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Essential oils of *Cinnamomum curvifolium* (Lour.) Nees and *Cinnamomum mairei* H. Lev

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Abstract
In this work, the stem bark and leaf essential oils of two Vietnamese species of the genus *Cinnamomum* were analyzed by gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC/MS). The results showed that *Cinnamomum curvifolium* (Lour.) Nees afforded oils dominated by α-copaene (14.2%) and 1,8-cineole (10.0%) in the stem bark as well as β-pinene (23.8%), sabinene (14.0%) and camphene (12.1%) in the leaf. The stem bark and leaf oils of *Cinnamomum mairei* H. Lev had an abundance of α-pinene (15.5% and 13.1%), 1,8-cineole (14.6% and 23.1%) and β-pinene (10.5% and 9.0%) respectively.

Keywords: *Cinnamomum curvifolium, Cinnamomum mairei*, Essential Oil, Terpenes

1. Introduction
Cinnamomum is a genus of evergreen aromatic trees and shrubs belonging to the family, Lauraceae. The genus contains over 300 species, distributed in some regions of the world [1]. The chemical constituents of essential oils some species grown in Vietnam have been published. The volatile contents are usually monoterpenes and sesquiterpenoid compounds of diverse structural patterns [2-5]. For example, *C. sericans* leaf consists mainly of sesquiterpenes spathulenol (14.5%), caryophyllene oxide (9.3%) while the leaf oil of *C. magnificum* contained sesquiterpenes bicyclogermacrene (33.9%) and β-caryophyllene (25.5%)[2]. Monoterpenes such as *ρ*-cymene (15.6%) and limonene. (13.9%) dominated in *C. durifolium* [2]. In this paper we report the volatile oils compositions from *Cinnamomum curvifolium* (Lour.) Nees and *C. mairei* H. Lev, growing in Vietnam. The plant of *C. curvifolium* is harvested from the wild for local use as a medicine and source of essential oil. The bark and roots are used in the treatment of abdominal pain [6]. The authors are aware of one report each on the volatile oils of *C. curvifolium* and *C. mairei* [3].

2. Materials and methods
2.1 Collection and authentication of plant sample
The leaves and stem bark of *C. curvifolium* and *C. mairei* were collected from each different trees growing at Pù Huống Natural Reserve, Nghệ An Province, Vietnam, in August 2013. Voucher specimens PHM15 and PHM9 respectively have been deposited at the Botany Museum, Vinh University, Vietnam.

2.2 Preparation of sample
Prior to hydrodistillation, the leaves and stem barks of the plants were air-dried (17^0C, without washing with water) under laboratory shade for two weeks to reduce the moisture contents. In addition, sediments and other unwanted materials were separated from the samples. Afterwards, samples were pulverized to coarse powder using a locally made grinder.

2.3 Hydrodistillation of essential oil
A total of 500 g of the pulverized plant samples of *C. curvifolium* and *C. mairei* were used for the experiment at different time. Known weight of samples was separately and carefully introduced into a 5-L flask and distilled water was added until it covered the sample completely. Essential oils were obtained by hydrodistillation procedure which was carried out in an all glass Clevenger-type distillation unit designed according to Vietnamese

Pharmacopoeia [7] as described previously [1, 5, 6]. All experiments were done in triplicate. The distillation time was 3 h and conducted at normal pressure. The volatile oils distilled over water and were collected by running through the tap in the receiver arm of the apparatus into clean and previously weighed sample bottles. The oils were kept under refrigeration (4 ºC) until the moment of analyses as described previously [2-5].

2.4 Analysis of the oil sample

The gas chromatography (GC) analysis of the essential oil was actualised using an Agilent Technologies HP 6890 Plus Gas chromatograph containing Flame Ionization Detector, fused with HP-5MS column (dimensions: 30 m x 0.25 mm; film thickness 0.25 µm). He (1 mL/min) was used as carrier gas. The inlet pressure was 6.1 kPa. The injector and detector temperatures were maintained at 250 ºC and 260 ºC respectively. The analysis was done by column temperature programmed starting from 40 ºC (2 min hold) and ending at 220 ºC (10 min hold) at 4 ºC/min. The volume of the sample injected was 1.0 µL and injection was done at the split ratio of 10:1. Each analysis was performed in triplicate. The relative amounts of individual components were calculated based on the normalized GC peak area (FID response).

For the experiment on gas-chromatograph-mass spectrometry analysis, a HP 6890N Plus gas chromatograph interfaced with a mass spectrometer HP 5973 MSD was used. The column employed was HP-5 MS (fused capillary, dimension: 30 m x 0.25 mm; film thickness 0.25 µm). The condition for the gas chromatograph was as described above. The conditions used for the Mass Spectrometry were ionization voltage of 70 eV, with mission current 40 mA. The acquisitions scan mass range of 35-350 amu at a sampling rate of 1.0 scan/s was maintained throughout the experiment.

