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= 단신 =

GC-MS에 의한 라일락 꽃 향기 분석

김남선 · 이동선★
서울여자대학교 화학과
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Characterization of Fragrances from Lilac Blossom by Gas Chromatography-Mass Spectrometry

Nam-Sun Kim and Dong-Sun Lee★
Department of Chemistry, Seoul Women's University, Seoul, 139-774 Korea
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요 약 : 라일락 꽃 향기 성분의 특성을 고체상 포집 용매추출법과 기체크로마토그래피 이온 포집형 질량분석법으로 연구하였다. 라일락 품종에 따라 향기성분의 조성이 현저한 차이를 보였다. 백색 라일락 꽃의 경우 벤즈알데히드, 페닐 아세트알데히드 및 알파-파네센인데 비하여 보라색 라일락 꽃은 벤즈알데히드, 알파 피넨 및 오시멘이 주된 향기성분으로 발견되었다 라일락 꽃 향기성분 중 알파-피넨의 거울상 이성질체의 본질을 분석한 결과 ( )형태임을 알 수 있었다.

Abstract : Fragrance components of lilac (*Syringa vulgaris*) blossom have been characterized in this paper. The accurate characterization of fragrances collected from lilac blossom was carried out by solid-phase trapping-solvent extraction and gas chromatography-ion trap mass spectrometry. According to lilac species, the chemical compositions were significantly different. Benzaldehyde, phenylacetaldehyde, and α-farnesene were found as the predominant component of white lilac blossom whereas benzaldehyde, α-pinene, and ocimene were those of pale purple lilac. The enantiomeric analysis of α-pinene in lilac blossom was found in the form of ( ).

Key words : *Syringa vulgaris*; lilac blossom ; fragrances; enantiomer; GC-MS.

1. Introduction

Lilacs are the most elegant and colorful of all early summer flowering shrubs. Lilac which has botanical name of *Syringa vulgaris*, belongs to the same plant family (Oleaceae) as olive trees, forsythia, ash and jasmine as well as provet. Lilacs belong to the genus *Syringa*, whose name comes from the Greek word *Syrinx*, meaning a pipe, referring to the hollow stem which is a characteristic of lilacs. The flower spike are made up of very small, individual tubular flowers. They are known for their beautiful long flower spikes with their complex variety of hues, often with a beautiful fragrance combining musk, spices and almonds. The

★ Corresponding author
Phone : +82+(0)2-970-7712 Fax : +82+(0)2-970-5972
E-mail : dslee@mail.swu.ac.kr

color-range in the many cultivars of lilac is from white through pink to blue and dark purple. The 22 species of lilac grow wild in eastern Asia, south easten Europe, the western Himalayas and through into the mountains of China, home to the greatest diversity of species.

The rapid expansion of the fragrance industry worldwide has been driven by the many demands for all natural fragrances. However, detail composition of fragrances emitted from lilac blossom is not studied by GC-MS. Furthermore, there is no report on the separation of chiral components of lilac blossom. Enantiomer can differ either in odour quality and properties or in odour intensity. Therefore, separation of enantiomer is of great importance in the fields of fragrances, not only to characterize analyte in quality assurance of natural fragrances, but also to identify possible adulterations. [1-2] Generally, the use of cyclodextrin in routine enantiomer recognition is now well established because of the high enantio-selectivity, stability and reproducibility of cyclodextrin capillary columns. [3-4]

The main purpose of this study is to characterize the fragrance composition emanated from lilac blossom. The screening of fragrance compounds and combination formulas for cosmetics, aromatherapy and many other applications is the final goal. In this study, solid-phase trapping-solvent extraction (SPTE) was used to collect fragrances emitted from lilac blossom. Then, fragrant compounds were analyzed by GC-MS with electron impact ionization (EI). In addition, separation of enantiomer of -pinene on a cyclodextrin capillary column was performed to identify chirality.

