CHEMICAL COMPOSITION OF ESSENTIAL OILS OF *ANNONA SQUAMOSA* L. AND *ANNONA RETICULATA* L. FROM VIETNAM

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The Annonaceae, a pantropic family, is well developed in the tropics and is subtropics of both New and Old World. Only a few species are distributed in warm temperature (*Asiminia*) and the islands of the Pacific. The Annonaceae is one of the largest family that include 130 genera and over 2300 species in the world, and the greatest number of genera and species is concentrated in Indo-Malaysian area of Asia [7, 13]. Economically, this family is an important source of edible fruits and oils, raw material for perfumery and folk medicine for various purposes [8].

The genus *Annona* is one of important genus of the family Annonaceae. This genus consists of about 125 species, widely distributed in Asia and Australia, American, Africa, especially in South East Asia, such as, Malaysia, Indonesia, Thailand and Indochina [3].

Some authors have investigated the composition of *Annona squamosa* and *A. reticulata*: Chavan M. J., Shinde D. B., Nirmal S. A. [4], Andrade H. A., Zoghbi M. B., Maia G. S., Fabricius H. and Marx F. [2], Ogunwande Isiaka A., Ekundayo A., Olusegun Olawore, Nureni O., Kasali Adeleke A. [10], Pino J. A., Aguero J., Marbot R. [11].

I. MATERIAL AND METHODS

1. Meterial

The leaves of *Annona squamosa* L., *Annona reticulata* L. were collected in April 2007, in Thanh Hoa and Nghe An provinces. A voucher specimen (DD110-DD111) was deposited at the Herbarium of the Institute of Ecology and Biological Resources and Vinh University.

Fresh leaves were shredded and their oils were obtained by steam distillation for 3h at normal pressure, according to the Vietnamese Pharmacopoeia, 1997 [9].

2. GC/MS

An Agilent Technology HP 6890N Plus Chromatograph was fitted with a fused silica capillary column HP-5 MS column (30 m × 0.25 mm, film thickness 0.25 μm). The condition of use was the same as described above with He as carrier gas, and interface with a mass spectrometer HP 5973 MSD (70eV). The temperature was programmed as reported above. Components identification was carried out by comparing MS data with those reported in Library Willey on Chemstation HP [10-13].

II. RESULTS AND DISCUSSION

The content of essential oil of *Annona squamosa* is 0.15% (fresh leaves) and of *A. reticulata* is 0.20% (fresh leaves).

The compounds detected in the leaf oil of *Annona squamosa* and *A. reticulata* from Vietnam are listed in table 1. Of the total 76 oil components, thirty five were identified in leaf oil of *A. reticulata*, that make up about 92.4%. The major constituent of the essential oil was β-elemene (36.5%). This major compound was accompanied by lesser quantities of germacrene D (16.0%), β-caryophyllene (5.3%), β-bourbonene (4.7%), α-copaene (4.3%). Other compounds consist with amount lesser than 1.0% to trace.

By analysing essential oil of the

A. squamosa the presence of β-caryophyllene (20.0%), camphene (11.5%), α-pinene (4.3%), α-humulene (3.7%), α-cadinol (3.7%), δ-elemene (3.5%), bicyclogermacrene (3.4%) cadina-1,4-diene (3.4%), β-elemene (3.2%) and cyperene (3.2%) was revealed.

Table

Chemical constituents of essential oils of *Annona squamosa* and *A. reticulata* from Vietnam

Nº	**Compounds**	**KI**	***A. squamosa***	***A. reticulata***
1	Tricyclene	926	0.4	-
2	α-thujene	931	0.1	0.4
3	α-pinene	939	4.3	1.0
4	**Camphene**	**953**	**11.5**	0.6
5	Sabinene	976	trace	1.8
6	6-methyl-5-hepten-2-one	978	0.1	-
7	β-pinene	980	0.6	0.5
8	myrcene	990	0.2	0.8
9	α-phellandrene	1006	trace	0.1
10	δ^3-carene	1011	trace	-
11	α-terpinene	1017	0.2	0.2
12	Anisole	1019	trace	-
13	p-ocymene	1026	0.1	0.1
14	limonene	1032	2.1	0.7
15	(Z)-β-ocimene	1042	0.2	0.6
16	(E)-β-ocimene	1052	0.4	0.9
17	γ-terpinene	1061	trace	0.3
18	terpinolene	1090	0.1	0.2
19	linalool	1100	0.1	-
20	alloocimene	1128	trace	0.4
21	camphor	1145	0.1	-
22	borneol	1167	0.1	-
23	rosefurane	1177	trace	-
24	α-terpineol	1191	trace	-
25	trans-caveol	1217	0.1	-
26	geraniol	1253	0.1	-
27	enethol	1253	-	0.1
28	bornyl acetate	1289	0.4	-
29	Tridecane	1300	Trace	-
30	z-citral	1318	0.2	-
31	cycloisolongifolene	1319	0.7	-
32	bicycloelemene	1327	-	2.0
33	δ-elemene	1340	3.5	-
34	α-cubebene	1351	0.2	0.6
35	cyclosativene	1371	-	0.3
36	α-copaene	1378	1.0	4.3
37	β-bourbonene	1385	2.2	4.7
38	β-cubebene	1388	1.3	1.8
39	**β-elemene**	**1391**	3.2	**36.5**
40	Cyperene	1399	3.2	-

