Comparation Between Chemical Compositions of Some Essential Oils Obtained by Hydrodistillation from Citrus Peels

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In the present study we have investigated the variation of extraction yields and chemical composition of five types of essential oils isolated from orange (Citrus sinesis), lemon (Citrus limon), red grapefruit (Citrus paradisi), white grapefruit (Citrus paradisi) and pomelo (Citrus grandis). The citrus oils were obtained from peels of fruits by hydrodistillation procedure and analyzed using the techniques of Gas Chromatography coupled with Mass Spectrometer (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR). Using GC-MS technique, a total number of 16, 21, 10 and 5 chemical constituents were identified in essential oils extracted from the fruits peel of orange, pomelo, lemon, red grapefruit and white grapefruit respectively. It was found that Limonene was the major component in the all five essential oils (80.26-98.68%). FTIR technique was used for the identification of functional groups of components present in essential oils. FTIR spectra of all five types of essential oils were characterized by the presence of the Limonene vibrational modes at 886 cm^{-1} (out of plane bending of terminal methylene group), 1435-1436 cm^{-1} (C-H asymmetric and symmetric bend) and 1644 cm^{-1} (C=O stretching vibration).

Keywords: citrus fruit, chromatography - mass spectrometry (GC-MS), FTIR spectroscopy

Volatile oils are mixtures of substances such as terpenoids, with characteristic odor and taste. They are called essential oils or aromatic essences. Essential oils are extracted from various aromatic plants generally localized in countries situated in regions having the climate from temperate to warm, like mediterranean and tropical countries, where they represent an important part of the traditional pharmacopoeia. They are liquid, volatile, limpid, rarely colored, soluble in lipids and in organic solvents, having generally lower densities than water.

Essential oils can be synthesized by all plant organs, i.e. buds, flowers, leaves, stems, twigs, seeds, fruits, roots, wood or bark, and are stored in secretory cells, cavities, canals, epidermic cells or glandular trichomes [1]. They are usually obtained by steam or hydro-distillation, techniques first developed in the Middle Ages by Arabs [1]. Known for their antiseptic, i.e. bactericidal, virucidal and fungicidal, and medicinal properties and their fragrance, they are used in embalmment, preservation of foods and as antimicrobial, analgesic, sedative, anti-inflammatory, spasmolytic and locally anesthesic remedies. Up to the present day, these characteristics have not changed and more than that now are known their mechanisms of action, particularly at the antimicrobial level [1, 2].

Genus *Citrus* has approximately 16 species in the family Rutaceae and are mainly cultivated in subtropical regions. The citrus essential oils make up the largest sector of the world production of essential oils [3, 4]. The oils are stored in cavities of fruits, lined with secretory cells that are continually enlarging and differences in the antimicrobial effects of the same type of citrus oil may be attributed to factors such as fruit quality, the stage of growth when is extracted or to the conditions of growing [3, 5]. The components of essential oils are very important as their qualitative and quantitative composition determines their characteristics [3, 6]. Citrus essential oils contain 85-99% volatile and 1-15% non-volatile components [3]. The volatile constituents are a mixture of monoterpenes hydrocarbons, sequiterpene hydrocarbons and their oxygenated compounds including [7]: aldehydes (citral), ketones, acids, alcohols (linalool) and esters [8, 9]. The main volatile compounds presenting in the *citrus* essential oils are pinene (there are two isomers: alpha–pinene and beta-pinene), limonene, citral, myrcene, linalool, á-terpineol (there are five isomers: alpha– terpineol, beta- terpineol, gamma- terpineol, delta- terpineol and 4- terpineol) present in different percentages.

