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Study on the Chemical Constituents of Essential Oils of Two Annonaceae Plants from Vietnam: *Miliusa sinensis* and *Artabotrys taynguyenensis*

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ABSTRACT
The compositions of essential oils obtained by hydrodistillation of two Annonaceae plants from Vietnam were reported. The essential oils were analysed for their constituents by means of gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectrometry techniques (GC-MS). The principal components of the leaf of *Miliusa sinensis* Fin. & Gagnep were β-caryophyllene (19.5%), δ-selinene (10.3%), caryophyllene oxide (10.1%) α-humulene (7.9%) and β-elemene (7.1%). The major compounds identified in the leaf oil of *Artabotrys taynguyenensis* Ban were valencene (40.1%) along with δ-selinene (8.8%), α-pinene (6.7%), α-muurolene (5.1%) and α-panasinsene (5.1%). However, bicycloelemene (25.1%), bicyclogermacrene (23.7%) and spathulenol (12.8%) were the principal compounds in the stem oil. This is the first report on the volatile constituents of these plant samples.

Keywords: *Miliusa sinensis, Artabotrys taynguyenensis,* essential oil composition, monoterpenes, sesquiterpenes

1. Introduction

In the present paper, the chemical constituents identified in two newly studied plant species were being reported. *Miliusa sinensis* Finet et Gagnep., is a tree that grows up to 6 m tall. Most parts are pubescent and densely when young. The leaf blades are elliptic while the inflorescences are axillaries. The inner petals are purplish red and ovate while the stamens are also apically connected. The flower usually one is pubescent. The seed are 1 or 2 per monocarp. Flowering takes place between April and September while fruiting occurs from July to December [1]. Phytochemical analyses revealed the isolation and characterisation of cytotoxic 4',6'-dihydroxy-2',3',4-trimethoxydihydrochalcone along with pashanone, dihydropashanone, pinostrobin, 5-hydroxy-7, 4'-dimethoxy flavanone, 5-hydroxy-6 ,7-dimethoxy flavanone , 5-hydroxy-7,8-dimethoxyflavanone,3,5-dihydroxy-7,3',4'trimethoxyflavone, liriodenine, 3,5-dihydroxy-7,3',4'-trimethoxyflavone and 24-methylencycloartane-3β,21-diol [2, 3], cytotoxic miliusanes [4], stigmasterol and β-sitosterol glucoside [2].

Artabotrys taynguyenensis Ban is a species of flowering plants. The leaves form alternately. The single flower is hermaphroditic. Flowering occurs between January and May while the fruiting period takes between April and August. This aromatic plant is used for flavouring and in the treatment of fever and inflammation [1].

Till now, there is no record of the chemical composition and biological activities of the essential oils of these plants in the literature. This prompted our interest in the research into their essential oil contents as part of our continued study on the chemical constituents of poorly studied species of Vietnamese plants [5, 6].

2. Materials and methods

2.1 Plants collection

Leaves of *M. sinensis* were harvested from Pù Huống Natural Reserve, NghệAn Province, Vietnam, in May 2013 respectively. Leaves and stem barks of *A. taynguyenensis* were collected from Lâm Đồng Province, Vietnam, in September 2013. Voucher specimens DND 283 and BVT 131 respectively were deposited at the Botany Museum, Vinh University, Vietnam. Plant samples were air-dried prior to extraction

2.2 Extraction of essential oils
0.5 Kg of each plant sample was shredded and the oil was obtained by hydrodistillation for 4 h at normal pressure, according to the Vietnamese Pharmacopoeia [7]. The yield content of the essential oils were 0.25% (v/w; *M. sinensis*, light yellow) and 0.21% (v/w; *A. taynguyenensis* for both the leaf and stem, light yellow and colourless respectively) calculated on a dry weight basis.

