SHORT REPORT

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Volatile Constituents of Three *Illicium* Plants

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Abstract: The chemical composition of volatiles from the leaves of three different *Illicium* species has been studied. The essential oils were obtained by hydrodistillation and analyzed by GC (FID) and GC-MS. The components by identified by MS libraries and their LRIs. The essential oil contents vary between 0.12% and 0.21% (v/w), calculated on a dry weight basis. *Illicium majus* J. D. Hooker & Thomson afforded oil whose major constituents were aromadendrene (13.0%), cuparene (8.2%), 1,8-cineole (8.1%) and calamenene (7.8%). However, 1,8-cineole (8.4%), linalool (7.7%), (*E*)-nerolidol (7.6%) and sabinene (7.1%) were the quantitatively significant compounds of the leaf oil of *Illicium micranthun* Dunn. The leaf oil of *Illicium tsaii* A. C. Smith comprised mainly of (*E*)-nerolidol (15.5%), β-caryophyllene (8.1%), β-cedrene (6.5%), 1,8-cineole (6.3%) and calamenene (6.3%). The chemical composition of the leaf essential oils of these plants from are being reported for the first time.

Keywords: *Illicium majus; Illicium micranthum; Illicium tsaii;* monoterpenes; sesquiterpenes. © 2016 ACG Publications. All rights reserved.

1. Plant Source

This paper, therefore report for the first time, the chemical compounds identified in the essential oils of the leaves of *I. majus, I. micranthum* and *I. tsaii* growing in Vietnam. Previously, the volatile constituents of some other Vietnamese plants have been studied and reported [1].

Leaves of *I. majus* were collected from Vũ Quang National Park, Hà Tĩnh Province, Vietnam, while those of *I. micranthum* and *I. tsaii* were obtained from Bat Xat Distrist Lào Cai, Province, Vietnam. All collections were done between June and September 2013. Botanical identification was performed by Dr. Dai DN. Voucher specimens DND 380, BVT 40 and BVT 47 respectively were deposited at the Botany Museum, Vinh University, Vietnam. Plant samples were air-dried prior to extraction.

2. Previous Studies

The essential oil of the pericarps of *I. majus* was found to contained high contents of safrole, linalool and limonene [2] while limonene (10.2%) and β-caryophyllene (10.1%) are the main

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compounds in pericarps oil of sample from China [3]. In the same vein, *I. micranthum* pericarps oil was known to contained high contents of safrole, linalool and limonene [3, 11]. The composition of the pericarps oil obtained from China [3] was dominated by limonene (17.9%) and β-caryophyllene (8.6%). 1,8-Cineole (21.47%), α-pinene (10.40%) and limonene (8.09%) were the significant compounds of the seed oil of *I. micranthum* [4]. No record of the composition of the essential oil of *I. tsaii* could be found in literature.

3. Present Study

The yields of essential oils were 0.12% ±0.01 (v/w, *I. majus*), 0.21% ±0.02 (v/w, *I. micranthum*) and 0.18% ±0.02 (v/w, *I. tsaii*) calculated on a dry weight basis. Oil samples were light yellow (*I. majus*), colourless (*I. micranthum*) and yellowish (*I. staii*). Table 1 indicates the chemical constituents present in the oil, their percentages as well as retention indices on HP-5MS column. Sesquiterpene compounds comprising of hydrocarbons (54.3%) and oxygenated sesquiterpenes (17.7%) are the main classes of compounds in the leaf oil of *I. majus*. The contents of monoterpene compounds are hydrocarbons (13.5%) and oxygenated (11.1%). The major compounds were aromadendrene (13.0%), 1,8-cineole (8.1%), cuparene (8.2%), calamenene (7.8%) and α-pinene (7.3%). Other compounds identified in sizeable quantity include τ-muurolol (5.6%), (*E*)-nerolidol (6.1%), bicyclogermacrene (6.1%) and β-caryophyllene (5.3%). The authors are not aware of any report on the volatile composition of the leaf of the plant. However, limonene, the main compound of the pericarps oils from China [11, 12] was not detected in the present study which also contained low contents of safrole and β-caryophyllene.