Terpineol is usually a mixture of these isomers having alpha-terpineol as major constituent. The chemical structures of the compounds listed above are shown in figure 1. The major chemical component of the citrus oils is *limonene* and it varies between 68-98% in sweet orange, 45-76% in lemon and 32-45% in bergamot [3, 10]. *Linalool* has concentrations of 0.018, 0.015 and 10.231% (v/v) in sweet orange, lemon and bergamot, respectively [3, 11]. The main component extracted from orange blossom is linalool with a concentration of 40% (w/v) [3, 12]. The aldehyde citral has been shown to be present in lemon, orange and bergamot essential oils often in the form of the stereoisomers neral and geranial [3, 13, 14]. In the present, the essential oils may be extracted now through different methods. These may include: the use of liquid carbon dioxide or microwaves, the low or high pressure distillation employing boiling water or hot steam, the cold pressing, the compression of the peel, the hydrodistillation and the supercritical fluid extraction [1, 15, 16, 18, 19]. Due to the

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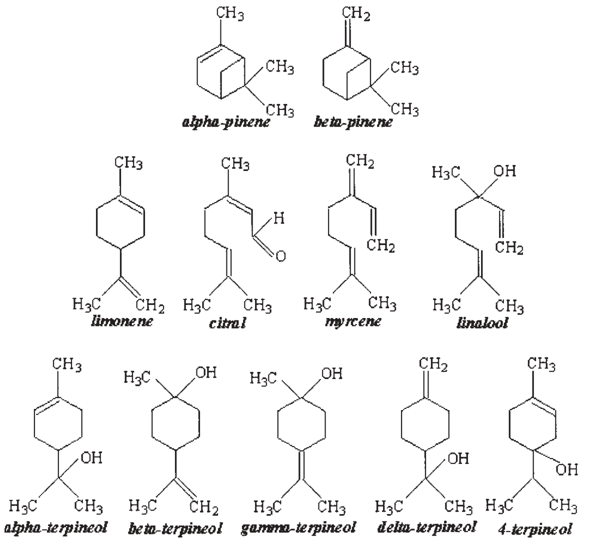

Fig. 1. The chemical structures of the main volatile compounds present in the citrus essential oils

bactericidal and fungicidal properties, their pharmaceutical and food uses are more and more widespread as alternatives to synthetic chemical products in order to maintain the ecological equilibrium.

In this case, the extraction by steam distillation or by expression, for example for *Citrus*, is preferred. For perfume uses, the extraction with lipophilic solvents and sometimes with supercritical carbon dioxide is favoured. Thus, the chemical profile of the essential oil products differs not only in the number of molecules but also in the stereochemical types of molecules extracted, according to the type of extraction, and the type of extraction is chosen according to the purpose of the use. The extraction product can vary in quality, quantity and in composition according to climate, soil composition, plant organ, age and vegetative cycle stage [1, 20, 21]. After extraction, the identification of the compounds in the oil is important and chromatography is the most-used alternative [15, 22, 23].

In the present paper, we reported the results of a study aimed to compare the properties of five essential oils obtained from five *Citrus* species: orange (*Citrus sinesis*), lemon (*Citrus limon),* red and white grapefruit (*Citrus paradisi*) and pomelo (*Citrus grandis).* The citrus oils were obtained from the peels of fruits, by hydrodistillation and analyzed using GC-MS (Gas Chromatography coupled to Mass Spectrometry) and FTIR (Fourier Transform Infrared Spectroscopy).

Experimental part

Materials

In the experiments were used mature citrus fruits purchased from the romanian market. All other used reagents were of analytical grade and were purchased from Sigma-Aldrich, Bucharest.

Fig. 2 The photograph of the Clevenger hydrodistillation installation

The essential oil extraction from the peels of fruits

A known quantity of fresh citrus peels was transferred in a balloon with a round bottom having the capacity of 2 L and over it was added 1 L of water. The balloon was connected to the Clevenger-type apparatus for distillation (fig. 2). Extraction time has varied according to the quantity of citrus, as shown in table 1. The distillate obtained has been dried over anhydrous sodium sulphate and stored in air tight amber-coloured bottle at 4°C until it was analized.

The analysis of the essential oil

The analysis of the volatile components of the obtained essential oil was carried out on a gas chromatograph coupled with a mass spectrometer of GC-MS Agilent 5975C type. The column used for the separation of the sample components was a DB5-MS capillary column (30 m length × 0.32 mm internal diameter, film thickness 0.25μm).