2. Experimental

The freshly picked flower samples of lilacs of white and pale purple color were collected at Seoul Women's University campus in May, 2002. Ethylvinyl bezene divinyl benzene copolymer (Porapak Q, 149-125 ㎛: 50-80 mesh) was purchased from Supleco (Bellefonte, PA, USA). Special precaution is required prior to use Porapak Q, because it contains *m-, o-, p-* isomers of diethylbenzene as impurities. Before use, Porapak Q particles were pre-rinsed with organic solvent in order to remove impurities. All fragrance standards were of analytical grade (purity, 99.9%) and were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Tokyo Kasei (Nihonbashi, Tokyo, Japan). All organic solvents of chromatographic grade were purchased from Sigma-Aldrich.

Fragrance compounds were collected from the lilac blossom by using a SPTE apparatus as described in our previous reports. [5-8] About 10 g of lilac flower samples were filled in a clean, dry barrel of the hypodermic glass syringe (50 mL, 3 cm I.D. × 14 cm long) with its plunger and needle removed. And then, two syringe barrels were fitted together with a polytetrafluoroethylene (PTFE, Teflon) spacer gasket and held by a joint clip. A Pasteur pipet (0.565 cm I.D. × 15 cm long) was used as a trap-housing which was packed with Porapak Q adsorbent (400 mg) and glass wool plugs. The inlet of the Pasteur pipet was attached to the luer taper tip of the barrel containing the flower cut. An oil-free electric vacuum pump (Vacuubrand GMBH, Wertheim, Germany, diaphragm ME2 model, 2.4 m^3/h) and a PTFE valve restrictor were connected with Tygon tubing to the outlet end of the trap via glass-manifold. A purified nitrogen gas (purity, 99.99%) flow at *ca.* 400 mL/min was passed into a couple of barrels and out through the adsorbent trap under reduced pressure. The collection was continued for 1 h at ambient temperature. After a run, the trap was then removed and the trapped fragrance compounds were eluted by two extractions with 2 mL of petroleum ether in portions to the new syringe to which the trap was attached and forcing the solvent through with the syringe plunger. Aliquots were analyzed by GC-MS.

GC-MS was performed on a Trace GC 2000 with GC-Q Plus ion trap MS (Thermoquest-Finnigan, Austin, TX, USA) gas chromatograph-mass spectrometer with Xcalibur software system. The columns were used a 5% phenyl poly dimethylsiloxane (SPB-5, Supelco, 30 m × 0.32 mm × 0.25 m film thickness) fused silica column to characterize fragrances and a 30% heptakis (2,3-di-O-methyl-6-O-t-butyldimethyl-silyl)-β-cyclodextrin (Cyclosil-B, J&W, 30 m × 0.25 mm × 0.25 ㎛ film thickness) column to analyse enantiomers from lilac

blossom. The oven temperature program for SPB-5 column was 50 ℃(3 min)-5 ℃/min-240 ℃ (10 min). Injector temperature and transfer line temperature were 250 ℃ and 275 ℃, respectively. Carrier gas (He, 99.9995%) was adjusted to a flow of 1.0 mL/min, the sample volume injected was 1μL. The split ratio was 1:30. The EI mass spectrometer was operated as follows: ionization voltage, 70 eV; ion source temperature, 200 ℃. The oven temperature program of the Cyclosil-B column was 50 ℃(1 min) - 5 ℃/min - 200 ℃ (5 min); injector, 200 ℃; transfer line, 230 ℃; the other conditions were the same as those of the SPB-5 column. The mass spectrometer was operated in positive ion EI ionization was used. The volatile constituents were positively identified by comparing their retention times as well as their EI mass spectra by comparing mass spectra of unknown peaks with NIST and Wiley libraries, and those of authentic substance used as reference standards. Kovats retention indices were determined by using a solution containing the homologous series of normal alkanes (C_8-C_{20}).

