ХИМИЧЕСКИЕ НАУКИ

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GAS-CHROMATOGRAPHIC ANALYSIS OF THE VOLATILE SECONDARY METABOLITES OF HALIMODENDRON HALODENDRON (PALL.) VOSS

G.Zh. Baisalova[1], G. Ozek[2], K.H.C. Baser[2], R.Sh. Erkasov[1]

[1]Department of Chemistry, Faculty of Natural sciences, Eurasian national university, 010008, Astana, Kazakhstan

[2]Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470, Eskisehir, Turkey

The genus Halimodendron (Leguminosae) is represented by only one species mostly in steps, sandy and clayey deserts, by springs and saline soils in Kazakhstan. Is used in designing fences and planting deserts.

Halimodendron halodendron (Pall.) Voss. (H. halodendron) is a silvery thorny bush with a height of from 0,5 up to 3 meters, young twigs are covered with grey-silvery filament. Leaves are complicated, with a little prickle at the top (up to 3 mm), with the length that goes up to 3,5 centimeters, densely covered with silky filaments. Flowers are of bright-violet, pale-purple, pink color, with the length of 1, 5 cm. It blossoms abundantly 11-20 days in May- July. The fruit is oval, a swollen bean with the length of 2,5 cm and of brown-yellow color. Grows in somber forests, in sands and near sandy soil waters, in steps, along the road. Is spread in Middle Asia, West Siberia, West Europe, in Mongolia and Iran [1].

The researches [2] show that in the leaves of H. halodendron 0,79% , and in the fruits 0,31% of flavonoids can be found. The other researches [3] show that in fruits, twigs and leaves of H. halodendron contain 2, 46 % and 1,94% of tannic substances.

In the mineral composition of the ashy residue of leaves 42 elements were found with iron, phosphorus and aluminium as major constituents. Extracts from the aerial part of H. halodendron show high antioxidant activity [4]. Practically, there is no more information on the chemical content of H. halodendron in the literature therefore phytochemical research upon the plant was carried out.

The aim of the present work embraced the determination of the volatile secondary metabolites of the different organs of the aeral part of H. halodendron. The volatiles were obtained from the dried and crushed fruits, leaves, seeds by microdistillation using an Eppendorf MicroDistiller followed by simultaneous

GC/FID and GC/MS techniques. The results are shown in Table 1. Thus, it was possible to identify 34 components in the volatiles extracted from leaves, representing 91,7% of the total volatiles. The seven major components identified were farnesyl acetone (10,2%), hexadecanoic acid (9,0%), dihydroactinidiolide (8,7%), (E)-geranyl acetone (5,7%), phytol (5,3%), 1-octen-3-ol (4,9%), 4-vinyl guaiacol (4,3%). In the volatiles from fruits we identified twenty-seven compounds, representing 87,5% of the total volatiles. The two major constituents identified were hexadecanoic acid (35,8%), nonacosane (21,5%), hexahydrofarnesyl acetone (3,9%). 32 components were characterized, representing 84,3% of the total volatiles of seeds. Hexadecanoic acid (47,3%), (Z)-9-hexadecanoic acid (10,2%) tetradecanoic acid (4,1%), dodecanoic acid (3,9 %) were found in seeds as the main constituents.

Table 1

Chemical composition of the volatile compounds of Halimodendron halodendron

RRI	Compound	leaf, %	fruit, %	seed, %
1	2	3	4	5
1244	Amyl furan			0.8
1300	Tridecane			0.2
1360	Hexanol			0.5
1400	Nonanal	1.4	0.1	0.4
1400	Tetradecane			0.6
1452	1-Octen-3-ol	4.9	0.8	
1506	Decanal		0.6	
1507	(E,E)-2,4-Heptadienal	2.7		
1525	Theaspirane A	1.6		
1541	Benzaldehyde		0.8	0.9
1553	Linalool	3.6		
1569	Theaspirane B	2.2		
1600	Hexadecane		0.2	1.5
1602	6-Methyl-3,5-heptadien-2-one	tr		
1611	Terpinen-4-ol	1.7		
1621	2-Octen-1-ol	1.8		
1638	B-Cyclocitral	0.5		
1654	(E,E)-2,5-Epoxy-6,8-megastimadiene	tr		
1656	Benzene acetaldehyde		3.1	
1671	Acetophenone		2.6	
1700	Heptadecane		0.8	1.7
1706	α-Terpineol	1.9		