Monoterpenes (19.7% hydrocarbons vs. 21.6% oxygenated) and sesquiterpenes (33.5% hydrocarbons vs. 19.2% oxygenated) compound dominated in the essential oil of *I. micranthum.* The chemical constituents of the leaf oil of *I. micranthum* was characterized by the abundance of 1,8-cineole (8.4%), linalool (7.7%), (*E*)-nerolidol (7.6%) and sabinene (7.1%). The minor compounds present in the oil are α-pinene (4.2%), β-caryophyllene (4.2%), α-cadinol (4.1%), δ-cadinene (3.7%), zingiberene (3.6%), *ar*-curcumene (3.6%) and bicyclogermacrene (3.5%). Although no report could be seen on the leaf oil content of this plant, the chemical pattern was found to differ from those of the pericarps and seed oils. The main variations are the conspicuous absent of limonene and lower content of α-pinene, 1,8-cineole and β-caryophyllene when compared with the pericarps [2, 3] and seed [4] oils.

Sesquiterpene compounds made up of 44.2% hydrocarbons and 24.2% oxygenated counterpart occurred in higher quantity in the essential oil of *I. tsaii.* The content of monoterpene compounds was hydrocarbons (11.4%) and oxygenated derivatives (15.9%). However, (*E*)-nerolidol (15.5%), β-caryophyllene (8.1%), β-cedrene (6.5%), 1,8-cineole (6.3%), calamenene (6.3%) and α-pinene (5.1%) were the quantitatively significant compounds of the oil. There are sizeable quantity of aromadendrene (4.9%), δ-cadinene (4.3%), β-pinene (3.3%), linalool (3.2%) and germacrene D (3.0%). There is dirt of literature information on the essential oil constituents of this plant and this finding may represent the first of its kind.

The chemical compositions of essential oils from other *Illicium* plants from Vietnam and other part of the world have been reported. When the results of the present analysis were compared with the constituents of the leaves oils of other *Illicium* plants from Vietnam and elsewhere [5-26], it was found that each sample has its own composition pattern different from other. Several compounds that were present in other *Illicium* oils were not identified in the studied oils of *Illicium* plants. This observation may be explained in term of the different nature of the plant, handling and processing procedure as well the differences in the environmental and climatic conditions between the various places of collections. Considering the chemical constituents of studied *Illicium* oils, three groups of chemotypic forms are encountered. They are oils with abundant of phenylpropnaoids, ones in which a phenylpropene and oxygenated monoterpene predominates and those with high contents of different kind of terpene compounds. These are;

Group A: phenylpropenes chemotypes

i. Oils containing larger proportions of safrole as seen in pericarps of *I. micranthum* [2], root of *I. griffithii* [5].

ii. Oil dominated by myristicin, α-asarone and methyl isoeugenol common to the root of *I lanceolatum* [6], leaf and stem of *I. griffithii* [7] and branch of *I. parviflorum* [8].
iii. Essential oils with abundance of *trans*-anethole commonly encountered with all parts of *I. verum* [9-16].
iv. Oils rich in safrole and myristicin which occurred in *I. henryi* [17, 18].
v. Methoxyeugenol dominated oil common only to *I. difengpi* [20].

Group B: phenylpropene and oxygenated monoterpene chemotypes

i. Oils with large contents of safrole and linalool e.g. *I. difengpi* [19, 20], fruits of *I. griffithii* [21] and fruits of *I. majus* [2].
ii. Oils with some percentages of myristicin and linalool seen in fruits of *I. griffithii* [22].
iii. Oils containing elemicin and linalool analysed in the leaf of *I. lanceolatum* [23].

Group C: terpene dominated chemotypes

i. Linalool/linaly acetate type e.g. leaf and branch of *I. floridanum* [11].
ii. α-Terpineol/ carvone type e.g. *I. fargesii* [24].
iii. Limonene rich oil e.g. pericarps of *I. micranthum* [3], fruits of *I. lanceolatum* [23], *I. pachyphyllum* [13] and *I. simonsii* [25].
iv. 1,8-Cineole/linalool rich oil displayed by *I. anisatum* fruit [26], seed oil of *I. micranthum* [4] and leaf of *I. micranthum* (present study).
v. β-Caryophyllene dominated oil e.g. fruit of *I. simonsii* [25] and pericarps of *I. majus* [3].
vi. Oil rich in (*E*)-nerolidol as seen in *I. tsaii* (present study).
vii. Oil with high amount of aromadendrene e.g. *I. majus* (present study)

Conclusions

For the first time, the compositions of the leaf essential oils of the Vietnamese *I. majus, I. micranthum* and *I. tsaii* were elucidated. Due to the very limited amount of published data on the essential oils of these plants, comparison of the present results with other studies from Vietnam or other countries was limited. Although, some compounds such as α-pinene, (E)-β-ocimene, 1,8-cineole, linalool and β-caryophyllene were identified in all the samples; each species has its own compositional pattern different from others.