Hydrogen (99.999% high purity) was used as the carrier gas (inlet pressure 82 737 Pa at a flow rate of 1.6667 × 10^{-8} m^3 s^{-1} (1 mL min^{-1}) (splitting ratio 40:1). Oven temperature was initially 40°C and then was raised progresively to 80°C with a rate of 3 ° C/min, to 180° C at a rate of 5° C/min and finally was raised to 280°C at a rate of 8°C/min and mentained there for 20 min. 30μL of each sample, dissolved in 1 mL hexane were injected. The injector temperature was 280 °C. The mass spectrometry conditions were as follows: ionization voltage of 70 eV, emission current of 35 mA, scan rate of 2.8 scan/s, mass range of 10–350 Da and ion source temperature of 200°C. The percentage composition (area percent) of the oils was computed by the normalization method from the GC peak areas, by means of three injections from each sample, without using correction factors. The constituents of the volatile oils were identified by two methods: by comparing their calculated GC retention indices with literature data and by library searching. A mixture of aliphatic hydrocarbons (C8–C24) in hexane was injected as under the above-mentioned temperature programme and to

Table 1
RECEIPES FOR ESSENTIAL OILS EXTRACTION

Fruits	Peels quantities (g)	Ratio between peels quantity and water (w:V)	Extraction time (h)
orange (*Citrus sinesis*)	350	1:2.86	3
lemon (*Citrus limon*)	353.03	1:2.83	4.45
red grapefruit (*Citrus paradisi*)	242.15	1:4.13	5
white grapefruit (*Citrus paradisi*)	235.94	1:4.23	5
pomelo (*Citrus grandis*)	168.58	1:5.93	6

calculate the retention indices the generalized equation of Van den Dool and Kratz (1963) was used.

Kovats retention indices are calculated using the formula:

$$K = 100 \times \left[n + \frac{\log t_{Rx} - \log t_{Rn}}{\log t_{Rn+1} - \log t_{Rn}} \right]$$

where:

- x is the test compound;

- n is the alkane with n carbon atoms into the molecule, whose peak is placed in the left side of the analyzed peak from the chromatogram;

- $n+1$ is the alkane with n carbon atoms into the molecule, whose peak is placed in right side of the analyzed peak from the chromatogram.

Fourier Transform Infrared Spectroscopy (FTIR)

The IR fingerprint of the citrus essential oils was highlighted using a FTIR spectrophotometer – Thermo SCIENTIFIC Nicolet 6700 Model 912A063, by ATR measurement method. The spectra of the samples are the averages of 32 scans, in the range of 4000 – 800 cm^{-1}, with a resolution of 4 cm^{-1}.

Results and discussion

The extraction yields of essential oils from five types of citrus peels are shown in figure 3. Species had significant effect on essential oil yield. Red grapefruit has exhibited the highest extraction yield (2.47%) followed by lemon (2.26%), white grapefruit (2.12%) and orange (1.08%) while pomelo has showed the smallest value of extraction yield (0.53%). The extractions parameters are known because of their strong influence upon the essential oil yield [24-26]. On the other hand, the water supply during ripening was reported to influence considerably the essential oil content with an enhancement of the yield under moderate water shortage conditions [24, 25, 28]. The yields obtained in our study were higher in some cases or comparable in other than those reported in the literature. For example, Soumaya et al. [24] have reported yields varying from 0.46 to 2.70% for citrus varieties from Tunisia and Ahmad et al. [29] between 0.30 to 1.21% for citrus from Pakistan.

