

Volatile Components of Parsley Leaf and Seed (*Petroselinum crispum*)

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Abstract: The volatile oils of the fresh leaf and seed of parsley (*Petroselinum crispum*) were isolated by simultaneous steam distillation and extraction procedure. The compositions of the resulting oils were investigated by gas chromatography and gas chromatography-mass spectrometry. The volatile oil contents of leaf and seed were 0.06 % and 3.11 %, respectively. Fifty-eight components including 15 partially characterized components were identified in leaf oil and 23 components in seed oil. Seven of them are suggested as new parsley leaf volatiles. Terpenoids were represented as much as 46.4 % of total leaf volatiles and 49.3 % of total seed volatiles. The leaf volatiles contained a lot of myrcene (3.02 %), 4-isopropenyl-1-methyl benzene (4.52 %) and p-1,3,8-menthatriene (10.49 %), but the seed volatiles were characterized by greater quantities of the isomers, α -pinene (22.28 %) and β -pinene (16.20 %), although these compounds were contained only trace in leaf volatiles. Of the components identified in both oils, the most abundant component was myristicin, constituting 21.80 % of the leaf volatiles and 47.54 % of the seed volatiles (Received January 4, 1990, Accepted February 22, 1990).

Parsley (*Petroselinum crispum* (Mill.) Nym. or *Petroselinum crispum* Hoffm., Umbelliferae)¹⁾, which is native to the Mediterranean region, is an annual or biennial herb. The three major types of parsley are curly leaf (var. *crispum*), plain leaf (var. *neopolitanum* Danert) and Hamburg or turnip-rooted parsley (var. *turberosum* (Bernh.) Crov.), which are cultivated for its enlarged edible stem²⁾. The fresh and dried leaves are used as a garnish, stuffing, sauces and flavoring agents for their attractive aroma. The essential oils obtained by steam distillation from the leaf or ripe seed are used as a flavoring agent in drinks, various meat products and sauces or fragrance in perfumes, soaps and creams.

Several reports about parsley leaf volatiles have already been published. In 1972, Kasting et al.³⁾ identified 42 volatile components from steam distillate, isopentane extract and headspace vapor. In 1985, MacLeod et al.⁴⁾ identified 45 components including 11 not previously reported as parsley leaf volatiles from a desert parsley leaf of Lib-

yan origin. More recently, Shaath et al.⁵⁾ compared the chemical compositions of both parsley herb (leaf) oil and seed oil and investigated the chemical compositions of five commercial seed oils. Also in 1988, Simon and Quinn²⁾ examined 104 parsley accessions of different chemotypes, the authors found that the chemical composition of essential oils in plants is influenced by the developmental stage, environmental condition, chemotypic variation and different geographical origins^{2, 6)}.

In this paper, we now report the results of our study on the volatile components of the leaf and seed of parsley which was cultivated in Korea.

Materials and Methods

Materials

Fresh curly leaf parsley and ripe seed (*Petroselinum crispum*) used in this study were Paramount variety obtained from a local farm, located near Taejon.

Isolation of the volatile components

Three hundred grams of fresh leaf and thirty grams of seed were homogenized with five volumes of distilled water for 2 min in Waring blender, and the volatile components were isolated by means of simultaneous steam distillation and extraction(SDE) at atmospheric pressure in a modified Likens and Nickerson type apparatus using distilled n-pentane-diethyl ether(1 : 1, v/v) for 2 hours⁷⁾. The volatile extracts were dried over anhydrous Na₂SO₄ and concentrated to a volume of 0.5 ml by Vigreux column(20 cm).

Gas chromatography and mass spectrometry (GC-MS)

Gas chromatographic analysis of the essential oil was performed on a Hewlett-Packard(HP) 5880 GC equipped with FID. Two different fused silica

capillary columns coated SPB-1(50 m×0.32 mm ID) and Supelcowax 10(30 m×0.32 mm ID) with 0.25 μm phase thickness were used. Subsequent operating GC conditions in the runs were identical in both columns. Oven temperature was programmed from 60 °C with a 5 min initial hold and then 2 °C/min increased to a final temperature of 230 °C. Carrier gas was nitrogen at a stream of 1.2 ml/min and the split ratio was maintained at 80 : 1. The temperatures of injector and detector were 250 °C, respectively.