Table 1. Volatile constituents of *I. majus, I. micranthum* and *I. tsaii* from Vietnam

			Percentage composition (±SD[a])		
Compounds[b]	**RI[c]**	**RI[d]**	***I. majus***	***I. micranthum***	***I. tsaii***
α-Thujene	930	926	0.1	0.2	0.1
α-Pinene	939	932	7.3	4.2	5.1
Camphene	953	946	0.1	0.1	0.2
Sabinene	976	964	0.5	7.1	-
β-Pinene	980	976	1.3	-	3.3
β-Myrcene	990	988	0.3	0.8	0.9
α-Phellandrene	1006	1004	0.6	0.3	0.2
δ-3-Carene	1011	1008	2.3	-	-
α-Terpinene	1017	1014	0.1	1.8	0.3
p-Cymene	1026	1020	0.6	-	-
1,8-Cineole[g]	1034	1032	8.1	8.4[e]	6.3
(*E*)-β-Ocimene	1052	1044	0.1	1.5	0.5
γ-Terpinene	1061	1056	0.1	2.6	0.5
cis-Sabinene hydrate	1071	1065	-	0.1	-
α-Terpinolene	1090	1089	0.1	1.0	0.3
Linalool [g]	1100	1095	1.6	7.7	3.2

allo-Ocimene	1128	1128	-	0.1	-
trans-Pinocarveol	1139	1135	0.2	-	0.2
Pinocarvone	1165	1160	0.2	-	0.2
Terpinen-4-ol	1177	1175	0.2	2.8	1.2
α-Terpineol	1189	1186	0.2	1.7	1.2
Myrtenal	1207	1195	0.4	-	-
trans-Piperitol	1209	1207	-	0.1	-
Cumin aldehyde	1226	1238	0.1	-	-
Geraniol	1253	1249	-	0.4	0.9
Safrole	1287	1285	0.9	-	-
Bornyl acetate	1289	1287	0.1	0.1	0.9
2-Undecanone	1291	1293	0.2	0.2	-
o-Thymol	1293	1289	-	-	0.5
Bicycloelemene	1327	1338	0.3	1.8	0.9
α-Cubebene	1351	1345	0.1	0.1	-
α-Ylangene	1375	1373	-	0.1	-
α-Copaene	1377	1374	0.3	0.9	0.3
Geranyl acetate	1381	1379	-	0.2	0.3
β-Bourbonene	1385	1387	-	0.4	-
β-Elemene	1391	1389	1.1	2.0	0.7
α-Gurjunene	1412	1409	-	0.1	-
β-Caryophyllene	1419	1417	5.3	4.2	8.1
β-Cedrene	1421	1419	-	-	6.5
Widdrene [g]	1431	1432	4.1	-	-
β-Gurjunene	1434	1431	0.2	-	-
trans-α-Bergamotene	1435	1431	-	1.1	-
Aromadendrene	1441	1439	13.0	1.6	4.9
α-Humulene	1454	1452	0.2	1.6	1.5
Geranyl propanoate	1476	1476	-	0.1	-
γ-Gurjunene	1477	1475	-	-	0.5
ar-Curcumene	1480	1479	2.2	3.6	0.7
Germacrene D	1484	1484	-	0.2	3.0
α-Amorphene	1485	1484	0.5	2.7	1.9
β-Selinene	1486	1486	-	-	0.1
Zingiberene	1494	1493	0.8	3.6	0.7
Cadina-1,4-diene	1496	1496	-	1.0	-
Bicyclogermacrene	1500	1500	6.1[e]	3.5	-
α-Muurolene	1502	1500	-	-	0.6
Cuparene	1506	1504	8.2	-	-
δ-Cadinene	1525	1522	1.0	3.7	4.3
α-Cadinene	1539	1537	-	0.2	-
δ-Calacorene	1546	1544	1.5	1.1	2.1
Elemol	1550	1548	1.1	0.3	-
Germacrene B	1561	1559	0.6	-	2.1
(*E*)-Nerolidol	1563	1561	6.1	7.6	15.5[e]
Spathulenol	1578	1577	4.9	-	1.4
Viridiflorol	1593	1592	-	0.5	1.9
β-Oplopenone [g]	1608	1607	-	0.1	-
τ-Muurolol	1646	1640	5.6	2.7	2.0
β-Eudesmol	1651	1649	-	0.3	-
α-Cadinol	1654	1652	-	4.1	2.0
α-Bisabolol	1682	1685	-	-	0.8
Vulgarol B	1688	1690	-	0.2	-
Calamenene	1702	1702	7.8	-	6.3
(*E,E*)-Farnesol	1718	1722	-	1.1	0.6

