CHEMICAL COMPOSITION OF THE ESSENTIAL OIL OF *MILIUSA BAILLONII* PIERRE (ANNONACEAE) FROM VIETNAM

TRAN MINH HOI
Institute of Ecology and Biological Resources
DO NGOC DAI, TRAN DINH THANG
Vinh University
NGUYEN XUAN DUNG
Hanoi National University

ABSTRACT: The leaf oil of *Miliusa baillonii* Pierre (Annonaceae) collected of Phong Nha - Ke Bang national park, Vietnam, in March 2007 was isolated by steam distillation to give oil yield 0.15% and analyzed by Capillary GC and GC/MS. Forty six components have been identified accounting more than 92.8% of the oil. The major constituents of this oil appeared to be z-citral (41.2%), β-caryophyllene (10.6%) and α-humulene (6.2%).

The genus *Miliusa* Lechen ex A. DC. comprises about 50 species that are widely distributed through the Indian subcontinent, Burma, Indo-China, Malaysia and Australia [1, 2]. The different species of *Miliusa* are invariably small to large trees and are found in a wide range of rainforest communities. Whilst the phylogeny of the Annonaceae remains to be satisfactorily resolved, *Miliusa* is thought to be allied to the genera *Orophea* Blume, *Mezzettiopsis* Ridley, *Plioenicanthus* Alston, *Alphonsae* Hook. f. & Thorns., *Platymitra* Boerl. and *Mezzettia* Becc. [2, 3]. Only three species of *Miliusa* occur in Australia, with two essential oil these being endemic [4]. Some extra species of *Miliusa* have been reported to contain alkaloids.

Two new isoquinoline alkaloids, 2,10-dimethoxy-3,11-dihydroxy-5,6-dihydroprotober -berine and 1,9-dihydroxy-2,11 -dimethoxy-4,5-dihydro-7-oxoaporphine, together with thirteen known alkaloids, were isolated from the ethanolic extracts of the stem and leaves of *M. cuneata* (Graib) [4]. Selective toxicity was also observed for 10-methoxyliriodenine (lauterine) and 10-hydroxyliriodenine, two oxoaporphine alkaloids isolated from *M. banacea* [5]. Until now only 6 *Miliusa*, *M. baillonii, M. balanse*, *M. banpoientes*, *M. campanulata*, *M. sinensis* and *M. velutima* were found in Vietnam [7].

The leaf oil obtained from *M. traceyi* contained a mixture of mono- and sesquiterpenes. The principal monoterpenes were the hydrocarbons α-pinene (10-19%) and β-pinene (13-19%). The only other monoterpene present at > 1% was limonene (2-4%). While the usually encountered monoterpene hydrocarbons were present, they did not account individually for more than 0.3%. A large number of sesquiterpenes were present in the oil, but only a few accounted for more than 5%. The main members were β-caryophyllene (9-14%), germacrene D (4-6%), bicyclogermacrene (3-10%) [6].

Miliusa horsfield presented leaf oil which was essentially sesquiterpenic. The full suite of monoterpene hydrocarbons were present, but in total accounted for less than 2%. The major sesquiterpenes encountered in the leaf oil were α-copaene (5-8%), β-caryophyllene (12-21%), α-liuinulciie (3-4%), α-and β-selincne (each t-3%), bicyclogerniacrene (2-4%), δ-cadinene (3-5%) and caryophyllene oxide (12-15%). Unidentified oxygenated sesquiterpenes accounted for up to 10% of the oil. The oil yield, based on fresh leaves, was 0.1% [6].

Miliusa braliei gave oil in which sesquiterpenes predominated to a very large extent. The major sesquiterpenes encountered were β-caryophyllene (10-25%), α-humulene (10-13%), germacrene D (1-6%), α- and β-selinene (both 1-3%), bicyclogermacrene (0.7-13%), globulol (3-7%), viridiflorene (1-3%), spathulenol (3-5%) and caryophyllene oxide (1-5%). The major monoterpenes detected were (Z)-β-ocimene (0.4-3%), linalool (0.6-8%, the majority being > 5%), α-terpineol (3-7%), geraniol (1-3%) and geranyl acetate (0.1-0.3%). It is, presumably, these latter oxygenated monoterpenes which are responsible for the 'raspberry jelly tree' name given to the species that pertains to the smell of the crushed foliage [6].

M. baillonii Pierre 15-30 m tall, is found in Dak Lak, Dong Nai, An Giang, Quang Binh (Phong Nha - Ke Bang) and Cambodia [6].

To the best of our knowledge, nothing is known about the chemical composition of essential oil of *M. baillonii*. For this reason, the objective of this study is to identify the volatile constituents (of the leaf oil) of *Miliusa baillonii* from Phong Nha - Ke Bang national park, Vietnam.

I. EXPERIMENTAL

1. ***Source*** - The leaves of *Miliusa baillonii* were collected in April 2007, in Phong Nha - Ke Bang national park, Quang Binh province and identified by Assoc. Prof. Dr. Vu Xuan Phuong of Institute of Ecology and Biological Resources. A voucher specimen (DD110) was deposited at the Herbarium of the Institute of Ecology and Biological Resources, Vietnamese Academy of Science and Technology.

Fresh leaves were shredded and their oil was obtained by steam distillation for 3h at normal pressure, according to the Vietnamese Pharmacopoeia [8]. The yield of the fresh leaf oil was 0.15%.

2. ***GC-*** About 15mg of oil, which was dried with anhydrous sodium sulfate, was dissolved in 1 ml of n-hexane (for spectroscopy or chromatography).