1722	Dodecanal	0.7		
1766	Decanol		0.3	
1800	Octadecane			1.0
1827	(E,E)-2,4-Decadienal			0.6
1838	(E)-β-Damascenone	1.4		
1861	1-Methylethyl dodecanoate	0.9	0.6	0.5
1868	(E)-Geranyl acetone	5.7		0.7
1910	1-Isobutyl-4-isopropyl 2,2-dimethyl succinate	3.2	0.4	0.9
1933	Tetradecanal	2.0		
1958	(E)-β-Ionone	2.7		0.4
1973	Dodecanol	1.3	0.6	
1992	Neophytadiene	2.1		
1995	trans-β-Ionone-5,6-epoxide	0.8		0.1
2046	Isopropyl myristate		0.4	0.5
2080	Cinnamaldehyde		0.9	
2131	Hexahydrofarnesyl acetone	1.9	3.9	0.4
2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	2.3	0.7	0.8
2179	Tetradecanol		0.8	
2198	Thymol	0.7		
2218	4-Vinyl guaiacol	4.3	1.7	0.4
2220	3,4-Dimethyl-5-pentyl-5H-furan-2-one	0.8	0.5	0.3
1	2	3	4	5
2226	Methyl hexadecanoate			0.3
2287	Ethyl hexadecanoata			1.0
2310	Methyldihydrojasmonate	0.9		0.9
2380	Dihydroactinidiolide	8.7		
2384	Hexadecanol		3.0	
2397	Farnesyl acetone	10.2		
2472	Ethyl octadec-9-enoate			0.5
2500	Pentacosane			0.8
2503	Dodecanoic acid	0.9	3.2	3.9
2509	(Z,Z)-9,12-methyl octadecadienoate			0.5
2538	Ethyl octadecadienoate			1.0
2607	1-Octadecanol			0.6
2622	Phytol	5.3		
2670	Tetradecanoic acid	3.6	1.2	4.1
2822	Pentadecanoic acid		2.0	

2840	γ-Palmitolactone		1.0	
2900	Nonacosane		21.5	
2931	Hexadecenoic acid	9.0	35.8	47.3
3200	(Z)-9-Hexadecenoic acid			10.2
	Total	91.7	87.5	84.3

RRI – Relative retention indices calculated against n-alkanes; % calculated from FID data; tr Trase (<0.1%);

Thus, the volatile constituents of H. halodendron were investigated by gas chromatography method.

EXPERIMENTAL

Plant Material and Isolation Procedure

Aerial parts of H. halodendron. were collected in September 2008 from Ayagus province of the Eastern Kazakhstan during the fruiting stage.

Aerial parts of H. halodendron were dried at room temperature, crushed plant were microdistilled using a Eppendorf MicroDistiller.

Analysis

The volatiles were analyzed by capillary Gas Chromatography-Flame Ionization detection (GC/FID) and Gas Chromatography–Mass spectrometry (GC/MS) using an Agilent 5975 GC-MSD system. The same column and analysis conditions were used for both GC/MS and GC/FID. HP-Innowax FSC column was used with helium as a carrier gas. GC oven temperature was kept at 600C for 10 min and programmed to 2200C for 10 min and then programmed to 2400C at a rate of 10C/min. The split ratio was adjusted at 40:1. Flame ionization detection and injector temperature were perfomed at 2500C. Mass spectrums were taken at 70 eV. Mass range was from m/z 35 to 450. The GC-FID analysis was carried out using an Agilent 6890N GC system. In order to obtain same elution order with GC/MS, simultaneous injection was done by using the same column and appropriate operational conditions. Identification of the volatile constituents was achieved by parallel comparison of their retention indices and mass spectra with data stored in the Wiley GC/MS Library, MassFinder software 3.0, Adams Library, NIST Library and Baser Library of Essential Oil Constituents. Relative percentage amounts of the separated compounds were calculated from FID chromatograms.

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Түйіндеме

Алғаш рет ГХ/ЖИД және ГХ/МС көмегімен H. halodendron жер үсті бөлігінің ұшқыш екіншілік метаболиттерінің химиялық құрамы талданған. H. halodendron жемістерінің, дәндерінің және жапырақтарының ұшқыш қосылыстарының сандық және сапалық құрамдары бір-бірінен ерекшеленеді. H. halodendron жемістері үшін - 26, дәндері үшін - 32 және жапырақтары үшін 34 қосылыс идентификацияланған.

Резюме

Впервые ГХ/ПИД и ГХ/МС анализирован химический состав летучих вторичных метаболитов надземной части H. halodendron. Качественный и количественный состав летучих соединений фруктов, сенены, листьев H. halodendron отличаются друг от друга. Идентифицированы 26 соединений для фруктов, 32 – семены и 34 – листьев H. halodendron.

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ТЕРМИЧЕСКИЕ И ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ПОЛИМЕРНЫХ И НЕПОЛИМЕРНЫХ ФОСФАТОВ КАЛЬЦИЯ

З.С. Нуркина

Евразийский Национальный Университет им. Л.Н. Гумилева, г. Астана

Фосфатам кальция присуща слабая растворимость в воде. Согласно справочным данным [1] произведение растворимости гидроксиапатита не превышает 10^{-59} , что ставит эту соль в ряд самых трудно растворимых неорганических веществ. В действительности у большинства из фосфатов кальция способность растворяться не столь мала, особенно если речь идет об аморфных разновидностях веществ или циклических формах. В целом, благодаря именно слабой растворимости, фосфорнокислые соли кальция, но крайней мере, те из них, которые имеют среднюю природу, способны осаждаться в ходе ионообменных реакций между растворимыми фосфатами и соединениями кальция. Как правило, в результате таких реакций формируются тонкодисперсные суспензии веществ, которые, после расслаивания дают