Name	Formula	Retention time (min.)				
		lemon	orange	grapefruit		pomelo
				red	white	
α-Fellandrene	$C_{10}H_{16}$	7.023				
Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (±)-	$C_{10}H_{16}$	7.215	7.170	7.250	7.208	7.205
4-Pentenal, 2-ethyl-	$C_7H_{12}O$					8.299
Myrtenol	$C_{10}H_{16}O$				8.891	
L-β-pinene; -α-pinene	$C_{10}H_{16}$	8.940 9.840	8.857 9.798	9.887	9.831	8.913 9.857
2-Norpinene, 3,6,6-trimethyl	$C_{10}H_{16}$			8.933		
Octanal	$C_8H_{16}O$				10.378	
4-Hydroxy-non-2-ynoic acid, ethyl ester	$C_{11}H_{18}O_3$			10.427		
3-Carene; (+)-2-Carene	$C_{10}H_{16}$	14.917 10.819	10.442			
o-Cymol	$C_{10}H_{14}$	11.201				
Limonene	$C_{10}H_{16}$	11.465	11.451	11.655	11.465	11.432
β-trans-Ocimene	$C_{10}H_{16}$	12.486				
trans-á-Terpinyl benzoate	$C_{17}H_{22}O_2$			12.531		
Terpinene, α	$C_{10}H_{16}$	12.832				
Diazirine	CH_2N_2			13.696		
Terpinolen	$C_{10}H_{16}$	14.181				
Bergamol	$C_{12}H_{20}O_2$		14.876			
Bicyclo[6.1.0]nonane, 9-(1-methylethylidene)	$C_{12}H_{20}$					14.895
Bicyclo[2.2.1]heptan-2-one, 4,7,7-trimethyl-, semicarbazone	$C_{11}H_{19}N_3O$		16.282			
p-Mentha-1(7),8(10)-dien-9-ol	$C_{10}H_{16}O$					16.292
4-Terpineol and 1-Terpinen-4-ol (4-Carvomenthenol)	$C_{10}H_{18}O$	18.207		18.247		
Terpineol; à-Terpineol; Terpineo	$C_{10}H_{18}O$	18.795	18.775	18.830		
trans-2-Decenol	$C_{10}H_{20}O$			19.594		
cis-p-Mentha-2,8-dien-1-ol	$C_{10}H_{16}O$		23.360 23.680 25.107			19.901 20.323
cis-Verbenol	$C_{10}H_{16}O$		20.324			
Geranyl bromide	$C_{10}H_{17}Br$	20.341				
Carvol	$C_{10}H_{14}O$					20.760
Verbenol	$C_{10}H_{16}O$	20.783				
Isogeraniol	$C_{10}H_{18}O$					21.302
Ethanol, 2-(3,3-dimethylcyclohexylidene)-, (Z)-	$C_{10}H_{18}O$	21.320				
Citral	$C_{10}H_{16}O$	21.825				
6-Isopropenyl-3-methoxymethoxy-3-methyl-cyclohexene	$C_{12}H_{20}O_2$		22.959			22.962 23.363
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl-	$C_{12}H_{20}O_2$		24.458			
Carveol	$C_{10}H_{16}O$		24.666			
β-Terpinyl acetate	$C_{12}H_{20}O_2$	24.788				
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl	$C_{12}H_{20}O_2$					25.107
Aromadendrene	$C_{15}H_{24}$	26.155				
trans-α-Bergamotene	$C_{15}H_{24}$	26.685				24.667
γ-Muurolene	$C_{15}H_{24}$					27.821
Valencen	$C_{15}H_{24}$		28.143			
α-Himachalene	$C_{15}H_{24}$	28.630				

Table 2
THE RETENTION TIME OF THE VOLATILES, IN VARIOUS ESSENTIAL OILS OBTAINED FROM CITRUS PEEL (MIN.)