GC-MS analytical runs were performed on an HP 5890 GC connected with a quadrupole HP 5970 mass spectrometer. For GC-MS, a fused silica capillary column coated with SE-30(16 m×0.20 mm ID) was used. Oven temperature was programmed from 60 °C with a 5 min initial hold to 200 °C at 2

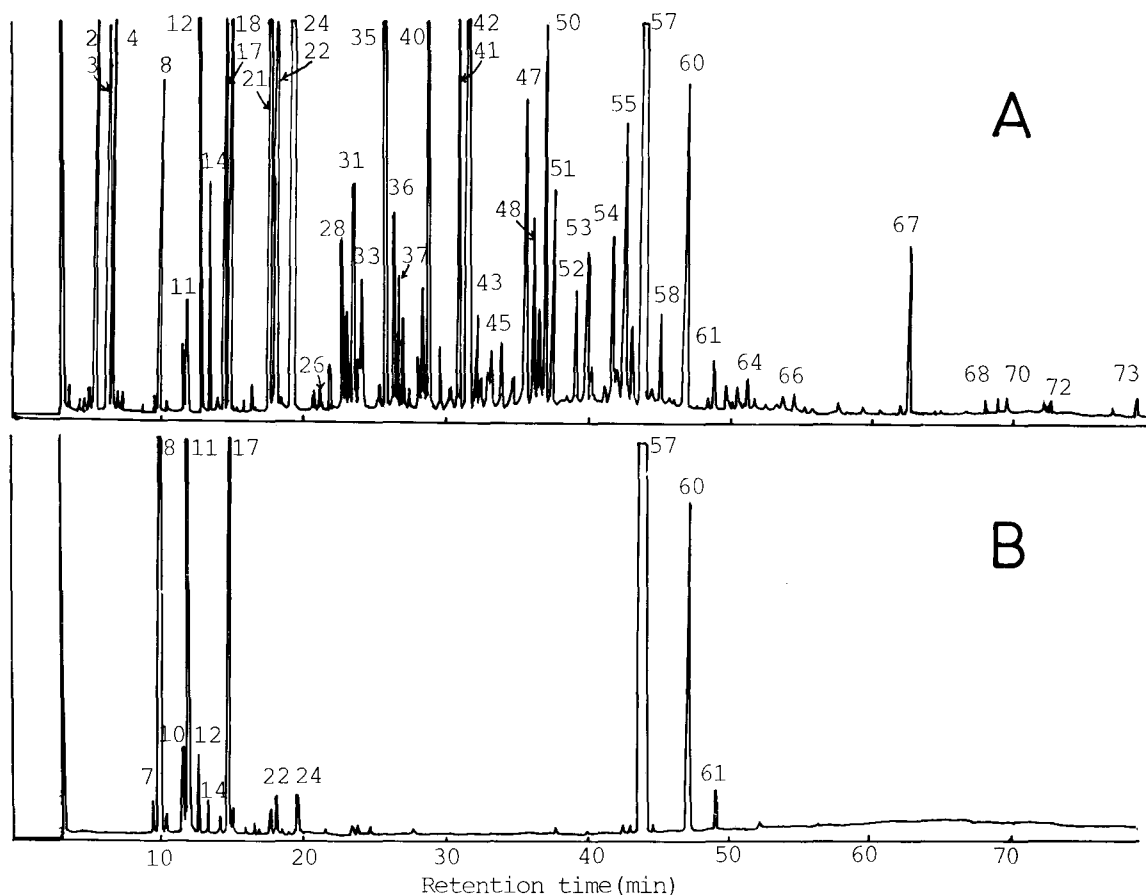


Fig. 1. Gas chromatograms of the volatile oils isolated from parsley leaf(A) and seed(B) on SPB-1(non-polar) column

