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Essential oil constituents of *Desmos cochinchinensis* Lour, and *Polyalthia longifolia* var. *Pendula* Hort from Vietnam

Tran Dinh Thang[1, *], Do Ngoc Dai[2], Tran Minh Hoi[2], Isiaka A. Ogunwande[3, *]

[1]Faculty of Chemistry, Vinh University, 182-Le Duan, Vinh City, Nghe An Province, Vietnam
[2]Faculty of Biology, Vinh University, 182-Le Duan, Vinh City, Nghe An Province, Vietnam
[3]Natural Products Research Unit, Department of Chemistry, Faculty of Science, Lagos State University, Badagry Expressway, Ojo, Lasu Post office, Ojo, Lagos, Nigeria

Email address:
thangtd@vinhuni.edu.vn (T. D. Thang), daidn23@gmail.com (D. N. Dai), isiaka.ogunwande@lasu.edu.ng (I. A. Ogunwande), tran.minhhoi@yahoo.com (T.M. Hoi)

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Abstract: The essential oils obtained by hydrodistillation from two Annonaceace plants from Vietnam were analysed by gas chromatography (GC) coupled with mass spectrometry (GC/MS). The main conpounds identified in bark oil of *Polyalthia longifolia* var. *pendula* Hort were zingiberene (26.7%), β-caryophyllene (11.1%) and β-bisabolene (7.9%). The major compounds in the flower oil of *Desmos cochinchinensis* Lour., were the monoterpenoids camphor (59.1%), limonene (8.9%), α-pinene (8.6%) and camphene (6.0%).

Keywords: Annonceae, *Desmos Cochinchinensis*, *Polyalthia Longifolia* var. *Pendula*, Essential Oils, GC/MS, Terpenoids

1. Introduction

In continuation of our studies on the volatile oil composition of Vietnamese flora [1], we report herein the essential oil constituents of two species in the Annonanaceae family. *Desmos* Lour., is a small genus in the family Annonaceae. About 25-30 species are endemic to tropical and subtropical Asia. *Desmos cochinchinensis* Lour., or Dwarf Ylang Ylang shrub, is a spreading shrub that likes shady places and may develop into a higher climber. The flowers open between April and July. Young flowers are green and inconspicuous. Only mature yellow flowers have strong lemon-like fruity scent that can be detected at a distance, especially during the evenings. *D. cochinchinensis* as a folk medicine is used for treatment of malaria in China [2]. Studies have shown that the plant is a source of biologically active compounds [3]. There are relatively fewer studies on the analyses of the content and composition of flower essential oil from Desmos species. Trans-caryophyllene (56.2%) and spathulenol (61.5%) respectively were the main compounds identified in the young and ripened flowers of D. cochinchinensis [4]. β-Caryophyllene (28.9%), bicyclogermacrene (11.5%), α-humulene (7.2%), germacrene D (7.2%) and β-elemene (6.4%) occurred in higher amounts in *Desmos chinensis* [5]. Most studies have focused on the leaf oil constituents of *Desmos* species [6-8].

A handsome ornamental of the family is the weeping form of the mast tree, *Polyalthia longifolia* var. *pendula* Hourt. Its shining, brilliant green, willowy, wavy-edged leaves hang from pendant branches that almost clasp the tall, straight trunk. The leaves are used as temple decorations in India. It is a lofty evergreen tree, commonly planted due to its effectiveness in alleviating noise pollution. It exhibits symmetrical pyramidal growth with willowy weeping pendulous branches and long narrow lanceolate leaves with undulate margins. The tree is known to grow over 30 ft in height. Extracts and compounds isolated from the plants have been reported to possess a number of biological activities [9, 10]. There is only one literature information on its volatile oil components [11].

2. Materials and Methods

2.1. Plants Collection

The stem barks of *P. longifolia* var. *pendula* were obtained from Thanh Hóa Province, Vietnam, in September 2011.

However, the flower of *D. cochinchinensis* were harvested from Vũ Quang, National park, Hà Tĩnh Province, Vietnam, in September 2011. Voucher specimens DND 63 and, DND 195 respectively for *D. cochinchinensis* and *P. longifolia* var. *pendula* have been deposited at the Botany Museum Vinh University, Vietnam, for future references.

2.2. Extraction of the Oils

About 0.5 kg of air-dried sample of each plant was shredded and their oils were obtained by hydrodistillation for 3h at normal pressure, according to the Vietnamese Pharmacopoeia [12]. The plant samples yielded a low content of essential oils: 0.15% (v/w; *D. cochinchinensis*); and 0.10% (v/w; *P. longifolia* var. *pendula* stem bark), calculated on a dry weight basis. Both oils were h light yellow in colouration.