Levomenol[f]	1720	1725	-	0.4	-
α-Costol [g]	1778	1773	-	1.9	-
Benzyl cinnamate	2096	2092	-	0.1	-
Phytol	2125	2119	-	0.2	-
	Total		**97.7**	**94.8**	**96.1**
Monoterpene hydrocarbons			**13.5**	**19.7**	**11.4**
Oxygenated monoterpenes			**11.1**	**21.6**	**15.9**
Sesquiterpene hydrocarbons			**54.3**	**33.5**	**44.2**
Oxygenated sesquiterpenes			**17.7**	**19.2**	**24.2**
Diterpenes			**-**	**0.2**	**-**
Phenylpropanoids			**0.9**	**0.3**	**0.4**
Non-terpenes			**0.2**	**0.3**	**-**

[a] Standard deviation were insignificant and were excluded from the Table except where stated; [b] Elution order on HP-5MS column; [c] Retention indices on HP-5MS column; [d] Literature retention indices (see Experimental); [e] Standard deviation, SD ± 0.02; [f] Tentative identification; [g] Further identification was performed by co-injection with authentic standard; - Not identified

References

[1] D.N. Dai, B.V. Thanh, L.D.N. Anh, N.K. Ban, T.D. Thang and I.A. Ogunwande (2015). Composition of Vietnamese species of *Kadsura* (Schsandraceae), *Rec Nat Prod.* **9**, 386-393.

[2] J. Huang, C. Yang and R. Zhao (1996). GC-MS analysis of essential oils from the pericarps of *Illicium majus* Hook.f.et. Thoms. and *I. micranthum* Dunn, *China J Chinese Mat Med*. **21**, 679-681.

[3] M.J.R. Howes, C.K. Geoffrey and M.S.J Simmonds (2009). Distinguishing Chinese star anise from Japanese star anise using thermal desorption-gas chromatography-mass spectrometry, *J Agric Food Chem*. **57**, 5783-5789.

[4] H.G. Li and G.L. Wang (1996). Studies on the chemical constituents of the seeds of *Illicium micranthum* Dunn, *Nat Prod Res Develop*. **6**, 18-22.

[5] N.T. Tam, L.A. Ha, A. Bighelli, M. Alain and J. Casanova (2005). Advances in the chemical composition of essential oils from *Illicium grifffithii* Hook. f. et Thoms. from Vietnam, *J Essent Oil Res*. **17**, 79-81.

[6] J. Liang, H. Baokang and W. Guowei (2012). Chemical composition, antinociceptive and anti-inflammatory properties of essential oil from the roots of *Illicium lanceolatum*, *Nat Prod Res*. **26,** 1712-1714.

[7] N.X. Dũng, D.C. Nguyêñ and P.A. Leclercq (1995). Volatile constituents of the fruit oil of *Illicium griffithii* Hook. f. et Thorns. from Vietnam, *J Essent Oil Res.* **7**, 451-452.

[8] A.O. Tucker and M.J. Maciarello (1999). Volatile oils of *Illicium floridanum* and *I. parviflorum* (Illiciaceae) of the southeastern United States and their potential economic utilization, *Econ Bot.* **53**, 435-438.

[9] M.B. Gholivand, M. Rahimi-Nasrabadi and H. Chalabi (2009). Determination of essential oil components of star anise (*Illicium verum*) using simultaneous hydrodistillation-sStatic headspace liquid-phase microextraction-gas chromatography mass spectrometry, *Anal. Lett.* **42**, 1382-139.

[10] M. Miyagawa, T. Satou, C. Yukimune, A. Ishibashi, H. Seimiya, H. Yamada, T. Hasegawa and K. Koike (2014). Anxiolytic-like effect of *Illicium verum* fruit oil, *trans*-anethole and related compounds in mice, *Phytother Res.* **28**, 1710-1712.

[11] G. Singh, M. Sumitra, M.P. de Lampasona and C. Cesar (2006). Chemical constituents, antimicrobial investigations and antioxidative potential of volatile oil and acetone extract of star anise fruits, *J. Sci Food Agric*. **86**, 111-121.