2.3 Analysis of the oils
Gas chromatography (GC) analysis was performed on an Agilent Technologies HP 6890 Plus Gas chromatograph equipped with a FID and fitted with HP-5MS column (30 m x 0.25 mm, film thickness 0.25 µm, Agilent Technology, Berkshire, United Kingdom). The analytical conditions were: carrier gas H_2 (1 mL/min), injector temperature (PTV, programmed temperature vaporisation) 250 °C, detector temperature 260 °C, column temperature programmed from 40 °C (2 min hold) to 220 °C (10 min hold) at 4 °C/min. Samples were injected by splitting and the split ratio was 10:1. The volume injected was 1.0 µL. Inlet pressure was 6.1 kPa.
An Agilent Technologies HP 6890N Plus Chromatograph fitted with a fused silica capillary HP-5 MS column (30 m x 0.25 mm, film thickness 0.25 µm) and interfaced with a mass spectrometer HP 5973 MSD was used for the GC/MS analysis, under the same conditions as those used for GC analysis. The conditions were the same as described above with He (1 mL/min) as carrier gas. The MS conditions were as follows: ionization voltage 70 eV; emission current 40 mA; acquisitions scan mass range of 35-350 amu at a sampling rate of 1.0 scan/s.

2.4 Identification of the constituents
The identification of constituents was performed on the basis of retention indices (RI) determined by co-injection with reference to a homologous series of *n*-alkanes, under identical experimental conditions. Further identification was performed by comparison of their mass spectra with those from NIST 08 Libraries (on ChemStation HP) and Wiley 9th Version and the home-made MS library built up from pure substances and components of known essential oils, as well as by comparison of their retention indices with literature values [8, 9].

3. Results & Discussion
Table 1 indicates the identities of forty-seven compounds identified in the oil of *M. sinensis*, accounting for 95.1% of the total oil content. They consist of 11 monoterpene hydrocarbons (5.2%), 3 oxygenated monoterpenes (0.2%), 18 sesquiterpene hydrocarbons (67.1%), 7 oxygenated sesquiterpenes (14.7%), 1 diterpene (0.3%), 2 fatty acids (0.5%) and 4 non-terpenes (6.8%). Sesquiterpenes were the most prominent class of compounds present in the oil. The main constituents of the oil were β-caryophyllene (19.5%), δ-selinene (10.3%) and caryophyllene oxide (10.1%). There were significant amounts of α-humulene (7.9%), β-elemene (7.1%), aromadendrene (6.6%), β-selinene (6.2%) and germacrene D (5.8%).
The authors are aware of only two reports on the volatile oils of the genus *Miliusa*. In an investigation [10], it was reported that *Miliusa traceyi* gave oil in which α-pinene (18.7%), β-pinene (18.6%) and β-caryophyllene (13.5%) were the major components. *Miliusa horsfieldii* comprised mainly of β-caryophyllene (20.2%) and caryophyllene oxide (12.5%), while β-caryophyllene (12.8%), α-humulene (11.3%) and bicyclogermacrene (12.9%) were the principal components of *Miliusa brahei*. However, (*Z*)-citral (41.2%), β-caryophyllene (10.6%) and α-humulene (6.2%) were the main constituents of *Miliusa baillonii* from Vietnam [11]. The high contents of β-caryophyllene and caryophyllene oxide make the composition of the oil similar to that of *M. horsfieldii* from Australia. It was noted that β-caryophyllene featured prominently in this oil of *M. sinensis* as well as other namely *M. traceyi* (13.5%), *M. horsfieldii* (20.2%), *M. brahei* (12.8%) and *M. baillonii* (10.6%) and may therefore be of chemotaxonomic interest.
Monoterpene hydrocarbons (2.6% and 20.2%), oxygenated monoterpenes (0.1% and 0.7%), sesquiterpene hydrocarbons (73.9% and 75.4%) and oxygenated sesquiterpenes (2.7% and 20.8%) were the classes of compound present in the oils of *A. taynguyenensis* (Table 1). The main constituents of the leaf oil were valencene (40.1%) along with δ-selinene (8.8%), α-pinene (6.7%), α-muurolene (5.1%) and α-panasinsene (5.1%). Minor constituents include β-agarofuran (4.0%), α-humulene (3.3%), limonene (3.0%), δ-3-carene (2.4%), α-copaene (2.4%) and β-caryophyllene (2.4%). However, bicycloelemene (25.1%), bicyclogermacrene (23.7%) and spathulenol (12.8%) were the principal compounds in the stem oil. Other notable constituents were β-caryophyllene (4.1%), isospathulenol (3.6%), α-humulene (2.3%), α-copaene (2.2%) and α-calacorene (2.2%). The principal sesquiterpenes of the leaf oil were not identified in the stem bark and vice versa.
Literature information has shown that the main constituents of *Artabotrys pallens* from Vietnam [6] were α-gurjunene (21.9%), α-phellandrene (20.1%) and bicyclolemene (9.6%). *Artabotrys vinhensis* [12] had its main compounds as α-pinene (16.7%), limonene (15.4%), germacrene D (14.4%) and benzyl benzoate (8.8%). The main constituents of *Artabotrys hexapetalus* [13] were caryophyllene oxide (31.5%) and β-caryophyllene (114%). However, spathulenol (13.7%), β-caryophyllene (6.6%), γ-elemene (6.3%) and δ-cadinene (6.3%) were the principal components of *Artabotrys hongkongensis* [14].
It could be seen that the compositional patterns of the oils of *A. taynguyenensis* were quite different from other species