3. Results and discussion

Fig. 1 shows total ion chromatograms (TIC) of fragrances collected by SPTE from lilac blossom with white (*Syringa emodi*) and pale purple color (*Syringa swenginzowil*). The Kovats retention indices (*I*) estimated, and characteristic mass ions for sixteen components on polar stationary phase are listed in *Table* 1. Compositions of lilac blossom collected from two different species were investigated as shown in *Table* 2. Lilac species showed different compositions in this investigation. Pale purple lilacs have complex variety of beautiful fragrances than white lilacs. The most predominant component of lilac blossom from two species was benzaldehyde. Benzaldehyde was also found from maehwa (meihua, ume: *Prunus mume*) by our previous investigation [9]. Benzaldehyde has a characteristic odor of volatile oil of almond, and is found in kernels of bitter almond. However, phenylacetaldehyde and α-farnesene were also found as the major component of

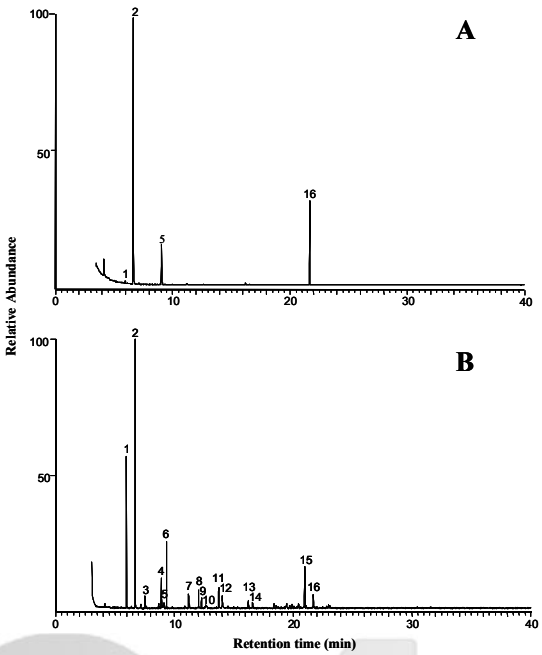

Fig. 1. Total ion chromatograms of fragrances of lilac blossom collected by SPTE.; obtaind by using 5% phenylpoly(dimethylsiloxane) (Supelco SPB-5, 30 m × 0.32 mm × 0.25 m) column. A, white lilac; B, pale purple lilac. Peak numbers correspond to the numbers indicated in *Table* 1. For analytical conditions, see experimental section.

white lilac blossom whereas α-pinene, and ocimene were those of pale purple lilac. However, minor components of pale purple lilac blossom contained α-pinene, benzyl methyl ether, phenethyl alcohol, cinnamyl alcohol, and α-farnesene.

The enantiomeric analysis of α-pinene in lilac blossom was undertaken using a Cyclosil-B, column. Chiral compounds from natural origins usually exist as one predominant optical isomer. As shown in *Fig*. 2, the enantiomer of α-Pinene in the fragrances emitted from lilac was found in the form of ( ). Enantiomers show different odour properties. For example (+)-limonene was found to have an orange odor, while ( )-limonene was found of turpentine type. [1] There have been previous reviews on the enantiomeric separation and enantio-selective perception of chiral odorants.[1,3,10]

Table 1. Characteristic mass spectral ions of volatile compounds assigned from floral fragrances of lilacs(*Syringa*) using a 5% phenylpoly(dimethylsiloxane) column

