Journal of Chromatography
Separation Techniques

Wu et al., J Chromatogr Sep Tech 2014, 6:1
DOI: 10.4172/2157-7064.1000261

Research Article Open Access

Gas Chromatography-Mass Spectrometry Analysis of Photosensitive Characteristics in Citrus and Herb Essential Oils

Pei-Shan Wu[1], Yu-Ting Kuo[1], Shen-Ming Chen[2]*, Ying Li[2] and Bih-Show Lou[1]*

[1]Chemistry Division, Center for General Education, Chang Gung University, 259 Wen-Hwa 1st Road, Kwei-Shan, Tao-Yuan 333, Taiwan, ROC
[2]Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106,Taiwan, ROC

Abstract

Essential oils (EOs) are commonly used in aromatherapy and offer a number of health benefits. However, the photosensitivity of citrus EO family limits their applications. It is important to characterize the compositional changes of EOs upon possible factors affecting their stability, such as light and water content. In this study, we used gas chromatography equipped with mass spectrometry detector to investigate the constituents of commercial citrus EOs (lemon, orange) and herb EOs (clary sage, lavender). The result indicated that limonene was the most abundant compound in citrus EOs and followed by β-pinene or β-myrcene. Linalyl acetate and β-linalool were the major constituents in herb EOs. It is surprised to find that almost no change in chemical composition under sunlight exposure for 2hr. In contrast, the amount of terpene hydrocarbons decreased greatly in citrus OEs with H_2O addition and under sunlight exposure, which might be converted to oxidative compounds, such as carveol, *ρ*-cymene and limonene oxide. However, herb EOs was much less photosensitive, which are more potential to become a stable material for daily used products application.

Keywords: Essential oil; Citrus; Herb; Photosensitive; Gas Chromatography-Mass Spectrometry (GC-MS)

Introduction

Essential oils (EOs) are complex mixture and highly concentrated hydrophobic liquid containing volatile plant secondary metabolites belong to terpenoids and aromatic groups. They are usually extracted from various parts of plants (flower, leaf or fruit) by different methods such as steam/water distillation, solvent extraction or cold expression, etc. The natural source and pleasant flavor characters make EOs widely used in the medicine, cosmetic, household products and food industry. EOs was also reported to contain many bioactive compounds, such as terpenoids, alkaloids, flavonoids and carotones. These components make EOs are extensively represent a green alternative in the pharmaceutical, neutritionanl argticultural field due to their antimicrobial, antiviral, insecticidal, antioxidant, antiinflamatory and stress-repellent properities [1-3].

Citrus fruits are the most common subtropical crops in the world, such as lemon and orange. We usually eat citrus fruits' sweet and juicy fleshes, though recently, people have started to pay attention to reusing of fruits peels. The main reasons are that citrus peels are easily obtained and naturally high in pectin, their antioxidant activity, and relative benefits from vitamin C and flavonoids [1]. Furthermore, when they are made into EOs, the main product, limonene, has been proved to inhibit cancer cells initiation, promotion and progression [4]. Another widespread EOs is extracted from spices and their constituents mainly depend on the plant species such as sage and lavender. Sage is a small evergreen shrub with grayish leaves, blue to purplish flowers and has therapeutic properties of antiinflammatory, antibacterial, antioxidant and stimulant for medicinal purposes [5]. Lavender belongs to mint family and used for centruies as an herbal remedy due to its' sweet overtones. It is also believed to be benefit for stress, exhaustion, headaches, depression and digestion problems, and even have application of food preservation [2].

Gas chromatography equipped with mass spectrometry (GC-MS) as detector is a widely used platform for analyzing volatile complex compounds [6]. A tool with good selectivity and high sensitivity is necessary for natural EOs because they are usually composed of many different ingredients or flavonoids. GC-MS can offer a quick qualitative function based on the integrity of a compound database (ex: NIST), and the quantification can be more precise when isotope standards and selected ion mode (SIM) are used together.

Meanwhile, due to the various components in oil extracts, some of them are light-, oxygen-, temperature- or moisture-sensitive. Most of commercial EOs is highly concentrated and need to be diluted before used to avoid skin or respiratory damage [7]. Proper storage and safe usage become an important issue for EOs to ensure the effectiveness and quality for future development in the medicinal field [8,9]. The effect of sunlight exposure on the hydrolysis or oxidation reaction in the citrus and herb EOs is not revealed yet. In this work, a photosensitivity experiment was designed to understand the composition changes when EOs coexisted with water under sunlight treatment.

Materials and Methods

Chemicals and reagents

Alkane standard solution (contains C8-C20, ~40 mg/L each, in hexane) and LC/MS-grade methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA).

***Corresponding author:** Bih-Show Lou, Chemistry Division, Center for General Education, Chang Gung University, 259 Wen-Hwa 1st Road, Kwei-Shan, Tao-Yuan 333, Taiwan, ROC, Tel: +886 3 2118800 ext 5018; Fax: +886 3 2118700; E-mail: blou@mail.cgu.edu.tw

Shen-Ming Chen, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106,Taiwan, ROC, Tel: +886 2270 17147; fax: +886 2270 25238; E-mail: smchen78@ms15.hinet.net

Received October 26, 2014; **Accepted** December 23, 2014; **Published** December 29, 2014

Citation: Wu PS, Kuo YT, Chen SM, Li Y, Lou BS (2014) Gas Chromatography-Mass Spectrometry Analysis of Photosensitive Characteristics in Citrus and Herb Essential Oils. J Chromatogr Sep Tech 6: 261. doi:10.4172/2157-7064.1000261

EO samples

Commercial citrus and herb essential oils were provided from an aroma products company (EASECOX, Germany), and the original material plant source was Italy. Before experiment, EOs were kept in dry environment and prevented from light at room temperature. All samples were diluted 1:15 (v/v) in methanol prior to GC-MS analysis.

Photosensitive experiment

EOs were added H_2O (group C) with the ratio 5:1 (EO: H_2O, v/v) and with a non-H_2O added sample (group B) as positive control. The sample vials were sealed well and irradiated with UVA (320-400nm) and UVB (290-320nm) of 100 mW/cm^2 from sunlamps (Xe lamp, 1.5AM) for 2 hours. The irradiated samples and stock without treatment (group A) were collected and prevented from light before GC-MS analysis.

GC-MS analysis

GC-MS analysis was performed on Agilent Technology (Little Falls, California, USA) 6890 series gas chromatography (GC) system, equipped with 5973 mass spectrometry (MS) detector and a 7683 series auto-injector was used. Compounds were separated on Rtx®-Wax capillary column (30 m × 0.25 mm, film thickness 0.25 μm; RESTEK, Pennsylvania, USA). Helium (5N5 grade) was used as carrier gas, with a flow rate of 0.8 mL/min, and the split ratio was 60:1. Sample injection volume was 1 μl and the injector temperature was 230°C. The column oven temperature was held at 70°C for 2 min, and then programmed to 130°C at 30°C/min and change the gradient to 230°C with 10°C/min. Finally, held at 230°C for 6 min and the total run time was 20 min. An electron ionization (EI) system with ionization energy 70 eV was used for detection. The ion source temperature was set at 230°C, the interface temperature was 250°C, detector voltage was 2 kV. The mass spectrum was acquired in scan mode at a scan rate 0.98 scan/sec within a mass range of 20-800 amu. The measurement was performed in duplicate for each sample with solvent delay for 2 min.