Table 1. Compounds identified from the volatile oils of parsley leaf and seed

Peak No ^a	Compound	Rt ^b	Peak area(%)		Peak No ^a	Compound	Rt ^b	Peak area(%)	
			Leaf	Seed				Leaf	Seed
1	n-Hexanal	774	0.06	-	38	43, 137, 41, 135, 91, 152(M ⁺)		0.32	-
2	trans-2-Hexenal	821	2.08	-	39	Geraniol	1243	0.21	-
3	43, 41, 55, 70, 71, 69 ^c		0.82	-	40	43, 109, 124, 41, 69, 152(M ⁺)		0.54	-
4	cis-3-Hexen-1-ol	838	3.10	-	41	43, 109, 124, 95, 41, 152(M ⁺)		2.77	-
5	trans-2-Hexenol	846	0.03	-	42	43, 109, 155, 81, 55, 196		4.57	-
6	n-Hexanol	854	0.04	-	43	43, 79, 81, 108, 123, 95		0.34	-
7	α -Thujene	928	0.02	0.19	44	43, 91, 41, 105, 119, 150(M ⁺)		0.24	-
8	α -Pinene	932	0.83	22.28	45	α -Cubebene	1337	0.31	-
9	Camphene	938	0.04	0.13	46	43, 41, 55, 69, 79, 154(M ⁺)		0.08	-
10	Sabinene	966	0.09	0.87	47	α -Copaene	1359	1.32	-
11	β -Pinene	969	0.40	16.20	48	β -Elemene	1368	0.90	-
12	Myrcene	984	3.01	0.54	49	43, 95, 108, 123, 161, 196		0.37	-
13	δ -3-Carene	991	0.02	-	50	43, 95, 41, 123, 81, 79, 196		1.94	-
14	α -Phellandrene	995	0.72	0.28	51	α -Gurjunene		0.82	-
15	α -Terpinene	1009	0.04	-	52	β -Caryophyllene	1410	0.41	-
16	p-Cymene	1013	0.24	0.11	53	Bicyclogermacrene		0.86	-
17	β -Phellandrene	1019	9.96	7.52	54	β -Farnesene	1456	0.65	0.08
18	Limonene	1022	2.63	0.10	55	Germacrene D		1.15	-
19	cis- β -Ocimene		0.03	-	56	β -Selinene	1483	0.28	-
20	r-Terpinene	1077	0.07	0.10	57	Myristicin	1496	21.80	47.54
21	Terpinolene	1083	5.51	0.14	58	β -Bisabolene	1512	0.46	0.07
22	4-Isopropenyl-1-methyl benzene		4.52	0.28	59	α -Nerolidol	1527	0.03	-
23	Linalool	1088	0.02	-	60	Elemicin		3.04	2.64
24	ρ -1, 3, 8-Menthatriene		10.49	0.28	61	δ -Cadinene	1581	0.23	0.35
25	4-Isopropyl cyclohex-2-enone		0.07	-	62	Apiole		0.06	0.07
26	p-Menthatriene		0.06	-	63	43, 95, 121, 41, 79, 161, 204(M ⁺)		0.18	-
27	p-Menthatrienol		0.14	-	64	α -Cadinol		0.03	-
28	p-Methyl acetophenone	1160	0.61	0.10	65	43, 107, 41, 55, 79, 151, 204(M ⁺)		0.09	-
29	43, 91, 119, 137, 109, 152(M ⁺)		0.28	-	66	o-Methylbenzyl acetate	1700	0.06	-
30	43, 137, 91, 109, 119, 152(M ⁺)		0.44	-	67	Tetradecanal	1820	0.64	-
31	p-Cymene-8-ol	1168	0.73	0.09	68	Diels-Alder adduct(M ⁺ 268)		0.02	-
32	Terpinen-4-ol	1173	0.12	-	69	Diels-Alder adduct(M ⁺ 268)		0.02	-
33	α -Terpineol	1179	0.45	0.07	70	Hexadecenoic acid		0.04	-
34	Esteragole		0.27	-	71	Diels-Alder adduct(M ⁺ 268)		0.05	-
35	p-Menthatrienol		3.05	-	72	43, 71, 41, 55, 69, 81, 135, 222(M ⁺)		0.03	-
36	Carveol	1212	0.65	-	73	Pentatriacontane		0.03	-
37	Neral	1216	0.49	-					

^aThe peak numbers refer to Fig. 1. ^bRetention indices on SPB-1.