GC analysis was performed on an Agilent Technologies HP 6890 Plus Gas chromatograph equipped with a FID and fitted with HP-5MS column (L = 30 m, ID = 0.25 mm, film thickness = 0.25μm). The analytical conditions were: carrier gas H_2, injector temperature (PTV) 250°C, detector temperature 260°C, temperature programmed 60° (2 min hold) to 220° (10 min hold) at 4°C/min.

3. ***GC/MS-*** An Agilent Tech HP 6890 N Plus Chromatograph was fitted with a fused silica capillary col. HP-5MS column (L = 30 m, ID = 0.25 mm, film thickness = 0.25 μm). The condition of use were 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. Component identification was carried out by comparing MS data with those reported in Library Willey on Chemstation HP, and in some cases substances identified from oils known composition and also with standard substances [9-12].

II. RESULTS AND DISCUSSION

Table 1

Chemical constituent of essential oil of *Miliusa baillonii* Pierre from Phong Nha - Ke Bang national park, Vietnam

N°	Compounds	KI	%FID
1	6-methyl-5-hepten-2-one	978	0.7
2	myrcene	990	0.2
3	limonene	1032	0.4
4	furan (perillene)	1037	0.3
5	(E)-β-ocimene	1052	0.7
6	α-terpinolene	1090	1.5
7	linalool	1100	2.7
8	alloocimene	1128	0.1

9	cis verbenol	1141	0.2
10	cis-carveol	1229	0.2
11	geraniol	1253	0.5
12	**z-citral**	**1318**	**41.2**
13	bicycloelemene	1327	1.1
14	α-cubebene	1351	0.3
15	α-longipinene	1353	0.1
16	α-ylangene	1375	0.1
17	α-copaene	1377	0.3
18	α-copaene	1377	0.3
19	β-cubebene	1388	0.3
20	isolongifolene	1390	1.2
21	β-elemene	1391	3.5
22	β-elemene	1391	0.7
23	isocaryophyllene (bicyclo[7.2.0]undec-4-ene)	1409	2.6
24	**β-caryophyllene**	**1419**	**10.6**
25	calarene	1434	0.2
26	γ-elemene	1437	1.0
27	aromadendrene	1441	1.0
28	**α-humulene**	**1455**	**6.2**
29	dehydroaromadendrene	1463	0.2
30	naphthalene	1464	1.0
31	germacrene D	1485	1.2
32	cadina-1,4-diene	1496	0.2
33	(E,E)-α-farnesen	1508	0.4
34	δ-cadinene	1525	1.4
35	(Z)-nerolidol	1533	0.2
36	α-cadinene	1539	0.1
37	elemol	1550	1.7
38	germacrene B	1561	1.2
39	Ledol	1569	0.3
40	spathoulenol	1578	1.4
41	viridiflorol	1593	0.6
42	Guaiol	1601	0.2
43	allo aromadendrene	1641	0.3
44	τ-muurolol	1646	3.8
45	calamenene	1702	0.3
46	Lanceol	1761	0.1

Note: trace < 0.1%; KI: Kovas Index.

The leaf oil of *Miliusa baillonii* Pierre was isolated by steam distillation to give oil yield 0.15% and analyzed by Capillary GC and GC/MS. Forty six components have been identified accounting more than 92.8% of the oil. The major constituents of this oil appeared to be z-citral (41.2%), β-caryophyllene (10.6%), α-humulene (6.2%).

Less predominant constituents included τ-muurolol (3.8%), β-elemene (3.5%), linalool (2.7%), isocaryophyllene (2.6%), elemol (1.7%), α-terpinolene (1.5%), spathoulenol (1.4%), δ-cadinene 1.4%), isolongifolene (1.2%), germacrene B (1.2%), germacrene D (1.2%) and bicycloelemene (1.1%). All the other components were in concentration of less

than 0.1-1.0%.

III. CONCLUSIONS

The leaf oil of *Miliusa baillonii* Pierre collected from Phong Nha - Ke Bang national park, Quang Binh province in April 2007 was isolated by steam distillation to give oil yield 0.15% and analyzed by Capillary GC and GC/MS. Forty six components have been identified accounting more than 92.8% of the oil. The major constituents of this oil appeared to be z-citral (41.2%), β-caryophyllene (10.6%), α-humulene (6.2%).

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THÀNH PHẦN HÓA HỌC TINH DẦU LÁ LOÀI MẠI LIỄU BAILONI (*MILIUSA BAILONIII* PIERRE) Ở VIỆT NAM

TRẦN MINH HỢI, ĐỖ NGỌC ĐÀI, TRẦN ĐÌNH THẮNG, NGUYỄN XUÂN DŨNG

TÓM TẮT

Nghiên cứu thành phần hoá học tinh dầu lá loài mại liễu bailloni (*Miliusa bailonii* Pierre). Thu tại Vườn quốc gia Phong Nha - Kẻ Bàng vào tháng 3 năm 2007. Hàm lượng tinh dầu theo nguyên liệu tươi là 0,15%. Bằng phương pháp sắc ký khí (GC) và sắc ký khí khối phổ liên hợp (GC/MS) hơn 50 hợp chất đã được tách ra, trong đó đã xác định được 46 hợp chất (chiếm 92,8% tổng hàm lượng tinh dầu). Thành phần chính tinh dầu của lá là z-citral (41,2%), β-caryophyllen (10,6%), α-humulen (6,2%).

Ngày nhận bài: 4-9-2010