Data process and compound identification

The data was processed by software provided by Agilent Technology (MSD ChemStation D.03.00.611). The compounds identification were using their MS data compared to the on-site NIST98 mass spectral library and on-line NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/), and the retention indices (RIs) relative to C8-C20 *n*-alkanes obtained on a nonpolar Rtx®-Wax column.

Results and Discussion

A high throughput CG-MS methodology for essential oil analysis

In this study, we demonstrated that GC-MS is a quick and reliable platform for EOs analysis in both qualification and quantification. Natural plant essential oils were prepared simply by dilution with methanol and a short separation gradient of GC coupled with auto-sampler made this platform more efficient. MS detector provided high sensitivity and good selectivity in samples analysis. In addition, rich GC-MS database, such as NIST library, coupled with retention index supplied a credible method to identify compounds in a complex mixture [10].

Chemical composition of citrus and herb essential oils by GC-MS analysis

GC-MS chromatography for lemon and orange EOs prior to treatment are shown GC-MS chromatograms of lemon and orange EOs prior to treatment as control are shown in Figure 1 I-A and II-A, respectively. The most predominant compound of lemon OE was the limonene shown at the peak 6 of Figure 1 I-A accounting for the % area of 57.71, which is consistent with other reports [8,13-17], and followed compounds were β-pinene and 3-carene at the peak 3 with 13.57% and the peak 7 with 10.54%, respectively. Table 1 summarized peak number, retention time (RI), compound name, formula and % area for all the identified compounds of lemon OE found in this study. Similarly, limonene at the peak 4 of Figure 1 II-A was the highest contained compound with % area of 86.05 shown in Table 2 for orange EO, however, the next two abundance compounds were β-myrcene and L-carvone at the peak 3 with 2.22% and the peak 22 with 1.12 %, respectively. These compounds are common monoterpenoid hydrocarbons found in EO through the addition, cabocation and cyclication reaction of gernyl pyrophosphate under specitfic enzymic control in plants. The structures of major components for lemon and orange EOs were showed in Figure 3. Limonene is a single-cyclic terpenenoid with a strong citrus odor and bitter taste. α-pinene, β-pinene and 3-carene are bi-cyclic terpenenoids found major constituents of turpentine in nature. β-myrcene is a very widespread monoterpenoid in nature, especially in herbs and spices. Carvone is a common monoterpenoid ketone found in EOs and its enantiomers provides the characteristic odor of spearmint [11]. According to both Table 1 and 2, the contents of other type terpenoids, such as sesquiterpenoids (bergamotene and bisabolene), alcohols (β-linalool and α-terpieol), aldehydes (cis- and trans-citral), ketones (sulcatone), acids (octanoic acid) and oxides (cis- and trans-limonene oxide) were occupied low concentration in original citrus EOs before treatment (total amount is lass than % area of 10).

In herb EOs, the chromatograms of untreated clary sage and lavender EOs as control were showed in Figure 2 III-A and IV-A, respectively. Linalyl acetate and β-linalool were the two predominant components in both clary sage and lavender EOs with similar concentration ratio. In general, linalyl acetate found in many flower and spice plants is the acetate ester of linalool, and they both often exist as in accompany and possess antifungal activity [12]. Linalyl acetate was almost taken up half content in both clary sage and lavender shown at the peak 14 of Figure 2 III-A with % area of 46.43 and the peak 16 of Figure 2 IV-A with 33.81%, respectively. On the other hand, β-linalool was found at the peak 13 of Figure 2 III-A with 22.68% and the peak 15 of Figure 2 IV-A with 24.89% for clay sage and lavender, respectively. α-terpineol and 4-terpeneol are the two of four isomers of terpineol, which is a common monoterpene alcohol in herb EOs. Trans-geranyl acetate, a monoterpene with a pleasant floral aroma, was the third highest component in calry sage (peak 24, 4.80%). A bi-cyclic sesquiterpene and FDA approved food additive [9], caryophyllene was the fourth abundant compound (peak 18, 5.83%) in lavender EO. As compared with citrus EOs, the amounts of hydrocarbon terpenoids in clary sage and lavender existed relative low, such as β-myrcene, β-ocimene and germacrene D. Detail chemical compositions and their relative intensities were listed in Table 3 and 4 for clary sage and lavender, respectively. Grand viriability dependends on several factors including plant species, season, location, the part for extraction and the preparation method, and could result in different chemical constituents of citrus and herb Eos found in this study from other literatures [13-17].

Photosensitive investigation

Compared with the chromatograms between A and B of Figures 1 and 2 for both citrus and herb EOs, we found surprisedly that they were almost identical to each other and revealed no effect under sunlight

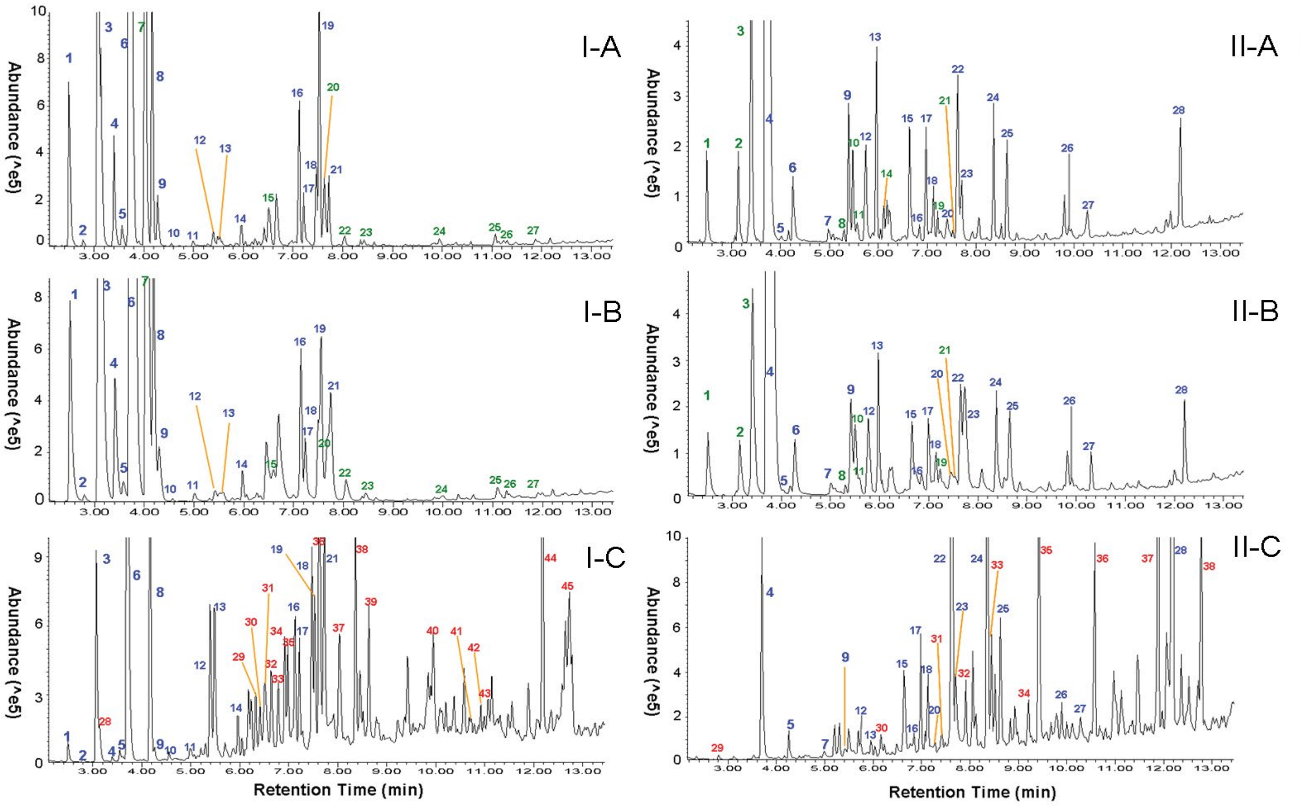

Figure 1: GC-MS total ion chromatography (TIC) of citrus essential oils in different experimental condition. I: lemon, II: orange. (A) control sample, stock storage well in the dark and dry environment, (B) after 2hr sunlight treatment sample, (C) H2O added (5:1, EO: H2O) and exposed to sunlight 2hr sample. Blue number: original identified compound before treatment; red number: new appeared compound after treatment; green number: disappeared compound after treatment.