^cMajor fragment ions in decreasing order of relative abundance, M⁺=molecular ion.

$^{\circ}$ C/min. Mass spectra were taken with the ionization voltage of 70eV and electron multiplier energy of 1,600V. Scan range was 40-500amu and vacuum was maintained at 1.6×10^{-5} torr. with the ion source temperature at 250 $^{\circ}$ C.

Retention indices(RI) were obtained from the

data on the relative retention behavior of the nalkane homologue mixtures(C₈-C₂₆)⁹⁾. Identification of each component was carried out by means of comparison of retention indices, and also by computer library matching and mass spectral data books⁹⁻¹²⁾.

Results and Discussion

The volatile oils of fresh parsley leaf and seed were isolated by simultaneous steam distillation and extraction procedure. The resultant oils were found to possess characteristic parsley aroma when the concentrates were re-diluted appropriately. The essential oil contents were 0.06 % and 3.11 % on a fresh weight base in leaf and seed, respectively. These results were similar to previous studies reporting essential oil contents ranged from 0.04 to 0.15 %, averaging 0.07 % in fresh leaves^{2, 12}, and 1.5-3.5 % in seeds¹³.

Fig. 1 shows a typical gas chromatograms for the volatile oils of parsley leaf and seed on SPB-1(non-polar) column and Table 1 gives the details of the components of the oils with the percentage compositions of each component. Overall, 73 components were detected in leaf oil, of which 43 components were positively identified, with further 15 partially characterized by mass spectral data only. The 15 unidentified components listed with dominant fragment ions in Table 1 were either presented in low amounts or the mass spectrum was too poor for interpretation.

Of the fully identified components, 7 components consisted of trans-2-hexenal, trans-2-hexenol, n-hexanol, o-methylbenzyl acetate, tetradecanal, hexadecenoic acid and pentatriacontane are found as new parsley volatiles. Among them, C₆ aldehyde and alcohols such as trans-2-hexenal and trans-2-hexenol could be considered as lipid degradation products¹⁴, and these components may be originated from unsaturated fatty acids by lipoxigenase and hydroperoxide lyase after homogenization of fresh leaf^{15, 16}. Tetradecanal was identified from cold pressed Mexican and Persian lime oils which were produced in Florida¹⁷, and its aroma character have a very faint, fruity-citrusy odor with an ambre-incense note¹⁸.

Both of the oils were very rich in terpene compounds, 43 terpenoids including 14 sesquiterpenoids

represented as much as about 46.4 % of the total leaf volatiles and about 49.3 % of the total seed volatiles. In leaf volatiles, 18 of them were monoterpene hydrocarbons(32.7 % of total volatiles), 11 oxygenated monoterpenes(6.20%), 12 sesquiterpene hydrocarbons(7.42%) and 2 oxygenated sesquiterpenes(0.09 %). And from seed volatiles, 19 terpenoids including 4 sesquiterpenoids were identified, 13 of them were monoterpene hydrocarbons(48.8 %), 2 oxygenated monoterpenes(0.16 %), 3 sesquiterpene hydrocarbons(0.50 %) and 1 oxygenated sesquiterpene(0.07 %). It is apparent from these results that both parsley oils contain more terpene hydrocarbons than oxygenated terpenoids. However, a considerable difference is that, whereas the leaf volatiles contained a lot of myrcene(3.01 %), 4-isopropenyl-1-methyl benzene(4.52 %) and p-1, 3, 8-menthatriene(10.49 %), whereas the seed volatiles were characterized by greater quantities of the isomers, α -pinene(22.28 %) and β -pinene(16.20 %), although these components were contained only trace in leaf volatiles.