Denumire	Formula	Relative concentration (percentage of area, %)				
		lemon	orange	grapefruit		pomelo
				red	white	
α-Fellandrene	$C_{10}H_{16}$	0.208				
Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (±)- (-α-pinene)	$C_{10}H_{16}$	1.027	0.187	0.169	0.267	0.208
4-Pentenal, 2-ethyl-	$C_7H_{12}O$					0.156
Myrtenol	$C_{10}H_{16}O$				0.160	
L-β-pinene; -α-pinene	$C_{10}H_{16}$	5.266 0.760	0.064 0.594	0.604	0.728	0.914 14.545
2-Norpinene, 3,6,6-trimethyl	$C_{10}H_{16}$			0.179		
Octanal	$C_8H_{16}O$				0.160	
4-Hydroxy-non-2-ynoic acid, ethyl ester	$C_{11}H_{18}O_3$			0.072		
3-Carene; (+)-2-Carene	$C_{10}H_{16}$	0.139 0.210	0.137			
o-Cymol	$C_{10}H_{14}$	0.342				
Limonene	$C_{10}H_{16}$	80.229	97.825	98.617	98.686	82.936
β-trans-Ocimene	$C_{10}H_{16}$	0.090				
trans-á-Terpinyl benzoate	$C_{17}H_{22}O_2$			0.064		
Terpinene, α	$C_{10}H_{16}$	5.955				
Diazirine	CH_2N_2			0.077		
Terpinolen	$C_{10}H_{16}$	0.313				
Bergamol	$C_{12}H_{20}O_2$		0.183			
Bicyclo[6.1.0]nonane, 9-(1-methylethylidene)	$C_{12}H_{20}$					0.193
Bicyclo[2.2.1]heptan-2-one, 4,7,7-trimethyl-, semicarbazone	$C_{11}H_{19}N_3O$		0.054			
p-Mentha-1(7),8(10)-dien-9-ol	$C_{10}H_{16}O$					0.067
4-Terpineol and 1-Terpinen-4-ol (4-Carvomenthenol)	$C_{10}H_{18}O$	0.315		0.080		
Terpineol; à-Terpineol; Terpineo	$C_{10}H_{18}O$	0.345	0.045	0.062		
trans-2-Decenol	$C_{10}H_{20}O$			0.076		
cis-p-Mentha-2,8-dien-1-ol	$C_{10}H_{16}O$		0.150 0.047 0.204			0.104 0.135
cis-Verbenol	$C_{10}H_{16}O$		0.032			
Geranyl bromide	$C_{10}H_{17}Br$	0.067				
Carvol	$C_{10}H_{14}O$					0.130
Verbenol	$C_{10}H_{16}O$	0.113				
Isogeraniol	$C_{10}H_{18}O$					0.074
Ethanol, 2-(3,3-dimethylcyclohexylidene)-, (Z)-	$C_{10}H_{18}O$	0.102				
Citral	$C_{10}H_{16}O$	0.119				
6-Isopropenyl-3-methoxymethoxy-3-methyl-cyclohexene	$C_{12}H_{20}O_2$		0.174			0.128 0.133
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl-	$C_{12}H_{20}O_2$		0.064			
Carveol	$C_{10}H_{16}O$		0.167			
β-Terpinyl acetate	$C_{12}H_{20}O_2$	0.107				
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl	$C_{12}H_{20}O_2$					0.117
Aromadendrene	$C_{15}H_{24}$	0.102				
trans-α-Bergamotene	$C_{15}H_{24}$	0.104				0.089
γ-Muurolene	$C_{15}H_{24}$					0.071
Valencen	$C_{15}H_{24}$		0.073			
α-Himachalene	$C_{15}H_{24}$	0.140				

Table 3
THE RELATIVE CONCENTRATION OF THE VOLATILES, IN VARIOUS ESSENTIAL OILS OBTAINED FROM CITRUS PEEL (%)

The results of the chromatographic analysis (tables 2-4) show that a total of 41 compounds were identified in all five essential oils types as follows: 21 in the lemon, 16 in the orange and pomelo, 10 in the red grapefruit and 5 in the white grapefruit. The list of the identified compounds and their retention time, relative concentration and Kovats retention indices (K) for all essential oils obtained are presented in tables 2-4. From the analysis and comparison of the essential oils from orange, lemon, red grapefruit, white grapefruit and pomelo, it was found that principal compounds in these citric essential oils are the terpenes, such as α-pinene, β-pinene, α-terpinene, 1-terpinen-4-ol, terpinolen, o-cymol, 3-carene; (+)-2-carene, α-terpineol and d-limonene. The last terpene was the most abundant in all four types of citric fruits, having a concentration over 98% in red and white grapefruit, 97% in orange, 82% in pomelo and 80% in lemon. Also, it has been found that each type of citrus fruit has particular components present in minor quantities.

From the study of these citrus chromatograms is seen that there is a common compound namely limonene which showed, with very small differences, the same retention times and the same Kovacs indices (in accordance with tables 2 and 4). Also, there is a similarity between orange and pomelo chromatograms through the existence of some common compounds (L-β-pinen, cis-p-menta-2,8-dien-1-ol and Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (±)) and between red grapefruit and white grapefruit chromatograms through the existence of the α- pinene in addition to the compounds already mentioned as being common to all these citrus. The terpinneol is present in lemon and orange at the RT of 18.795 and 18.775 respectively, having the same Kovats index of 1.588×10^3. For lemon, a large percentage of area, about of 5.955%, is the α-terpinene.