exposure for 2hr. On the other way, a great effect was observed with H_2O addition and under sunlight exposure for 2hr in I-C and II-C of Figure 1 for both citrus EOs. The major component, limonene, decreased dramatically from 57.71% and 86.05% to 19.02% and 4.55% for lemon and orange EO, respectively, and considered that it was conversed into alcohols, aldehyde, ketones and oxides via oxidation, hydration and isomerisation. In lemon oil, many alcohols, ketone oxide compounds were appeared or increased significantly, such as caveol (0% to 5.85%), carvone (0% to 6.23%) and limonene oxie (0.38% to 6.07%). These compounds were the products from limonene hydration and oxidation under water-light combined action and a brief mechanism was proposed in Figure 4A. Limonene-1,2-diol (0% to 7.19%) was limonene involved in further epoxidation and the epoxides had been hydrated to limonene-diol [18]. α-, β-pinene and 3-carene at the peaks 1, 3 and 7 of Figure 1 I-C decreased obviously from 2.27% to 0.36%, 13.57% to 3.36% and 10.54% to 0%, respectively. The oxidative reactions of α-, β-pinene were proposed in Figure 4B [19]. The possible mechanism presented that α-, β-pinene were converted to their hydroperoxides with migration of the double bond under light exposion via myrtenol (peak 37, 0% to 2.44%) and trans-pinocarveol (peak 34, 0% to 1.43%) and finally produced terminal hydroperoxides, myrtenal (peak 33, 0% to 1.10%). The oxidation of 3-carene can be initiated by ozone and OH radical under humidity atmosphere and the ozonide or hydroxyl radical go further to generate different products [20]. The remainder generated monoterpenoid alcohols after water-light treatment, such as α-terpieol, cis- and trans-mentha-2,8-dien-1-ol were also the limonene hydrated and oxided products [21,22]. The aromatic monoterpene *p*-cymene at peak 8 of Figure 1 I-C increased from 2.92% to 6.66% after water and sunlight treatment, which has been reported for identification of aged EOs as increase during storage [7,19]. Geranic acid, cis- and trans-geranyl acetate were oxidized from citral shown in Figure 4C [7] and increased in a considerably range from 0% to 3.5 ~ 4%. Citral (mixture of neral and geranial at peaks 16 and 19) is a strong lemon odor aldehyde and is often used as index to estimate the quality of lemon EOs. For orange oil, most compositional changes were similar to lemon oil. An enormously limonene content dropped from 86.05% to 4.55% and the raise of carveol (cis- and trans-form, 1.28% to 12.95%), carvone (1.12% to 17.30%), limonene oxide (cis- and trans-form, 0% to 5.14%) and the major product limonen-1,2-diol (0.68% to 22.31%). Unlike lemon oil, orange oil had fewer hydrocarbon terpenoids, and the limonene hydration and oxidation become the main reaction in total compositional change. There are still aldehyde and ketone of monoterpenoid were observed increased at the peaks 38 and 37 from 0% to 3.36% and 0% to 7.16%, respectively, which might be resulted in the oxidation of limonene and β-linalool under water-light environment [9,23]. The CC profile provides a simple way to understand the compositional change between pre-and post-treatment. According to the color change, it is easier to figure out that the constituent changes of EO from monoterpenes to alcohols and ketones after water-light treatment were quite different between lemon and orange EOs shown in Figure 5 I and II, respectively.

In proportion of herb EOs, there were much less compositional changes in photosensitive experiment and suggested that major compound linalyl acetate was quite stable and not easily hydrated and oxidized under sunlight coupled water treatment. The evidence

Citation: Wu PS, Kuo YT, Chen SM, Li Y, Lou BS (2014) Gas Chromatography-Mass Spectrometry Analysis of Photosensitive Characteristics in Citrus and Herb Essential Oils. J Chromatogr Sep Tech 6: 261. doi:10.4172/2157-7064.1000261

Peak N°. a	RI b	Compounds	Formula	% Area c		
				A	B	C
Hydrocarbons						
1	1031	α-Pinene	$C_{10}H_{16}$	2.27	2.15	0.36
2	1078	Camphene	$C_{10}H_{16}$	0.07	0.05	0.07
3	1121	β-Pinene	$C_{10}H_{16}$	13.57	13.04	3.36
4	1166	β-Myrcene	$C_{10}H_{16}$	1.40	1.24	0.08
5	1189	*p*-Menthane	$C_{10}H_{20}$	0.28	0.13	0.23
6	1213	Limonene	$C_{10}H_{16}$	57.71	61.22	19.02
7	1255	3-Carene	$C_{10}H_{16}$	10.54	10.09	NA
8	1278	*p*-Cymene	$C_{10}H_{14}$	2.92	2.26	6.66
9	1292	Terpinolene	$C_{10}H_{16}$	0.59	0.59	0.27
15	1599	α-Bergamotene	$C_{15}H_{24}$	0.72	0.42	NA
20	1746	α-Bisabolene	$C_{15}H_{24}$	0.81	0.31	NA
22	1786	β-Bisabolene	$C_{15}H_{24}$	0.16	0.29	NA
28	1146	β-Terpinene	$C_{10}H_{16}$	NA	NA	0.66
31	1607	β-Bergamotene	$C_{15}H_{24}$	NA	NA	1.54
Oxides						
12	1459	cis-Limonene oxide	$C_{10}H_{16}O$	0.18	0.10	2.84
13	1471	trans-Limonene oxide	$C_{10}H_{16}O$	0.20	0.18	3.23
24	2003	cis-Caryophyllene oxide	$C_{15}H_{24}O$	0.13	0.07	NA
40	2007	trans-Caryophyllene oxide	$C_{15}H_{24}O$	NA	NA	2.06
Alcohols						
14	1538	β-Linalool	$C_{10}H_{18}O$	0.23	0.21	0.64
17	1698	α-Terpieol	$C_{10}H_{18}O$	0.52	0.43	1.39
23	1839	trans-Geraniol	$C_{10}H_{18}O$	0.07	0.08	NA
25	2182	(-)-Spathulenol	$C_{15}H_{24}O$	0.18	0.15	NA
27	2284	α-Bisabolol	$C_{15}H_{26}O$	0.11	0.06	NA
32	1624	cis-Mentha-2,8-dien-1-ol	$C_{10}H_{16}O$	NA	NA	1.32
34	1657	trans-Pinocarveol	$C_{10}H_{16}O$	NA	NA	1.43
35	1665	trans-Mentha-2,8-dien-1-ol	$C_{10}H_{16}O$	NA	NA	1.38
37	1788	Myrtenol	$C_{10}H_{16}O$	NA	NA	2.44
38	1832	trans-Carveol	$C_{10}H_{16}O$	NA	NA	3.81
39	1863	cis-Carveol	$C_{10}H_{16}O$	NA	NA	2.04
41	2140	Cuminol	$C_{10}H_{14}O$	NA	NA	0.26
42	2166	trans-p-Mentha-2,8-dienol	$C_{10}H_{16}O$	NA	NA	0.27
43	2182	(+)-Spathulenol	$C_{15}H_{24}O$	NA	NA	0.68
44	2333	Limonen-1,2-diol	$C_{10}H_{18}O_2$	NA	NA	7.19
Aldehydes						
11	1398	Nonanal	$C_9H_{18}O$	0.08	0.11	0.24
16	1687	cis-Citral (Neral)	$C_{10}H_{16}O$	1.72	1.20	1.56
19	1735	trans-Citral (Gernial)	$C_{10}H_{16}O$	2.91	1.64	1.94
33	1641	Myrtenal	$C_{10}H_{14}O$	NA	NA	1.10
Ketones						
10	1339	Sulcatone	$C_8H_{14}O$	0.03	0.02	0.12
29	1583	Camphenilone	$C_9H_{14}O$	NA	NA	0.94
30	1595	(+)-Nopinone	$C_9H_{14}O$	NA	NA	0.57
36	1747	Carvone	$C_{10}H_{14}O$	NA	NA	6.23
Acids						
26	2218	Nonanoic acid	$C_9H_{18}O_2$	0.05	0.06	NA
45	2412	Geranic acid	$C_{10}H_{16}O_2$	NA	NA	3.91
Esters						
18	1726	cis-Geranyl acetate	$C_{12}H_{20}O_2$	0.64	0.69	3.71
21	1756	trans-Geranyl acetate	$C_{12}H_{20}O_2$	0.72	0.98	3.40
Unknowns				1.20	2.25	13.09