[12] G. Park, E. Shin and J. Kim (2016). Insecticidal activities of essential oils, *Gaultheria fragrantissima* and *Illicium verum*, their components and analogues against *Callosobruchus chinensis* adults, *J. Asia-Pacific Entom.*, (*In Press*).

[13] P. Liu, X.-C. Liu, H.-W. Dong, Z.-L. Liu, S.-S. Du and Z.-W. Deng (2012). Chemical composition and insecticidal activity of the essential oil of *Illicium pachyphyllum* fruits against two grain storage insects, *Molecules.* **17**, 14870-14881.

[14] M. Asif, A.H.S. Yehya, M.A. Al-Mansoub, V. Revadigar, M.O. Ezzat, M.B.K. Ahamed, C.E. Oon, V. Murugaiyah, A.S. Abdul Majid and A.M.S. Abdul Majid (2016). Anticancer attributes of *Illicium verum* essential oils against colon cancer, *South Afr J Bot.* **103**, 156-161.

[15] Y. Huang, J. Zhao, L. Zhou, J. Wang, Y. Gong, X. Chen, Z. Guo, Q. Wang and W. Jiang (2010). Antifungal activity of the essential oil of *Illicium verum* fruit and its main component *trans*-anethole, *Molecules.* **15**, 7558-7569.

[16] A. Dzamic, S. Marina, S.R. Mihailo, G.J. Slavica, V. Jelena and D.M Petar (2009). Chemical composition and antifungal activity of *Illicium verum* and *Eugenia caryophyllata* essential oils, *Chem Nat Comp.* **45**, 259-261.

[17] L.X. Chao and L.Z. Long (2015). Analysis of the essential oil of *Illicium henryi* Diels root bark and its insecticidal activity against *Liposcelis bostrychophila* Badonnel, *J Food Prot.* **4**, 636-858.

[18] X.C. Liu, Q.Y. Liu, L. Zhou and Z.L. Liu (2015). Larvicidal activity of essential oil derived from *Illicium henryi* Diels (Illiciaceae) leaf, *Trop J Pharm Res*. **14**, 111-116.

[19] Y. Liu, X.C. Liu, Q.Y. Liu, C. Niu and Z.L. Liu (2015). Larvicidal activity of *Illicium difengpi* BN Chang (Schisandraceae) stem bark and its constituent compounds against *Aedes aegypti* L, *Trop J Pharm Res*. **14**, 103-109.

[20] S.S. Chu, C.F. Wang, S.S. Du, S.L. Liu and Z.L. Liu (2011). Toxicity of the essential oil of *Illicium difengpi* stem bark and its constituent compounds towards two grain storage insects, *J Insect Sci.* **11**, 1-10.

[21] S.C. Dutta, B.N. Saha, M.G. Pathak, P.B. Kanjilal and R.K. Mathur (1997). Essential oil of *Illicium griffithii* Hook. f. & Thorns, *J Essent Oil Res.* **9**, 227-228.

[22] A. Vijayakumar, B. Jeyaraj, M. Karunai Raj, I. V. S. Nimal Christhudas, C. Balachandran, P. Agastian and S. Ignacimuthu (2014). In vitro cytotoxicity, α-glucosidase inhibition, antioxidant, and free radical scavenging activities of *Illicium griffithii* Hook. f. & Thoms fruits, *Med Chem Res.* **23**, 2769-2779.

[23] B. Huang, L. Jie, W. Guowei and Q. Luping (2012). Comparison of the volatile components of *Illicium verum* and *I. lanceolatum* from East China, *J Essent Oil-Bearing Pl*. **15**, 467-475.

[24] C.F. Wang, P. Liu, K. Yang, Y. Zeng, Z.L. Liu, S.S. Du and Z.W. Deng (2011). Chemical composition and toxicities of essential oil of *Illicium fragesii* fruits against *Sitophilus zeamais*, *Afr J Biotch.* **10**, 18179-18184.

[25] S.S. Chu, S.L. Liu, G.H. Jiang and Z.L. Liu (2010). Composition and toxicity of essential oil of *Illicium simonsii* Maxim (Illiciaceae) fruit against the maize weevils, *Rec Nat Prod.* **4**, 205-210.

[26] J.Y. Kim, S.S. Kim, T.H. Oh, J.S. Baik, G. Song, N.H. Lee and C.G. Hyun (2009). Chemical composition, antioxidant, anti-elastase, and anti-inflammatory activities of *Illicium anisatum* (Illiciaceae) essential oil, *Acta Pharm*. **59**, 289-300.

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