The composition of the essential oil of citric fruits is generally of 90% terpenes, 5% oxygenated compounds and less than 1% of non-volatile compounds such as waxes and pigments [15, 30]. From the analysis and comparison of the essential oils of five citrus species it was found that most of the compounds are monoterpenes hydrocarbons and oxygenated monoterpenes, as is showed in table 5. Hydrocarbon monoterpenes account 95.5–99.7% from the identified constituents, while oxygenated monoterpenes account about 0.160% in white grapefruit and about 0.99% in orange. From all the monoterpenes hydrocarbons, the limonene was the most abundant compound in all four types citric fruits, as is showed in figure 4.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy is one of the most widely employed techniques for f functional groups identification. Figures 5 to 7 and table 6 showed the infrared spectra and the characteristic bands observed in all five citrus oils in the range of 4000-800 cm^{-1}. The spectrum presents characteristic bands at 2965 and 2917 cm^{-1}

Denumire	Formula	Kovats retention indices, K (x10^3)				
		lemon	orange	grapefruit red	grapefruit white	pomelo
α-Fellandrene	$C_{10}H_{16}$	0.649				
Bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl-, (±)-	$C_{10}H_{16}$	0.655	0.654	0.656	0.655	0.654
4-Pentenal, 2-ethyl-	$C_7H_{12}O$					0.683
Myrtenol	$C_{10}H_{16}O$				0.697	
L-β-pinene; -α-pinene	$C_{10}H_{16}$	0.698 0.717	0.696 0.716	0.781	0.717	0.697 0.717
2-Norpinene, 3,6,6-trimethyl	$C_{10}H_{16}$			0.697		
Octanal	$C_8H_{16}O$				1.035	
4-Hydroxy-non-2-ynoic acid, ethyl ester	$C_{11}H_{18}O_3$			1.037		
3-Carene; (+)-2-Carene	$C_{10}H_{16}$	1.133 1.047	1.037			
o-Cymol	$C_{10}H_{14}$	1.056				
Limonene	$C_{10}H_{16}$	1.062	1.062	1.067	1.062	1.061
β-trans-Ocimene	$C_{10}H_{16}$	1.085				
trans-á-Terpinyl benzoate	$C_{17}H_{22}O_2$			1.086		
Terpinene, α	$C_{10}H_{16}$	1.092				
Diazirine	CH_2N_2			1.011		
Terpinolen	$C_{10}H_{16}$	1.119				
Bergamol	$C_{12}H_{20}O_2$		1.132			
Bicyclo[6.1.0]nonane, 9-(1-methylethylidene)	$C_{12}H_{20}$					1.133
Bicyclo[2.2.1]heptan-2-one, 4,7,7-trimethyl-, semicarbazone	$C_{11}H_{19}N_3O$		1.532			
p-Mentha-1(7),8(10)-dien-9-ol	$C_{10}H_{16}O$					1.532
4-Terpineol and 1-Terpinen-4-ol (4-Carvomenthenol)	$C_{10}H_{18}O$	1.576		1.577		
Terpineol; à-Terpineol; Terpineo	$C_{10}H_{18}O$	1.588	1.588	1.589		
trans-2-Decenol	$C_{10}H_{20}O$			1.944		
cis-p-Mentha-2,8-dien-1-ol	$C_{10}H_{16}O$		2.302 2.313 2.361			1.954 1.967
cis-Verbenol	$C_{10}H_{16}O$		1.967			
Geranyl bromide	$C_{10}H_{17}Br$	1.967				
Carvol	$C_{10}H_{14}O$					1.980
Verbenol	$C_{10}H_{16}O$	1.980				
Isogeraniol	$C_{10}H_{18}O$					1.995
Ethanol, 2-(3,3-dimethylcyclohexylidene)-, (Z)-	$C_{10}H_{18}O$	1.996				
Citral	$C_{10}H_{16}O$	2.010				
6-Isopropenyl-3-methoxymethoxy-3-methyl-cyclohexene	$C_{12}H_{20}O_2$		2.287			2.288 2.302
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl-	$C_{12}H_{20}O_2$		2.340			
Carveol	$C_{10}H_{16}O$		2.346			
β-Terpinyl acetate	$C_{12}H_{20}O_2$	2.351				
Cyclohexene, 4-isopropenyl-1-methoxymethoxymethyl	$C_{12}H_{20}O_2$					2.361
Aromadendrene	$C_{15}H_{24}$	2.592				
trans-α-Bergamotene	$C_{15}H_{24}$	2.613				2.347
γ-Muurolene	$C_{15}H_{24}$					2.655
Valencen	$C_{15}H_{24}$		2.667			
α-Himachalene	$C_{15}H_{24}$	2.852				