[a] Peak number labeled on TIC
[b] Retention index relative to C8-C20 *n*-alkanes on Rtx®-Wax column
[c] A: control sample; B: 2hr sunlight treated sample; C: H_2O added and sunlight treated 2hr sample

Table 1: Chemical compositional changes and relative intensity (%) of lemon EO in photosensitive experiment analysis by GC-MS.

Peak No. a	RI b	Compounds	Formula	% Area c		
				A	B	C
Hydrocarbons						
1	1031	α-Pinene	$C_{10}H_{16}$	0.58	0.47	NA
2	1130	α-Phellandrene	$C_{10}H_{16}$	0.57	0.46	NA
3	1166	β-Myrcene	$C_{10}H_{16}$	2.22	1.71	NA
4	1213	Limonene	$C_{10}H_{16}$	86.05	87.82	4.55
5	1278	*p*-Cymene	$C_{10}H_{14}$	0.09	0.05	0.07
Oxides						
9	1459	cis-Limonene oxide	$C_{10}H_{16}O$	0.76	0.74	0.23
10	1471	trans-Limonene oxide	$C_{10}H_{16}O$	0.48	0.40	NA
33	1838	cis-Carvone oxide	$C_{10}H_{14}O_2$	NA	NA	1.52
35	1950	Limonene dioxide	$C_{10}H_{16}O_2$	NA	NA	5.14
Alcohols						
8	1447	1-Heptanol	$C_7H_{16}O$	0.08	0.06	NA
13	1538	β-Linalool	$C_{10}H_{18}O$	1.07	0.73	0.32
15	1629	trans-p-Mentha-2,8-dienol	$C_{10}H_{16}O$	0.89	0.43	1.82
16	1652	1-Nonanol	$C_9H_{20}O$	0.14	0.12	0.14
17	1671	cis-p-Menth-2,8-dienol	$C_{10}H_{16}O$	0.64	0.41	1.85
19	1698	α-Terpineol	$C_{10}H_{18}O$	0.11	0.21	NA
24	1832	Trans-carveol	$C_{10}H_{16}O$	0.72	0.65	10.46
25	1863	cis-carveol	$C_{10}H_{16}O$	0.56	0.91	2.49
26	2005	Perilla alcohol	$C_{10}H_{16}O$	0.04	0.04	0.84
28	2333	Limonen-1,2-diol	$C_{10}H_{18}O_2$	0.68	0.53	22.31
Aldehydes						
6	1291	Octanal	$C_8H_{16}O$	0.54	0.44	NA
7	1398	Nonanal	$C_9H_{18}O$	0.13	0.10	0.18
11	1482	Citronellal	$C_{10}H_{18}O$	0.04	0.12	NA
12	1503	Decanal	$C_{10}H_{20}O$	0.80	0.63	0.33
18	1687	cis-Citral (Neral)	$C_{10}H_{16}O$	0.19	0.34	0.81
20	1713	Dodecanal	$C_{12}H_{24}O$	0.19	0.17	0.15
21	1735	trans-Citral (Gernial)	$C_{10}H_{16}O$	0.03	0.15	NA
23	1753	β-Methylcrotonaldehyde	C_5H_8O	0.12	0.92	0.77
29	1074	Hexanal	$C_6H_{12}O$	NA	NA	0.10
38	2421	1,3,4-Trimethyl-3-cyclohexenyl-1-carboxaldehyde	$C_{10}H_{16}O$	NA	NA	3.36
Ketones						
22	1747	Carvone	$C_{10}H_{14}O$	1.12	0.27	17.30
30	1563	Limona ketone	$C_9H_{14}O$	NA	NA	0.35
31	1719	Umbellulone	$C_{10}H_{14}O$	NA	NA	0.26
32	1777	p-Acetyltoluene	$C_9H_{10}O$	NA	NA	0.99
34	1925	4-Hydroxy-3-methylacetophenone	$C_9H_{10}O_2$	NA	NA	0.85
36	2128	Cyclooctanone	$C_8H_{14}O$	NA	NA	3.15
37	2302	3-Isopropylidene-5-methyl-hex-4-en-2-one	$C_{10}H_{16}O$	NA	NA	7.16
Acids						
27	2089	Octanoic Acid	$C_8H_{16}O_2$	0.19	0.28	0.62
Esters						
14	1538	Linalyl acetate	$C_{12}H_{20}O_2$	0.13	NA	NA
Unknowns				0.81	0.85	11.87

[a] Peak number labeled on TIC
[b] Retention index relative to C8-C20 *n*-alkanes on Rtx®-Wax column
[c] A: control sample; B: 2hr sunlight treated sample; C: H_2O added and sunlight treated 2hr sample

Table 2: Chemical compositional changes and relative intensity (%) of orange EO in photosensitive experiment analysis by GC-MS.