2.3. Analysis of the Oils

About 15 mg of each oil sample, which was dried with anhydrous sodium sulfate, was dissolved in 1mL of hexane (for spectroscopy or chromatography). Gas chromatography (GC) analysis was performed on Agilent Technologies HP 6890 Plus Gas chromatograph equipped with a FID and fitted with HP-Wax and HP-5MS columns (both 30 m x 0.25 mm, film thickness 0.25 µm, Agilent Technology). The analytical conditions were: carrier gas H_2 (3 mL/min), injector temperature (PTV) 250 ^oC, detector temperature 260 ^oC, column temperature programmed 60 ^oC (2 min hold) to 220 ^oC (10 min hold) at 4 ^oC/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 column HP-5 MS column (30 m x 0.25 mm, film thickness 0.25 µm) and interface with a mass spectrometer HP 5973 MSD was used for the GC/MS analysis, under the same condition for GC analysis. The conditions were the same as described above with He (3 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. The MS fragmentation patterns was checked with those of other essential oils of known composition patterns with Wiley (Wiley 9th Version), NIST 08 Libraries (on ChemStation HP), with those in the literature and also with standard substances.

2.3.1. Identification of the Constituents

The identification of constituents was performed on the basis of retention indices (RI) determined with reference to the homologous series of n-alkanes, under identical experimental conditions, co-injection with standards (Sigma-Aldrich, St. Louis, MO, USA) or known essential oil constituents, MS library search (NIST 08 and Wiley 9th Version), and by comparing with MS literature data [13-15]. The relative amounts of individual components were calculated based on the GC peak area (FID response) without using correction factors.

3. Results and Discussion

The chemical composition of the oils is summarized in Table 1. Monoterpenes (95.1%) were the dominant class of compound identified in *D. cochinchinensis*. Camphor (59.1%) was the most singly abundant compound of these monoterpenoids. Other significant ones included limonene (8.9%), α-pinene (8.6%) and camphene (6.0%). Sesquiterpenes compound have been identified in flower oil from a previous studies on this species [4] and *D. chinensis* [5]. Among these, β-caryophyllene, bicyclogermacrene, α-humulene and germacrene D are common compounds identified in the two reports.

Sesquiterpenes, represented by zingiberene (26.7%), β-caryophyllene (11.1%) and β-bisabolene (7.9%) were the dominant class of compound of *P. longifolia* var. *pendula*. In a previous study [11], high quantities of δ-cadinene (24.5%), zingiberene (19.6%) and aromadendrene (119.1%) were identified in the oil. However, δ-cadinene was conspicuously absent in our result while caryophyllene was identified in low quantity in previous study [11].

From Table 2, four chemical forms of the oils of *Polyalthia* species may be proposed. These are oils with abundant of sesquiterpene hydrocarbons as could be seen in *P. longifolia* var. *pendula* [11], *P. longifolia* [16], *P. suaveolens* [17] and P. nitidissima [18]; oils relative amounts of hydrocarbon and oxygenated sesquiterpenes as exemplified by *P. australis* and *Polyalthia* sp. (Wyvuri B.P.) [18]; oils dominated by oxygenated sesquiterpenes as seen in *P. michaelii* [18]; oils consisting of monoterpene hydrocarbons which are found in the fruit of *P. suaveolens* [17] and *P. nitidissima* [18].

Table 1. *Percentage of compounds identified in the oil samples.*

Compounds	RI [a]	LRI [b]	*D.c*	*P.l*
Tricyclene	926	921	0.1	0.2
α-Thujene	931	924	0.6	-
α-Pinene	939	932	8.6	5.7
Camphene	953	946	6.0	1.8
Sabinene	976	959	0.8	0.1
β-Pinene	980	974	-	0.1
β-Pinene	990	988	3.8	1.7
α-Phellandrene	1006	1002	1.3	Tr
δ-3-Carene	1011	1008	0.1	-
α-Terpinene	1017	1014	0.2	Tr