41	α-gurjunene	1412	-	0.3
42	**β-caryophyllene**	**1419**	**20.0**	5.3
43	γ-elemene	1437	trace	-
44	aromadendrene	1441	0.4	0.3
45	α-humulene	1454	3.7	1.2
46	α-patchoulene	1457	0.8	-
47	γ-muurolene	1480	0.1	-
48	**germacrene D**	**1480**	2.5	**16.0**
49	α-amorphene	1485	2.4	-
50	β-selinene	1490	0.6	-
51	δ-selinene	1493	0.9	-
52	bicyclogermacrene	1495	3.4	0.2
53	cadina-1,4-diene	1496	0.3	-
54	α-muurolene	1500	0.8	-
55	α-farnesene	1506	-	0.2
56	germacrene A	1509	-	0.3
57	γ-cadinene	1514	-	0.2
58	δ-cadinene	1525	2.0	0.8
59	cadina-4,9-diene	1532	-	2.0
60	Nerolidol	1533	0.3	0.3
61	α-cadinene	1539	0.1	-
62	Elemol	1550	0.2	-
63	Germacrene B	1561	0.1	-
64	trans-isoelemicine	1570	0.1	0.1
65	spathoulenol	1576	1.6	0.5
66	caryophyllene oxide	1583	1.4	0.6
67	Viridiflorol	1593	0.2	-
68	β-oplopenone	1608	0.2	-
69	aromadendren epoxide	1623	0.2	-
70	α-cadinol	1641	3.7	0.5
71	α-selina-6-en-4-ol	1648	0.2	-
72	Heptadecane	1700	1.1	-
73	Calamenene	1702	0.2	-
74	Farnesol	1718	0.2	-
75	Mitsulfit	1741	0.1	-
76	Octadecane	1800	0.3	-

Notes: KI. Kovas Index; trace < 0.1.

According to Ogunwande Isiaka A. et al. (1992), [10] oil obtained by hydrodistillation from the leaves of *A. reticulata* L. consists of 18 monoterpenes amounting to 29.0%, 20 sesquiterpenes totaling 52.9% and one aromatic esters making up 10.9%. And the oil contains (E,E)-farnesyl acetate (19.0%), α-turmerone (12.0%), benzyl benzoate (10.9%) and γ-terpinene (7.4%) that are as the major constituents. The volatile components of bullock's heart (*A. reticulata*) has been studied [11] and in their study the volatile components of bullock's heart were isolated by simultaneous steam distillation/solvent extraction and analyzed by GC/MS. Forty-nine compounds were identified in the fruits. The major volatiles in bullock's hearts are α-pinene (28.3 ppm), β-pinene (22.2 ppm) and germacrene D (12.5 ppm) [11].

By GC and GC/MS the essential oil produced by hydrodistillation of *Annona squamosa* leaves was also investigated [4]. In their work eighteen compounds have been identified accounting for 86% of the oil. The oil of *A. squamosa* was made up of monoterpene hydrocarbons (2.5%), sesquiterpene hydrocarbons (76.0%) and oxygenated sesquiterpenes (7.1%). β-caryophyllene (23.0%), germacrene D (21.3%), bicyclogermacrene (8.5%) and β-elemene (7.8%) are the major constituents of the oil. The volatile constituents of *Annona squamosa* L. bark were identified from the essential oil obtained by steam distillation and studied by GC/MS. Six major components are identified as 1H-Cycloprop(e)azulene (3.46%), germacrene D (11.44%), bisabolene (4.48%), caryophyllene oxide (29.38%), bisabolene epoxide (3.64%) and kaur-16-ene (19.13%). The oil was also screened for its antimicrobial activity that is as exhibited a significant antimicrobial activity against *Bacillus subtilis* and *Staphylococcus aureus* [4]. The chemical composition of the fruit pulp of *Annona squamosa* growing in the Brazilian Amazon is also studied [2]. In their work the result was compared with data of specimens occurring in Southeast Asia. In accordance with the sweet taste of the fruit pulp the amounts of sugars are found to be quite high (58% of dry mass) and the triglyceride concentration was found to be very low. The presence of the diterpenoid compound kaur-16-en-18-oic acid in a considerable amount (0.25% of dry mass) was detected in the lipid fraction. The essential oil of the fruit pulp is obtained and its volatile constituents are identified by GC-MS. The major compounds are α-pinene (25.3%), sabinene (22.7%) and limonene (10.1%). The occurrence of the isoricinoleic acid previously reported in the seed oil could not be confirmed [2].

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THÀNH PHẦN HÓA HỌC TINH DẦU LOÀI NA (*ANNONA SQUAMOSA* L.) VÀ BÌNH BÁT (*ANNONA RETICULATA* L.) Ở VIỆT NAM

TRẦN MINH HỢI, ĐỖ NGỌC ĐÀI, TRẦN ĐÌNH THẮNG

TÓM TẮT

Hàm lượng tinh dầu trong lá của loài na (*Annona squamosa* L.) và bình bát (*Annona reticulata* L.) ở Việt Nam lần lượt là 0,2 và 0,3%. Bằng phương pháp sắc ký khí khối phổ liên hợp (GC/MS), 39 hợp chất được tách ra từ lá bình bát, chiếm 92,4% tổng lượng tinh dầu với các thành phần chính là β-elemen (36,5%), germacren D (16,0%), β-caryophyllen (5,3%), β-bourbonen (4,7%) và α-copaen (4,3%). Sáu mươi tám hợp chất được tách ra từ tinh dầu lá loài na, chiếm 84,4% tổng lượng tinh dầu, trong đó β-caryophyllen (20,0%), camphen (11,5%), α-pinen (4,3%), α-humulen (3,7%), α-cadinol (3,7%), δ-elemen (3,5%), bicyclogermacren (3,4%), cadina-1,4-dien (3,4%), β-elemen (3,2%) và cyperen (3,2%).

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