Table 4
THE KOVATS RETENTION INDICES (K) OF THE VOLATILES, IN VARIOUS ESSENTIAL OILS OBTAINED FROM CITRUS PEEL

Chemical classes	orange	lemon	red grapefruit	white grapefruit	pomelo
Monoterpenes hydrcarbons	98.807	95.539	99.569	99.681	98.603
Oxygenated monoterpenes	0.645	0.994	0.218	0.160	0.510

Table 5
RELATIVE VOLATILE OIL COMPOSITION (%)

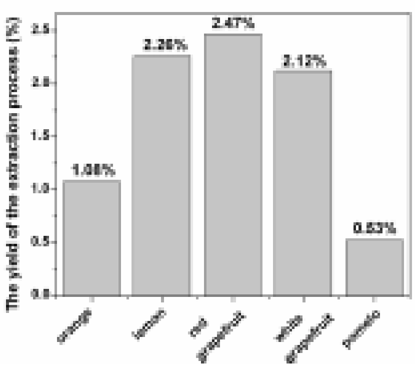

Fig. 3 The yield of the extraction process by hydrodistillation method (%)

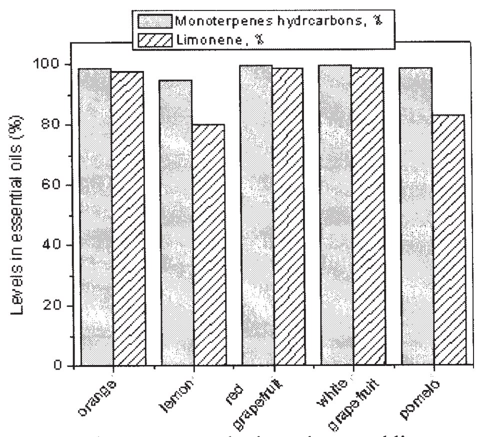

Fig. 4 The levels of monoterpene hydrocarbons and limonene, in citrus oil

corresponding to CH_2 asymmetric and symmetric stretching vibrations. The signals which appeared between 2920 and 2850 cm^{-1} are caused by the asymmetrical and symmetrical stretching vibrations of C–H groups. Carbonyl compounds are often the strongest band in the spectrum that lies between the 1825 and 1575 cm^{-1}, its exact position being dependent on its immediate substituent. For a double-bonded functionality, conjugation plays an important role in the observed carbonyl frequency. This includes the connection to an aromatic ring or the conjugation to a C=C or another C=O [30]. The band which