Compounds	RI [a]	LRI [b]	*D.c*	*P.l*
ρ-Cymene	1026	1020	0.5	Tr
Limonene	1032	1024	8.9	0.4
1,8-Cineole	1034	1026	1.5	-
(*Z*)-β-Ocimene	1043	1032	-	0.1
(*E*)-β-Ocimene	1052	1044	0.1	2.2
γ-Terpinene	1061	1054	0.4	0.1
cis-Sabinene hydrate	1070	1065	0.1	-
α-Terpinolene	1089	1086	1.0	0.1
2-Nonanone	1090	1087	-	Tr
Linalool	1100	1095	0.1	Tr
allo-Ocimene	1128	1128	-	0.1
Camphor	1146	1141	59.1	-
1-Nonene [d]	1149	-	-	0.2
Borneol	1169	1165	0.4	-
Terpinen-4-ol	1177	1175	0.5	-
α-Terpineol	1189	1186	0.6	-
Bornyl acetate	1289	1287	0.4	1.6
Bicycloelemene	1327	1338[c]	-	Tr
Neryl acetate	1362	1359	-	0.1
α-Ylangene	1375	1373	-	0.1
α-Copaene	1377	1374	-	0.1
β-Elemene	1391	1389	0.1	0.1
Longifolene	1408	1407	-	Tr
α-Cedrene	1412	1410	-	0.2
β-Caryophyllene	1419	1417	0.2	11.1
γ-Elemene	1435	1432	-	1.7
trans-α-Bergamotene	1437	1434	Tr	-
α-Guaiene	1440	1437	-	0.1
Aromadendrene	1441	1439	-	5.7
α-Humulene	1454	1452	-	4.4
(*E*)-β-Farnesene	1457	1454	-	3.0
ar-curcumene	1481	1479	-	1.9
γ-Curcumene	1483	1481	-	1.4
Germacrene D	1486	1484	0.2	-
β-Selinene	1490	1489	0.4	0.8
Zingiberene	1494	1493	-	26.7
Cadina-1,4-diene	1496	1495	-	0.1
α-Selinene	1498	1498	-	2.2
β-Bisabolene	1505	1505	-	7.9
(*E,E*)-α-Farnesene	1506	1505	-	0.3
cis-α-Bisabolene	1507	1506	-	0.7
γ-Cadinene	1514	1513	-	0.2
trans-γ-Bisabolene	1515	1514	-	0.3
cis-(Z)-α-Bisabolene epoxide [d]	1515	-	-	0.6
β-Sesquiphellandrene	1523	1521	-	1.6
δ-Cadinene	1525	1522	Tr	-
α-Calacorene	1546	1544	-	0.1
Germacrene B	1561	1559	0.1	-
(*E*)-Nerolidol	1563	1561	-	0.1
Palustrol	1566	1567	-	0.6
α-Caryophyllenyl alcohol	1572	1570	-	1.1
Spathulenol	1576	1577	-	0.1
Caryophyllene oxide	1583	1582	-	1.3
Globulol	1585	1590	-	0.9
Viridiflorol	1593	1592	-	0.4
allo-Aromadendrene	1641	1639	-	0.5

Compounds	RI [a]	LRI [b]	*D.c*	*P.l*
α-Muurolol	1644	1644	-	0.4
τ-Cadinol [d]	1659	-	-	0.8
α-Bisabolol	1686	1685	-	0.8
(*Z,Z*)-Farnesol	1718	1724	-	1.3
Benzyl benzoate	1760	1759	Tr	-
Eicosane	2000	2000	-	Tr
Abietatriene	2057	2055	-	Tr
Total			96.1	94.1
Monoterpene hydrocarbons			62.7	12.6
Oxygenated monoterpenes			32.4	1.2
Sesquiterpene hydrocarbons			1.0	72.0
Oxygenated sesquiterpenes			-	8.3
Diterpenes			-	Tr
Others			Tr	0.2

[a] Retention indices on HP-5MS column; [b] Literature retention indices (Adams, 2007, see Experimental); [c] Retention indices from Joulain and Koenig (see Experimental); [d] Identification by MS pattern, column retention indices and use of authentic home- made spectral; Tr, trace amount < 0.1%; - not identified and not found in Literature reference; D.c = Desmos cochinchinensis; P.l = Polyalthia longifolia var. pendula

Table 2. *Chemical forms of essential oils of P. longifolia species*

Chemical forms	Species	Major components	Origin	Ref
Oils with abundance of sesquiterpene hydrocarbons	*P. longifolia* var. *Pendula*	β-caryophyllene (30.0%), zingiberene (21.7%), aromadendrene (15.2%) and β-selinene (9.1%)	Vietnam	**This study**
	,,	δ-cadinene (24.5%), zingiberene (19.6%) and aromadendrene (19.1%)	"	11
	P. longifolia	allo-aromadendrene (19.7%), caryophyllene oxide (14.4%), and β-caryophyllene (13.0%)	Nigeria	16
	P. longifolia [a]	α-copaene/ α-muurolol (ca. 8.7%), β-selinene (8.6%), viridiflorene (8.1%), α-guaiene (7.8%) and allo-aromadendrene/δ-cadinene (ca.7.4%)	"	"
	P. suaveolens	β-caryophyllene and humulene (both 34%)	Gabon	17
Oils with relative amounts of hydrocarbon and oxygenated sesquiterpenes	*P. nitidissima* [#]	β-caryophyllene, aromadendrene, germacrene D, bicyclogermacrene, δ-cadinene, and spathulenol	Australia	18
	P. australis [#]	β-caryophyllene, germacrene D, bicycligermacrene, caryophyllene oxide and spathulenol	"	"
	Polalthia sp. (Wyvuri B.P.) [#]	γ-elemene, germacrene D, bicycolgermacrene, germacrene B, ledol, globulol and spathulenol.	"	"
Oils dominated by oxygenated sesquiterpenes	*P. michaelii* [#]	spathulenol	"	"
Oils consisting of monoterpene hydrocarbons	*P. nitidissima* [#]	α-pinene, limonene and (E)-β-ocimene	"	"
	P. suaveolens [#, b]	myrcene, β-pinene and limonene	Gabon	17

[a]Stem bark sample ; [b] Fruit sample; Others are from the leaves; [#] Quantitative data not available

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