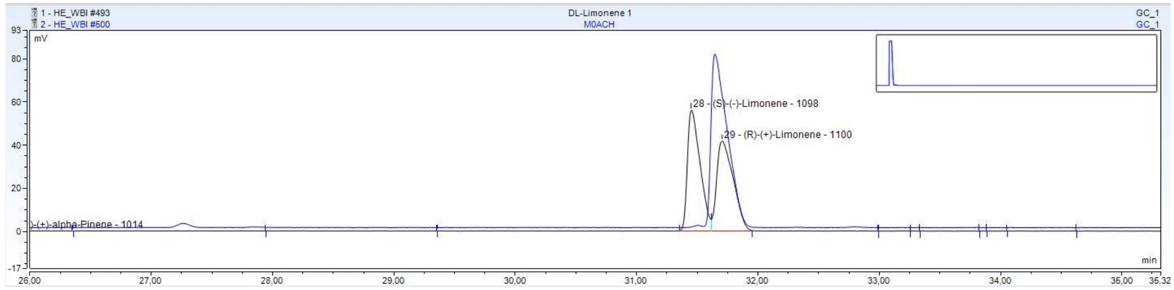

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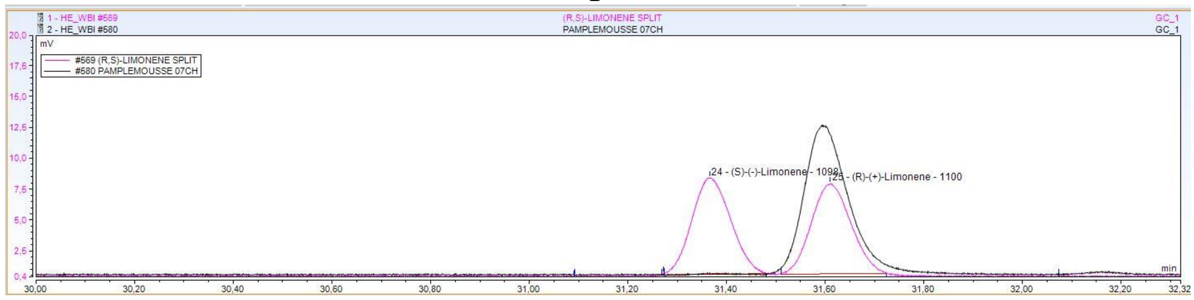

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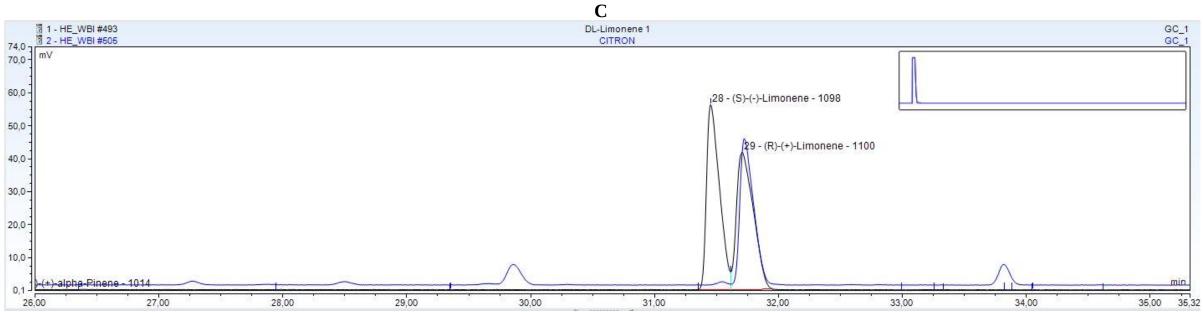
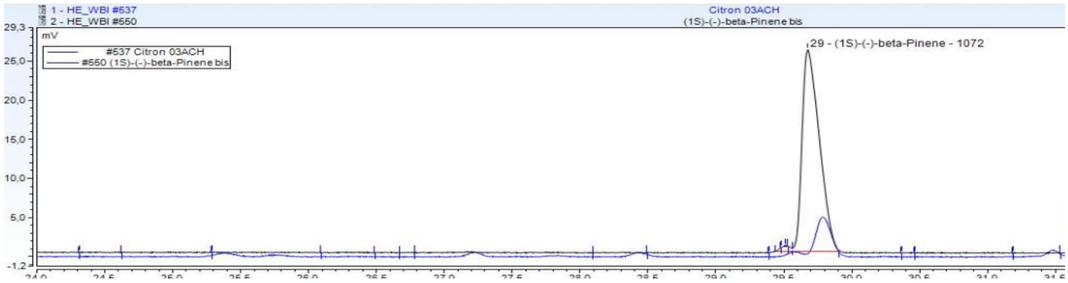


D

Figure 1. Chromatogram of racemic limonene and C. sinensis, *C. reticulata*, *C. maxima* and *C. aurantifolia* essential oils stack
A= racemic limonene and *C. sinensis*, B= racemic limonene and *C. reticulata*, C= racemic limonene and *C. maxima*, D= racemic limonene and *C. aurantifolia*



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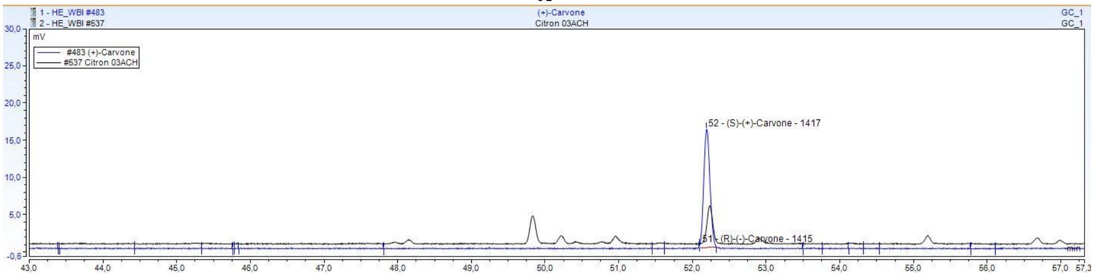

B

Figure 2. Chromatogram of (S)-(-)-β-pinene (S)-(+)-carvone,
and *Citrus aurantifolia* essential oil stack
A= (S)-(-)-β-pinene *C. aurantifolia* and B= (S)-(+)-carvone and *C. aurantifolia*