Citation: Wu PS, Kuo YT, Chen SM, Li Y, Lou BS (2014) Gas Chromatography-Mass Spectrometry Analysis of Photosensitive Characteristics in Citrus and Herb Essential Oils. J Chromatogr Sep Tech 6: 261. doi:10.4172/2157-7064.1000261

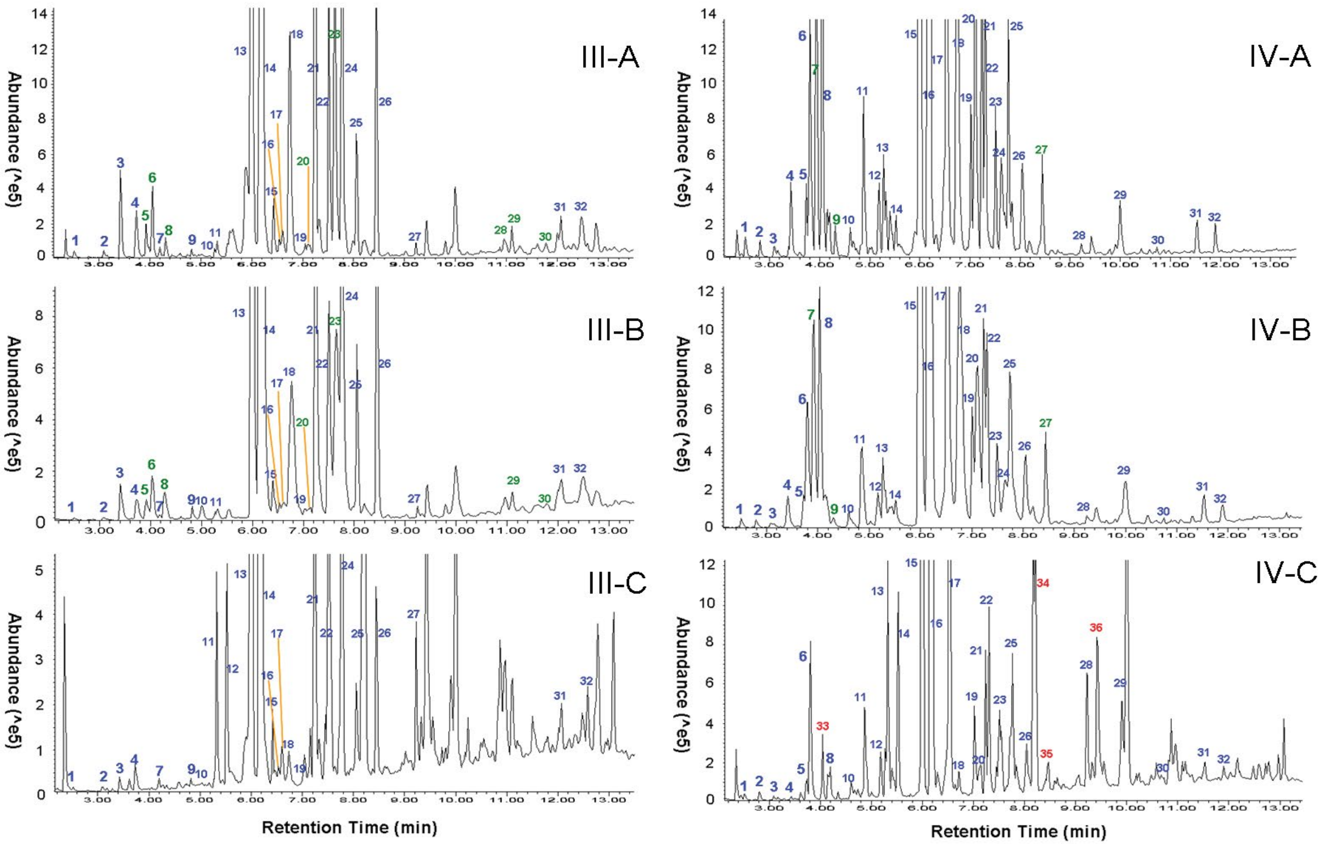

Figure 2: GC-MS total ion chromatography (TIC) of herb essential oils in different experimental condition. III: clary sage, IV: lavender. (A) control sample, stock storage well in the dark and dry environment, (B) after 2hr sunlight treatment sample, (C) H2O added (5:1, EO: H2O) and exposed to sunlight 2hr sample. Blue number: original identified compound before treatment; red number: new appeared compound after treatment; green number: disappeared compound after treatment.

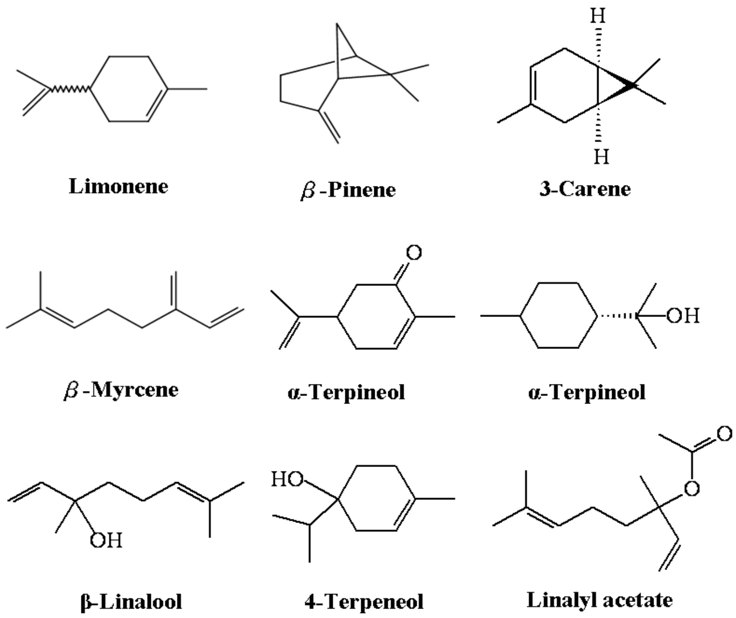

Figure 3: Structures of the major three compositional compounds in citrus and herb essential oils.

Citation: Wu PS, Kuo YT, Chen SM, Li Y, Lou BS (2014) Gas Chromatography-Mass Spectrometry Analysis of Photosensitive Characteristics in Citrus and Herb Essential Oils. J Chromatogr Sep Tech 6: 261. doi:10.4172/2157-7064.1000261

PeakNo.[a]	RI [b]	Compounds	Formula	% Area [c]		
				A	B	C
Hydrocarbons						
1	1031	α-Pinene	$C_{10}H_{16}$	0.07	0.02	0.01
2	1121	β -Pinene	$C_{10}H_{16}$	0.06	0.02	0.02
3	1166	β-Myrcene	$C_{10}H_{16}$	0.69	0.32	0.07
4	1213	Limonene	$C_{10}H_{16}$	0.48	0.23	0.16
5	1237	trans-β-Ocimene	$C_{10}H_{16}$	0.32	0.20	NA
6	1254	cis-β-Ocimene	$C_{10}H_{16}$	0.61	0.40	NA
7	1278	*p*-Cymene	$C_{10}H_{14}$	0.08	0.05	0.05
8	1292	4-Carene	$C_{10}H_{16}$	0.17	0.00	NA
17	1617	β-Elemene	$C_{15}H_{24}$	0.24	0.23	0.14
18	1624	Caryophyllene	$C_{15}H_{24}$	2.71	2.22	0.18
20	1687	cis-β-Farnesene	$C_{15}H_{24}$	0.05	0.09	NA
23	1730	Germacrene D	$C_{15}H_{24}$	2.79	2.18	NA
28	2169	Ledane	$C_{15}H_{26}$	0.18	NA	NA
30	2276	Guaiene	$C_{15}H_{24}$	0.11	0.30	NA
Oxides						
11	1447	Linalool, epoxydihydro-	$C_{10}H_{18}O_2$	0.11	0.09	0.90
12	1476	Linalool oxide	$C_{10}H_{18}O_2$	NA	NA	0.99
32	2368	Sclareoloxide	$C_{18}H_{30}O$	0.52	0.97	0.23
Alcohols						
9	1380	3-Hexen-1-ol	$C_6H_{12}O$	0.06	0.00	0.03
10	1440	1-Octen-3-ol	$C_8H_{16}O$	0.04	0.05	0.07
13	1538	β-Linalool	$C_{10}H_{18}O$	22.68	20.98	21.05
16	1608	4-Terpeneol	$C_{10}H_{18}O$	0.08	0.09	0.04
21	1699	α-Terpineol	$C_{10}H_{18}O$	6.72	5.68	5.18
25	1795	cis-Geraniol	$C_{10}H_{18}O$	0.99	1.07	0.48
26	1839	trans-Geraniol	$C_{10}H_{18}O$	2.02	2.47	0.91
27	1927	2,6-Dimethyl-3,7-octadiene-2,6-diol	$C_{10}H_{18}O_2$	0.09	0.11	0.65
29	2181	β-Spathulenol	$C_{10}H_{18}O$	0.22	0.33	NA
31	2306	β-Eudesmol	$C_{15}H_{26}O$	0.15	0.44	0.09
Esters						
14	1563	Linalyl acetate	$C_{12}H_{20}O_2$	46.43	53.85	51.22
15	1595	Linalyl formate	$C_{11}H_{18}O_2$	0.46	0.35	0.08
19	1672	Geranyl formate	$C_{11}H_{18}O_2$	0.06	0.10	0.18
22	1726	cis-Geranyl acetate	$C_{12}H_{20}O_2$	2.11	1.78	2.17
24	1756	trans-Geranyl acetate	$C_{12}H_{20}O_2$	4.80	4.00	3.95
Unknowns				3.89	1.40	11.16