On the other hand, Simon and Quinn² and Shaath et al.⁵ demonstrated the existence of the two isomers having a molecular weight of 268 in parsley herb oils. They suggested that these compounds were dimers resulting from a Diels-Alder type reaction of two molecules of p-1, 3, 8-menthatriene(MW 138). In this study, three peaks having a molecular weight of 268 were detected in only leaf volatiles, but total amounts of them were less than 0.1 %. The mass spectrum of one of three isomers having a molecular weight of 268 is presented in Fig. 2 for comparison with that of p-1, 3, 8-menthatriene. The mass spectrum in Fig. 2(A) indicates the dimer(MW 268) undergoes facile cleavage to the monomer(MW 134), as evidenced by the base peak at m/z 134. Furthermore, the reduced intensity of the fragment ions at m/z 119 and 91 relative to that of p-1, 3, 8-menthatriene is additional evidence the dimer results from more than simple hydrogen bonding^{2, 5}.

With regard to the characteristic odor of par-

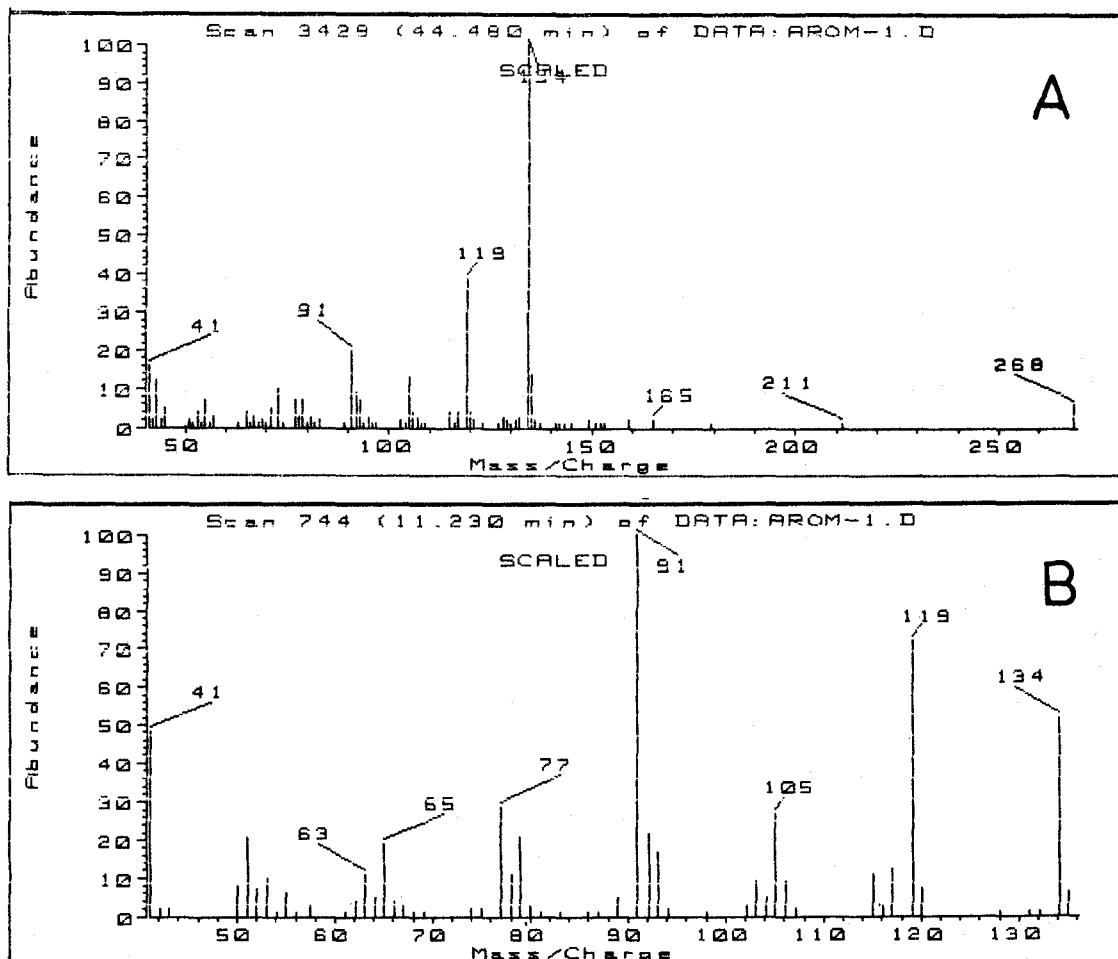


Fig. 2. Comparison of mass spectra of the molecular weight 268 dimer(A) and p-1, 3, 8-menthatriene(B)

sley oil, Ganero and Chretien-Bessiere¹⁹⁾ first suggested that p-1, 3, 8-menthatriene was responsible for the odor of parsley leaf, and Kasting et al.³⁾ later added β -phellandrene and the unseparated terpinolene and 4-isopropenyl-1-methyl benzene to this category. Freeman et al.²⁰⁾ separated the latter two compounds and suggested 4-isopropenyl-1-methyl benzene as being responsible for parsley leaf aroma. Recently, MacLeod et al.⁴⁾ agreed with Kasting et al.³⁾, but concluded that the compound having desirable parsley-like character was only apiole. On the content of apiole in parsley oil, MacLeod et al.⁴⁾ reported that apiole content was 18.3% in desert parsley oil of Libyan origin, and other investigators reported that its contents were