previously reported from Vietnam. Although the identities of the major constituents were quite different, *A. pallens* and *A. vinhensis* were characterised by abundance of monoterpene and sesquiterpene hydrocarbons; *A. hexaplus, A. hongkongensis* and *A. tayngyuenensis* (stem) also had large amounts of sesquiterpene (both hydrocarbons and oxygenated derivatives) while *A. tayngyuenensis* (leaf) was rich in sesquiterpene hydrocarbons only.

Table 1: Compounds identified in the essential oils of Vietnamese Annonaceae

Compounds [a]	**RI** [b]	**RI** [c]	**Percentages**		
			M.s	***A.tl***	***A.ts***
Tricyclene	926	926	-	-	0.1
α-Pinene	939	932	0.4	6.7	0.2
Camphene	953	946	Tr	0.6	0.2
Sabinene	976	969	0.8	-	-
β-Pinene	980	974	-	0.1	-
β-Myrcene	990	988	0.2	1.9	0.1
α-Phellandrene	1006	1002	0.2	1.5	0.1
δ-3-Carene	1013	1008	-	2.4	0.1
α-Terpinene	1016	1014	0.1	1.0	-
β-Phellandrene	1028	1025	0.8	-	-
Limonene	1032	1024	-	3.0	0.2
(*Z*)-β-Ocimene	1043	1032	0.1	0.3	0.5
(*E*)-β-Ocimene	1052	1043	2.4	0.2	0.1
γ-Terpinene	1061	1054	0.1	0.5	-
α-Terpinolene	1090	1086	0.1	1.4	-
Linalool	1100	1095	Tr	0.2	0.1
cis-p-2-Menthen-1-ol	1121	1121	-	0.1	-
allo-Ocimene	1128	1128	-	0.2	0.9
cis-3-Hexenyl isobutyrate	1145	1145	0.3	-	-
Terpinen-4-ol	1177	1176	0.1	-	-
α-Terpineol	1189	1186	-	0.2	-
p-allyl Anisole (Estragole)	1196	1196	-	0.1	-
(*Z*)-3-Hexenyl-2-methylbutanoate	1231	1231	0.6	-	-
Bornyl acetate	1289	1287	0.1	0.1	-
Bicycloelemene	1327	1338	0.8	-	25.1
α-Cubebene	1351	1345	0.1	-	0.1
Cyclosativene	1371	1369	0.1	0.1	0.1
α-Ylangene	1375	1373	0.3	-	-
α-Copaene	1377	1374	-	2.4	2.2
β-Elemene	1391	1389	7.1	0.2	1.1
Cyperene	1399	1398	-	0.1	0.2
α-Cedrene	1410	1412	-	0.2	-
α-Gurjunene	1412	1409	0.3	-	-
β-Caryophyllene	1419	1417	19.5	2.4	4.1
β-Gurjunene	1431	1431	-	0.9	0.2
trans-α-Bergamotene	1435	1434	-	0.2	0.6
γ-Elemene	1437	1434	-	-	1.7
α-Guaiene	1440	1439	0.5	-	-
Aromadendrene	1441	1439	6.6	-	1.5
α-Humulene	1454	1452	7.9	3.3	2.3