Peak No.	Compound	*I*	M_r	Base peak *m/z* (100%)	Characteristic mass spectral ions (EI) *m/z* (relative abundance %)
1	α-Pinene	933	136	91	64.1(7), 76.3(44), 92.5(35), 104.7(6), 136.0(17), 137.1(5)
2	Benzaldehyde	959	106	105	77.1(91), 106.9(16), 155.0(25),183.0(5)
3	Benzyl methyl ether	991	122	91	50.7(29), 76.9(32), 91.9(45), 120.9(59), 121.9(25), 122.9(3), 181.0(10)
4	Benzyl alcohol	1041	108	79	77(53), 91(20), 105(9), 108(89), 109(8)
5	Phenylacetaldehyde	1047	120	91	64.8(40), 91.8(29), 92.9(2), 120.8(1)
6	Ocimene	1056	136	93	79(45), 104(20), 121(25), 136(15)
7	Phenethyl alcohol	1121	122	91	64.8(31), 91.8(31), 92.8(2), 121.7(1)
8	Lilac aldehyde	1150	168	55	67(38), 93(41), 111(27), 153(10)
9	Lilac aldehyde	1158	168	55	66.7(82), 92.7(72), 110.6(91), 168.7(64), 169.8(57)
10	1,4-Dimethoxy-benzene	1171	138	123	62.6(87), 63.6(31), 64.6(26), 94.7(46), 137.8(83), 138.8(15)
11	Lilac alcohol	1197	170	171	54.6(95), 92.7(90), 106.8(80), 134.8(78), 171.7(75)
12	Lilac alcohol	1222	170	55	67(47), 71(24), 81(24), 93(70), 111(69), 155(13)
13	Indole	1304	117	89	63.0(22), 117.0(73), 117.9(7), 118.9(1)
14	Cinnamyl alcohol	1317	134	91	76.8(51), 91.8(47), 114.8(28), 115.8(8), 132.9(4)
15	Muulolene	1418	204	105	81(32), 91(37), 119(25), 133(14), 161(48), 189(10), 204(34)
16	α-Farnesene	1507	204	91	41(84), 77(47), 93(44), 204(0.22)

I = Kovat retention index; *M*r = relative mass.

Table 2. Fragrance composition of two different species of lilacs extracted by the SPTE

Peak No.	Compound	White lilac	Pale purple lilac
1	α-Pinene	1.06	20.15
2	Benzaldehyde	65.33	35.46
3	Benzyl methyl ether	-	1.97
4	Benzyl alcohol	-	4.77
5	Phenylacetaldehyde	15.65	1.08
6	Ocimene	-	10.31
7	Phenethyl alcohol	-	2.51
8	Lilac aldehyde	-	2.74
9	Lilac aldehyde	-	1.64
10	1,4-Dimethoxy-benzene	-	0.88
11	Lilac alcohol	-	3.84
12	Lilac alcohol	-	3.10
13	Indole	-	1.28
14	Cinnamyl alcohol	-	0.80
15	Muulolene	-	7.28
16	α-Farnesene	17.96	2.20

Unit: normalized peak area %.

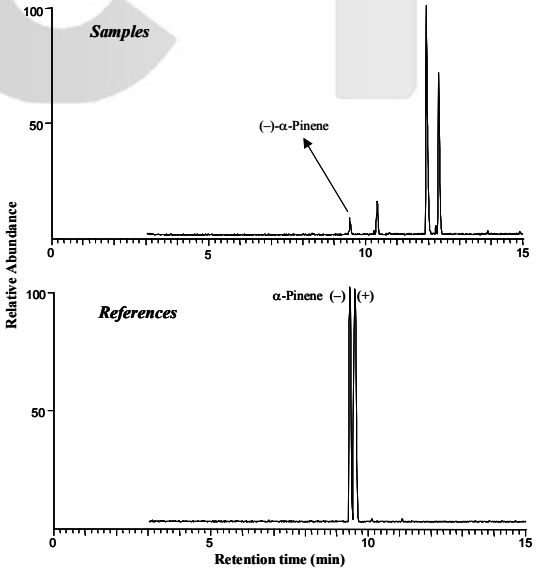

Fig. 2. Total ion chromatograms of α-pinene using 30% heptakis(2,3-di-O-methyl-6-O-t-butyldimethylsilyl)-β-cyclodextrin (Cyclosil-B, J&W, 30 m × 0.25 mm × 0.25 m) column. For analytical conditions, see experimental section.

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