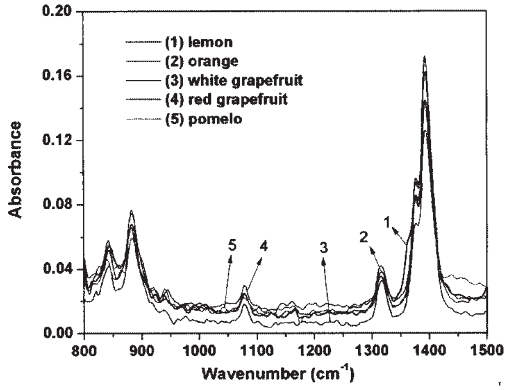

Fig. 5. FTIR spectra for all five citrus oils in the range of 800-1500 cm^{-1}

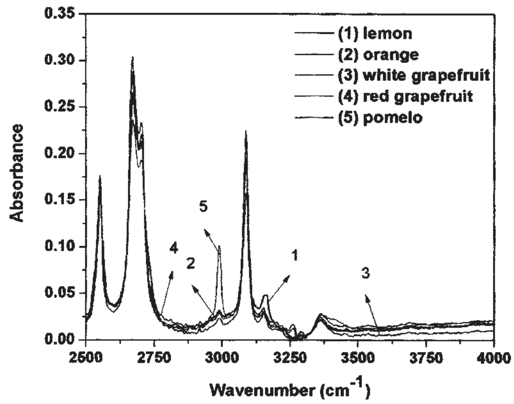

Fig. 7. FTIR spectra for all five citrus oils in the range of 2500-4000 cm^{-1}

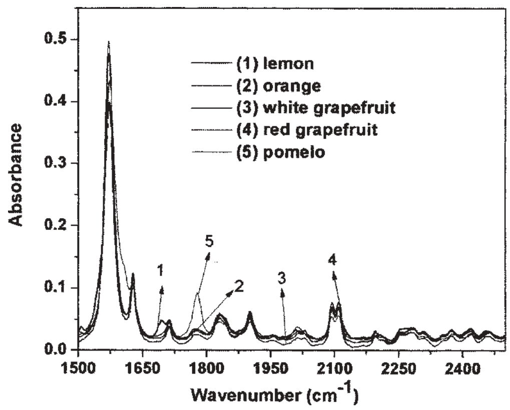

Fig. 6. FTIR spectra for all five citrus oils in the range of 1500-2500 cm^{-1}

Table 6

THE INFRARED CHARACTERISCTIC BANDS, OBSERVED IN CITRUS OILS

Band position (cm^{-1})	Class of Compounds
2917 and 2965	CH_2 asymmetric and symmetric stretching vibrations
2834	C–H stretching vibrations
1644	C=O stretching vibration
1435-1436	C-H asymmetric and symmetric bend
1376	C-H asymmetric and symmetric bend and OH bend (phenol or tertiary alcohol)
1147	C-O stretch (tertiary alcohol); C-O-C stretch (alkyl-substituted ether,
1051	C-O stretch (primary alcohol); C-O-C stretch (alkyl-substituted ether)
950-1225	$-CH_2-$ (methylene – cyclohexane ring vibrations), C-H in-plane bend (aromatic)
885-886	C-H out-of-plane bend (vinylidene), aromatic ring (aryl) group

appeared at 1644 cm^{-1} was attributed to the stretching vibration of C=O [31]. The strong methylene/methyl band which appeared at 1435-1436 cm^{-1}, the weak methyl band which appeared at 13175-1376 cm^{-1} and the methylene rocking vibration band which appeared at 758-759 cm^{-1} are indicative of a long-chain linear aliphatic structure [31, 32]. Bands which appeared at 1147 cm^{-1} and 1051 cm^{-1} were ascribed to the stretching vibrations of C-O-C and O-H, respectively. The absorption bands between 950-1225 cm^{-1} indicate the methylene- cyclohexane ring vibrations ($-CH_2-$) and aromatic C-H in-plane bend. Finally, the absorption which occurred at about 886 cm^{-1} was evidenced for the limonene presence. The FTIR analysis of all five kinds of essential oils has made us to notice a similitude of absorption bands and only small differences between their intensities.

Conclusions

Five types of essential oils isolated from orange (*Citrus sinesis*), lemon (*Citrus limon*), red grapefruit (*Citrus paradisi*), white grapefruit (*Citrus paradisi*) and pomelo (*Citrus grandis*) by hydrodistillation were obtained. The variations of extraction yields and chemical composition were investigated using the techniques of Gas Chromatography coupled with Mass Spectrometer (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR). From the analysis of the compositions of the studied essential oils, it was found that the principal compound in these citric essential oils is limonene and other terpenes and derivatives, such as: α-pinene, β-pinene, α-terpinene, 1-terpinen-4-ol, terpinolen, o-cymol, 3-carene; 2-carene, α-terpineol, can be found in significant amounts. Limonene was found in a concentration over 98% in red and white grapefruit, 97% in orange, 82% in pomelo and 80% in lemon. Also, it has been found that each type of citrus fruit has particular components present in minor quantities (area percents). The results were confirmed by FTIR technique by which the vibrational modes of limonene were identified at 886 cm^{-1} (out of plane bending of terminal methylene group), 1435-1436 cm^{-1} (C-H asymmetric and symmetric bend) and 1644 cm^{-1} (C=O stretching vibration).

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