0-22.1% in 104 accessions of parsley leaf oil including curly, plain leaf and Hamburg types²⁾ and 7.71-10.56% in five commercial seed oils³⁾. But considering that apiole contents of parsley leaf and seed oil in this result were less than 0.1%, characteristic odor of parsley leaf and seed used in the present study may be due to the combination of β -phellandrene, 4-isopropenyl-1-methyl benzene and p-1, 3, 8-menthatriene with apiole.

Of the components identified in both volatile oils, the most abundant component was myristicin, constituting 21.80% of the leaf volatiles and 47.54% of the seed volatiles. MacLeod et al.⁴⁾ reported that myristicin content from Libyan parsley leaf oil was 20.6% and Simon and Quinn²⁰⁾ reported

that amounts of myristicin from 104 accessions of parsley leaf oils ranged from 0 to 60.5 % due to genetic basis. More recently, Shaath et al.⁵⁾ reported that myristicin contents ranged from 46.57

to 48.56 % in five commercial seed oils. However, this lack of consensus in chemical compositions of parsley volatiles may originate from genetic basis, environmental and geographical differences.

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파슬리의 잎과 씨의 휘발성 성분

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초록 : 파슬리의 잎과 씨로부터 휘발성 향기 성분을 분리한 다음 GC-MS 및 GC에 의한 머무름 시간의 비교에 의해 성분을 확인하였다. 잎과 씨에서 휘발성 성분의 함량은 각각 0.06 %와 3.11 %이었다. 잎에서는 mass spectrum에 의해 잠정적으로 확인된 15종의 성분을 포함하여 58종 그리고 씨에서는 23종의 성분이 확인되었다. 그 중 43종의 terpene 화합물이 잎에서 분리한 휘발성 성분의 약 46.4 %를 차지하였고 씨에서는 49.3 %를 차지하였다. 잎에서 양적으로 많이 함유된 terpene 화합물은 myrcene(3.01 %), 4-isopropenyl-1-methyl benzene(4.52 %), ρ -1, 3, 8-menthatriene(10.49 %)인 반면 씨에서는 α -pinene(22.28 %)와 β -pinene(16.20 %)이었다. 한편 두 oil에서 가장 풍부하게 함유된 성분은 myristicin으로서 잎과 씨에서 각각 전체 향기성분의 21.80 % 및 47.54 %를 차지하였다.