[a] Peak number labeled on TIC
[b] Retention index relative to C8-C20 *n*-alkanes on Rtx®-Wax column
[c] A: control sample; B: 2hr sunlight treated sample; C: H_2O added and sunlight treated 2hr sample

Table 3: Chemical compositional changes and relative intensity (%) of clary sage EO in photosensitive experiment analysis by GC-MS.

Peak No.[a]	RI [b]	Compounds	Formula	% Area [c]		
				A	B	C
Hydrocarbons						
1	1031	α-Pinene	$C_{10}H_{16}$	0.12	0.09	0.08
2	1078	Camphene	$C_{10}H_{16}$	0.11	0.08	0.11
3	1121	β-Pinene	$C_{10}H_{16}$	0.08	0.03	0.06
4	1166	β-Myrcene	$C_{10}H_{16}$	0.47	0.35	0.04
5	1213	Limonene	$C_{10}H_{16}$	0.54	0.22	0.18
7	1237	trans-β-Ocimene	$C_{10}H_{16}$	3.31	1.98	NA
8	1254	cis-β-Ocimene	$C_{10}H_{16}$	3.67	2.20	0.49
9	1284	Terpinolene	$C_{10}H_{16}$	0.22	0.12	NA
18	1624	Caryophyllene	$C_{15}H_{24}$	5.83	4.88	0.28
20	1673	trans-β-Famesene	$C_{15}H_{24}$	2.95	2.62	0.52
24	1730	Germacrene D	$C_{15}H_{24}$	0.75	0.64	0.87
26	1779	γ-Muurolene	$C_{15}H_{24}$	0.76	0.93	0.96
31	2238	2-Isopropyl-5-methyl-9-methylenebicyclo[4.4.0] dec-1-ene	$C_{15}H_{24}$	0.24	0.39	0.44
Oxides						
14	1476	Linalool oxide	$C_{10}H_{18}O_2$	0.18	0.31	1.73
29	1991	Caryophyllene oxide	$C_{15}H_{24}O$	0.51	0.84	3.78
Alcohols						
6	1219	Eucalyptol	$C_{10}H_{18}O$	1.86	1.30	1.52
10	1345	1-Hexanol	$C_6H_{14}O$	0.18	0.11	0.13
13	1440	1-Octen-3-ol	$C_8H_{16}O$	0.35	0.26	0.05
15	1538	β-Linalool	$C_{10}H_{18}O$	24.89	26.83	24.80
17	1608	4-Terpeneol	$C_{10}H_{18}O$	8.59	7.22	6.39
19	1668	Lavandulol	$C_{10}H_{18}O$	0.99	0.94	1.01
21	1699	α-Terpineol	$C_{10}H_{18}O$	1.75	1.71	1.06
22	1708	Borneol	$C_{10}H_{18}O$	1.95	1.40	1.60
27	1839	trans-Geraniol	$C_{10}H_{18}O$	0.70	0.88	NA
28	1927	2,6-Dimethyl-3,7-octadiene-2,6-diol	$C_8H_{14}O_2$	0.06	0.18	1.22
30	2149	p-Cymen-7-ol	$C_{10}H_{14}O$	0.04	0.10	0.07
32	2281	α-Bisabolol	$C_{15}H_{26}O$	0.23	0.26	0.28
34	1801	7-Norbornanol	$C_7H_{12}O$	NA	NA	4.61
35	1830	Thymol	$C_{10}H_{14}O$	NA	NA	0.41
Ketones						
33	1256	3-Octanone	$C_8H_{16}O$	NA	NA	0.50
Esters						
11	1359	Octen-1-ol, acetate	$C_{10}H_{18}O_2$	1.23	0.88	1.16
12	1418	n-Hexyl butyrate	$C_{10}H_{20}O_2$	0.46	0.36	0.53
16	1563	Linalyl acetate	$C_{12}H_{20}O_2$	33.81	39.08	36.34
23	1726	cis-Geranyl acetate	$C_{12}H_{20}O_2$	0.92	0.88	1.69
25	1756	trans-Geranyl acetate	$C_{12}H_{20}O_2$	1.65	1.63	1.88
36	1939	cis-3-Hexenyl butyrate	$C_{10}H_{18}O_2$	NA	NA	1.71
Unknowns				0.59	0.28	3.47

[a] Peak number labeled on TIC
[b] Retention index relative to C8-C20 *n*-alkanes on Rtx®-Wax column
[c] A: control sample; B: 2hr sunlight treated sample; C: H_2O added and sunlight treated 2hr sample

Table 4: Chemical compositional changes and relative intensity (%) of lavender EO in photosensitive experiment analysis by GC-MS.