β-Agarofuran	1474	1474	-	4.0	0.1
β-Chamigrene	1476	1476	-	0.1	-
γ-Selinene	1484	1483	-	1.4	-
Ledene	1485	1482	-	-	1.1
Germacrene D	1485	1485	5.8	-	1.7
α-Amorphene	1485	1484	0.2	0.3	0.3
δ-Selinene	1486	1485	10.3	8.8	-
β-Selinene	1489	1489	6.2	0.7	-
Valencene	1490	1490	-	40.1	-
β-Guaiene	1491	1491	0.1	-	0.3
cis-Cadina-1,4-diene	1496	1495	-	0.2	0.9
α-Muurolene	1500	1500	-	5.1	-
Bicyclogermacrene	1500	1500	-	-	23.7
γ-Cadinene	1514	1513	-	-	1.5
α-Panasinsene	1518	1518	-	5.1	-
δ-Cadinene	1525	1522	0.8	-	1.2
α-Calacorene	1546	1544	-	0.1	2.2
Germacrene B	1557	1559	-	0.5	1.8
Cadala-1(10),3,8-triene	1562	1562	0.3	-	-
(*E*)-Nerolidol	1563	1561	0.2	0.1	0.6
Spathulenol	1579	1577	2.4	-	12.8
Caryophyllene oxide	1583	1582	10.1	0.5	-
Viridiflorol	1593	1592	1.4	-	1.1
β-Oplopenone	1608	1607	-	-	0.6
5-*epi*-Neointermedeol	1636	1637	-	0.9	-
Isospathulenol	1639	1639	-	-	3.6
α-Cadinol	1653	1652	-	1.2	1.2
α-Santalol	1671	1672	-	-	0.6
Ledene oxide II	1680	1682	0.2	-	-
α-Bisabolol	1683	1685	-	-	0.3
Mint sulphide	1741	1741	0.1	-	-
α-Cyperone	1706	1746	0.2	-	-
Benzyl benzoate	1760	1759	-	0.3	1.1
9,10-dehydro-Isolongifolene	1798	1796	0.2	-	-
1,2-Benzenedicarboxylic acid	1917	1917	4.0	-	-
n-Hexadecanoic acid	1982	1980	0.4	-	-
Phytol	2125	1947	0.3	-	-
Octadecanoic acid	2188	2200	0.1	-	-
(*Z*)-9-Octadecamide	2398	2398	1.9	-	-
TOTAL			**95.1**	**99.3**	**98.5**
Monoterpene hydrocarbons			**5.2**	**20.2**	**2.6**
Oxygenated monoterpenes			**0.2**	**0.7**	**0.1**
Sesquiterpene hydrocarbons			**67.1**	**75.4**	**73.9**
Oxygenated sesquiterpenes			**14.7**	**2.7**	**20.8**
Diterpenes			**0.3**	**-**	**-**
Fatty acids			**0.5**	**-**	**-**
Non terpenes			**6.8**	**0.3**	**1.1**

4. Conclusions

For the first time, the compositions of the leaf essential oils of the Vietnamese grown *M. sinensis* as well those of the leaf and stem of *A. tayngusyenensis* were elucidated. Although, ubiquitous terpenes were identified in all the samples, each species has its own compositional pattern different from other members of the genus. It is well known that variation exists between the chemical constituents in different plant parts. This and other factors such as the age of the plant, handling procedure, ecological and climatic conditions etc. may have been responsible for the observed differences in the chemical compounds identified in the species of each genus.

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