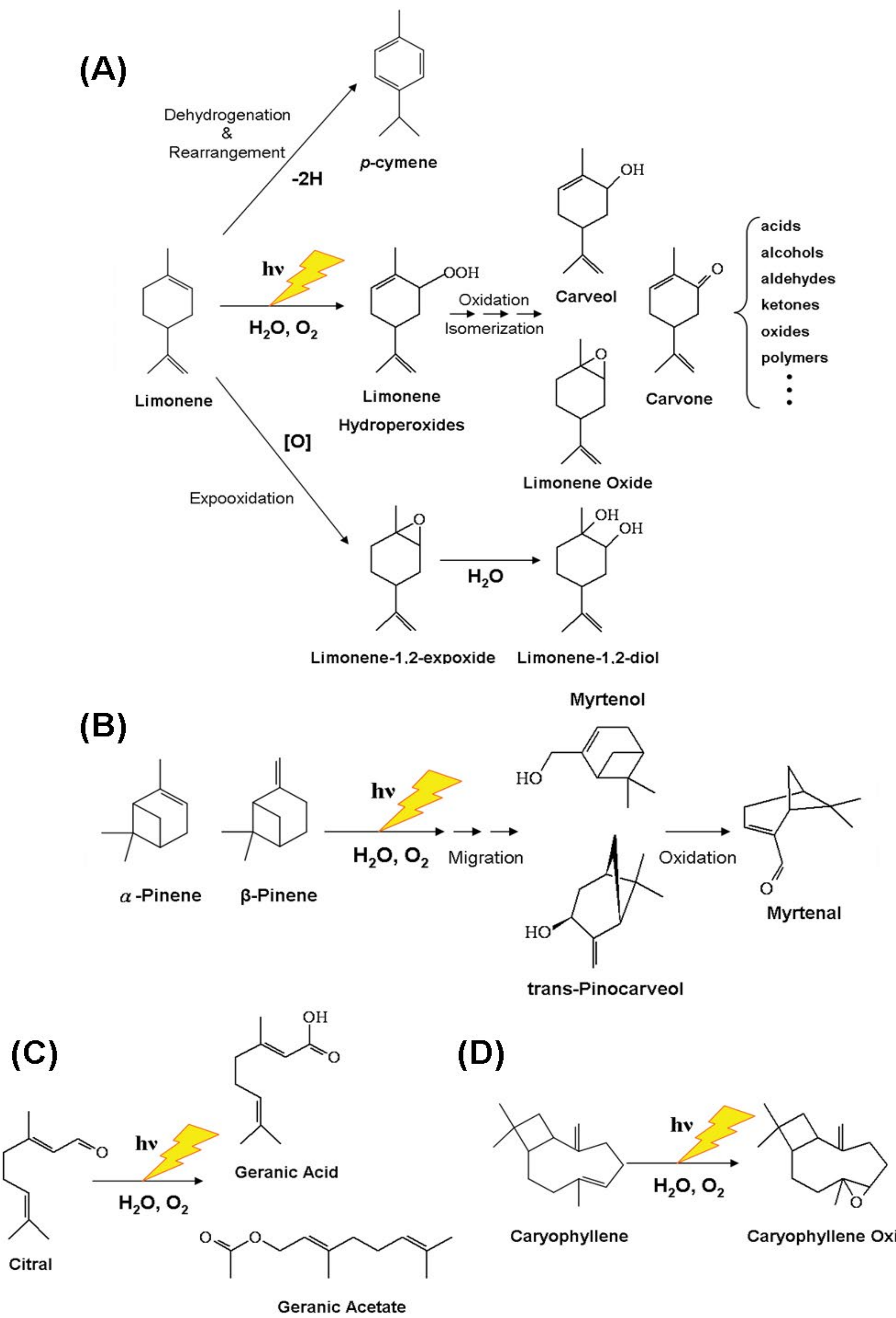

Figure 4: The reaction pathways of terpenes. (A) oxidation of limonene into various oxidative products, (B) the hydroperoxidation pathway of α-pinene and β-pinene , (C) oxidation of caryophyllene into its stable product, caryophyllene oxide, (D) citral oxidative and esterified products.

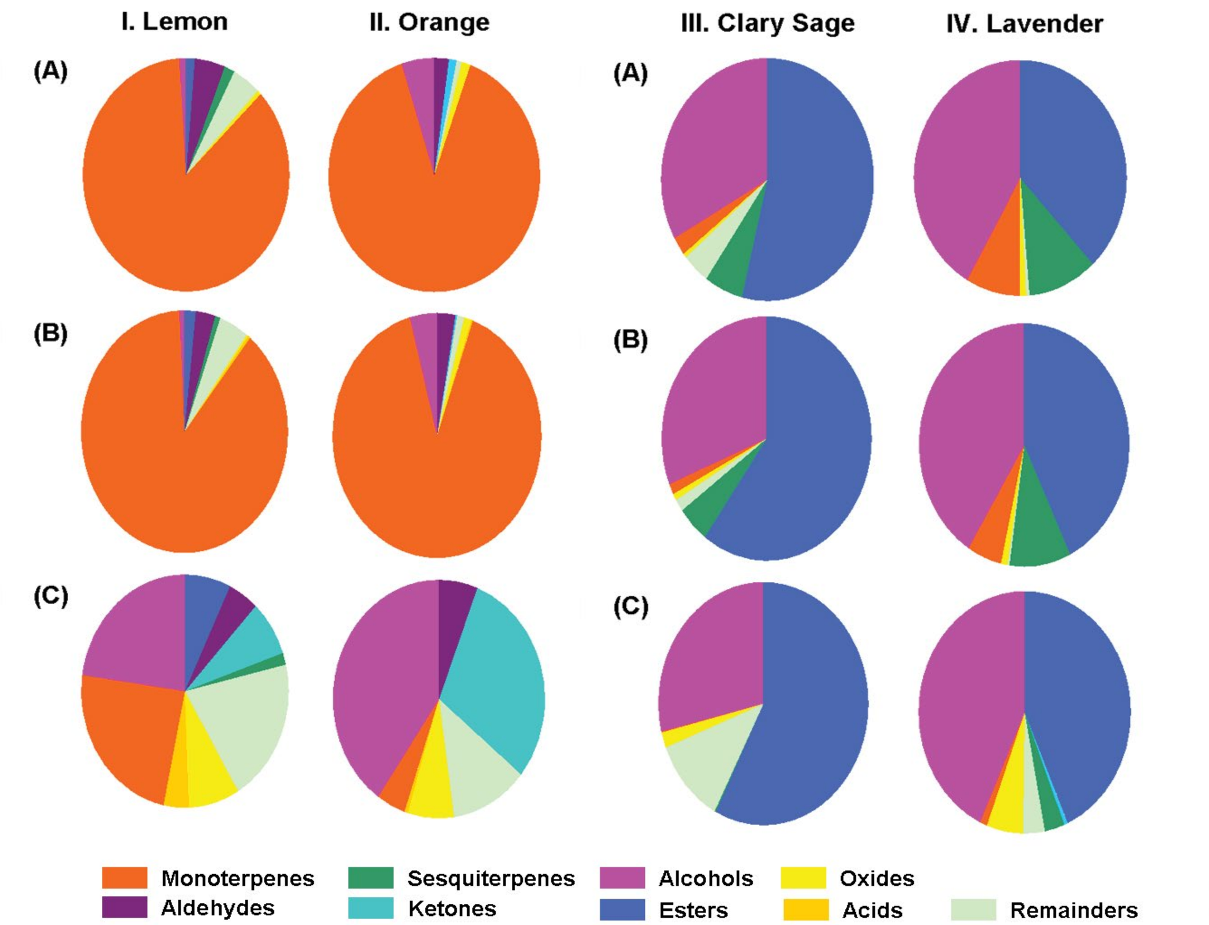

Figure 5: The citrus EO compositional changes in photosensitivity experiment expressed by CC profiles. I: lemon, II: orange, III: clary sage, IV: lavender. (A) control sample, stock storage well in the dark and dry environment, (B) after 2hr sunlight treatment sample, (C) H2O added (5:1, EO: H2O) and exposed to sunlight 2hr sample.

of this study suggested herb EOs become a better choice for skin care products. However, there was still some chemical reactions occurred for herb EOs under water-light environment. For instance, β-ocimene decreased 0.93% to 0% and 6.98% to 0.49% in clary sage and lavender, respectively, owing to the unstable properties in air [24]. Caryophyllene, β-famesene and germacrene D were sesquiterpenoids [11] and might converse into oxides or alcohols when H_2O co-exist with sunlight. Compare to lavender oil in group A and C experiment, caryophyllene (peak 18) decreased from 5.83% to 0.28% and caryophyllene oxide (peak 29) increased from 0.51% to 3.78% (Figure 4D). The sub-major compound, β-linalool sometime carries on esterification into linalyl acetate and increases the anticandidal ability [12]. β-linalool revealed a slight decreased in relative abundance and conversed into linalyl acetate for clary sage oil in both light and water-light experiment. According to the CC profiles of clary sage and lavender shown in Figure 5 III and IV, only few compositions varied for both herbs EOs after light/water treatment compare to citrus oils.

In this study, the present of H_2O had a great influence of citrus EOs in composition changes under solarization. The limonene was hydrated, oxidized and isomerized into its alcohol, ketone and oxide products. Those hydroperoxides may cause skin hypersensitivity, respiratory damage and allergic symptom [25-27]. For those reasons, citrus EOs might not be such a suitable material for skin or hair care products and their storage should avoid to moisture and sunshine. However, herb EOs were much less photosensitive than citrus due to their ester and alcohol composition. This might make herb EOs have more potential to become a stable material for daily used products application. But all type EOs should store in proper environment to reduce the risk of damage, and kept using quality from compositional change.

Conclusion

Citrus and herb EOs are described to contain many bioactive compounds in literature that make them useful in pharmaceutics as an antioxidant, antimicrobial and in aromatherapy as a stress repellent or stimulant [27]. These applications always involve EOs contacting skin or the respiratory tract directly, and the compositional changes may cause body damage or become an ineffective therapy depending on the storage and preparation of the EOs. The knowledge of EO compositional change as a result of different elements (light, water, oxygen and temperature, etc.) can ensure the effectiveness and quality of EOs, in addition to guaranteeing their safety [28,29]. The results in this study provided a suggestion of handing and storage for EO usage.

Acknowledgement

This work was supported by the Nation Science Council of Republic of China (NSC 101-2410-H-182-028) and Chang Gung University (UMRPD5A0071) to Bih-Show Lou.

References

1. Kalemba D, Kunicka A (2003) Antibacterial and antifungal properties of essential oils. Curr Medici Chem 10: 813-829.
2. Hui L, He L, Huan L, XiaoLan L, AiGuo G (2010) Chemical composition of lavender essential oil and its antioxidant activity and inhibition against rhinitis-relate bacteria. African J Microbio Res 4: 309-313.
3. Shabnam J, Ayesha J, Shaista N, Saeed MK, Zaid M, et al. (2014) Phytochemistry, GC-MS analysis, antioxidant and antimicrobial potential of eessential oil from five citrus species. J Agric Sci 6: 201-207.
4. Marti N, Mena P, Canovas JA, Micol V, Saura D (2009) Vitamin C and the role of citrus juices as functional food. Natur Product Commun 4: 677-700.
5. Genovaite B, Ona B, Danute M (2007) Essential oil composition variability in sage (*Salvia offoconalis L.*) CHEMIJA18: 38-43.
6. Luigi M, Alessandro C, Peter QT, Rosaria C, Paola D, et al. (2004) Fast GC for analysis of citrus oils. J Chrom Sci 42: 410-416.
7. Claudia T, Florian CS (2012) Stability of essential oils: a review. Comprehen Review Food Sci & Food Safety 12: 40-53.
8. Crupi ML, Costa R, Dugo P, Dugo G, Mondello L (2007) A comprehensive study on the chemical composition and aromatic characteristics of lemon liquor. Food Chem 105: 771-783.
9. Claudia T, Florian CS (2012) Impact of different storage conditions on the quality of selected essential oils. Food Res Internat 46: 341-353.
10. Oiao Y, JunXie B, Zhang Y, Zhang Y, Fan G, et al. (2008) Characterization of aroma active compounds in fruit juice and peel oil of *Jinchen* sweet orange fruit (citrus sinensis (L.) osbeck) by GC-MS and GC-O. Molecules 13: 1333-1344.
11. Husnu CB, Gerhard B (2010) Handbook of essential oils: science, technology, and application. Taylor & Francis CRC Press.
12. Yana H, Velizar G, Juergen W, Leopold J, Erich S, et al. (2013) Chemical composition ans antifungal activity of essential oil of *Salvia L.* from *Bulgaria* against clinical isolates of *Candida* species. J BioSci Biotech 2: 39-44.
13. Mauuel VM, Yolanda RN, Juana FL, Jose Angel PA (2007) Chemical composition of the essential oils obtained from some spices widely used in mediterranean region. Acta Chim Slov 54: 921-926.
14. Nimet K, Hasan B (2013) Determination of lavender and lavendin cultivars (Lavandula sp.) containing high quality essential oil in Isparat, Turkey. Turkis J Field Crops 8: 58-65.
15. Bhuiyan MN, Begum J, Sardar PK, Rahman MS (2009) Constituents of peel and leaf essential oils of Citrus Medica L. J Sci Res 1: 387-392.
16. Kamal GM, Anwar F, Hussain AI, Sarri N, Ashraf MY (2011) Yield and chemicalcomposition of *Citrus* essential oils as affected by drying pretreatment of peels. Internat Food Res J 18: 1275-1282.
17. ZhiSheng X, QunDi L, ZhiKun L, MingQian Z, XiaoXue Y, et al. (2013) The GC/MS analysis of volatile compenents extracted by different method from *Exocarpium Citri Grandis*. J Analyt Method in Chem 918406.
18. Earl R, John CL (1966) Reaction of the limonene 1,2-oxides. I. The stereospecific reactions of the (+)-*cis*- and (+)-*trans*-limonene 1,2-oxides. Reac of limonene Oxides 31: 1937-1944.
19. Sawamura M, Son US, Choi HS, Kim MSL, Phi NTL, et al. (2004) Compositional changes in commercial lemon essential oil for aromatherapy. Intern J Aromathera 14: 27-36.
20. Leonardo B, Lilian FF, Jacques FD, Edilson CS, Claudio Vinicius FS, et al. (2014) Theoretical study of Δ-3-(+)-carene oxidation. Phys Chem Chem Phys 16: 19376-19385.
21. Lindomar L, Geciane T, Débora O, Leda R, Cláudio D, et al. (2010) Microorganisms screening for limonene oxidation. Cilinc Tecnol Aliment 30: 399-405.
22. Gloria APS, Janeth APV, Claudia COL (2011) Microbial biotransromation of (R)-(+)-limonene by *Penicillium digitatum* DSM 62840 for producing (R)-(+)-terpineol. VITAE 18: 163-172.
23. Ines E, Manef A (2014) Kinetics of extraction of *Citrus aurantium* essential oil by hydrodistillation influence on the yield and the chemical composition. J Mater Environ Sci 5: 841-848.
24. Tomasz B, Agnieszka L, Elwira S, Krystyna SW, Jaroslaw W, et al. (2013) GC-MS analysis of essential oils from *Salvia Officinalis L.*: comparison of extraction methods of the volatile components. Acta Poloniae Pharmaceutica-Drug Res 70: 35-40.
25. Filipsson AF (1996) Short term inhalation exposure to turpentine: toxicokinetics and acute effects in men. Occupational Environ Med 53: 100-105.
26. Hausen B, Reichling J, Harkenthal M (1999) Degradation products of monoterpenes are the sentisizing agents in tea tree oil. Amer J Contact Dermatitis 10: 68-77.
27. Bertuzzi G, Tirillini B, Angelini P, Venanzoni R (2013) Antioxidative action of *Citrus limonum* essential oil on skin. Euorp J Med Plants 3: 1-9.
28. Nadia AA, Enas ND, Hasnaa SA (2013) The effect of enviromental stress on qualitative abd quantitatve essential oil of aromatic and medicinal plants. Archives Des Sci 66: 100-178.
29. Djilani A, Dicko A (2012) The Therapeutic Benefits of Essential Oils, Nutrition, Well- Being and Health, Dr. Jaouad Bouayed (Eds) InTech.