2.5 Identification of the oil constituents

The identification of constituents from the GC/MS spectra of *C. curvifolium* and *C. mairei* was performed on the basis of retention indices (RI) determined with reference to a homologous series of *n*-alkanes (C_6-C_{40}), under identical experimental conditions. In some cases, co-injection with known compounds or standards (Sigma-Aldrich, St. Louis, MO, USA) under the same GC conditions was employed. The mass spectral (MS) fragmentation patterns were checked with those of other essential oils of known composition (NIST 08 Libraries) [8] and with those in the literature as described previously [2-5].

3. Results & Discussion

The volatile compounds were displayed in Table 1, along with their percentages and retention indices calculated on a HP-5MS column. The yields of the essential oils from *C. curvifolium* were 0.73% and 0.32% (v/w) for the stem bark and leaf respectively. Quantitative amounts of monoterpene hydrocarbons (17.3%), oxygenated monoterpenes (15.2%), sesquiterpene hydrocarbons (31.2%) and oxygenated sesquiterpenes (28.1%) were identified in the bark oil of *C. curvifolium*. The main compounds of the oil were α-copaene (14.2%) and 1,8-cineole (10.0%). There are significant amounts of α-pinene (6.4%), δ-cadinene (5.9%), τ-cadinol (5.7%) and α-santalol (5.7%). On the other hand, monoterpene hydrocarbons (61.2%) and oxygenated monoterpenes (22.1%) constituted the bulk of the leaf oil of *C. curvifolium*. In addition, β-pinene (23.8%), sabinene (14.0%) and camphene (12.1%) were the present in higher quantity in the leaf oil. Moreover, (*E*)-cinnamaldehyde (8.9%) and *cis*-geraniol (7.3%) were also identified in sizeable amount. It should be noted that compounds such as benzyl cinnamate, benzyl benzoate, hexadecanoic acid and tetradecanol that were found in previous study on the leaf oil [3] were not identified in the present oil sample. The compositions of the bark oil are being reported for the first time.

C. mairei afforded yellow oils obtained in yields of 0.46% and 0.24% (v/w) for the stem bark and leaf. We have identified significant amounts of monoterpene hydrocarbons (46.4%), oxygenated monoterpenes (30.0%) and sesquiterpene hydrocarbons (15.2%) in the stem bark oil of *C. mairei*. The oil was devoid of any oxygenated sesquiterpene compounds. The major constituents of the oil were α-pinene (15.5%), 1,8-cineole (14.6%) and β-pinene (10.5%), along with sizeable amounts of α-copaene (7.5%), (*E*)-cinnamaldehyde (6.5%) and δ-3-carene (4.6%). In the same vein, monoterpene hydrocarbons (40.6%), oxygenated monoterpenes (36.5%) and sesquiterpene hydrocarbons (14.5%) in the leaf oil of *C. mairei*. The dominant compounds were1,8-cineole (23.1%), α-pinene (13.1%) and β-pinene (9.0%). It should be noted that compounds such as eugenol, eugenol acetate and neryl acetate that were found in previous study on the leaf oil [3], were not identified in the present oil sample. Also, the content of 1,8-cineole was also much higher than the previous study. The compositions of the bark oil are being reported for the first time.

Table 1: Compounds identified in the essential oil of studied *Cinnamomum*

Sr. No	Compounds[a]	RI[b]	RI[c]	*C. curvifolium*		*C. mairei*	
				Stem bark	Leaf	Stem bark	Leaf
1	1-Methyl-cyclopentanol	820		-	-	3.3	3.5
2	α-Pinene	939	932	6.4	0.6	15.5	13.1
3	Camphene	953	946	0.6	12.1	1.7	1.9
4	β-Thujene	968	964	2.1	4.9	1.3	1.2
5	Sabinene	976	969	0.6	14.0	2.0	2.2
6	β-Pinene	980	978	0.9	23.8	10.5	9.0
7	β-Myrcene	987	988	-	1.0	1.5	1.3
8	α-Phellandrene	1006	1004	0.2	0.9	-	-
9	δ-2-Carene	1008	1006	2.5	tr	3.0	2.5
10	δ-3-Carene	1011	1008	-	-	4.6	4.1
11	*p*-Cymene	1028	1020	1.6	1.1	1.5	1.3
12	Limonene	1032	1030	1.5	0.9	3.1	2.6
13	1,8-Cineole	1034	1032	10.0	0.3	14.6	23.1
14	(*E*)-β-Ocimene	1043	1040	tr	1.6	-	-

15	γ-Terpinene	1061	1056	-	0.3	-	-
16	α-Terpinolene	1090	1089	1.8	tr	1.7	1.4
17	Verbenol	1130	1132	-	0.4	-	-
18	(*Z*)-*p*-Menth-2-en-1-ol	1139	1140	0.6	-	1.2	1.0
19	Camphor	1145	1141	0.1	0.5	1.4	2.5
20	Terpinen-4-ol	1177	1177	1.5	0.8	1.3	1.7
21	α-Terpineol	1189	1188	1.1	0.4	1.9	3.7
22	*cis*-Geraniol	1239	1237	0.7	7.3	2.2	1.6
23	(*E*)-Citral	1259	1259	tr	2.5	-	-
24	(*E*)-Cinnamaldehyde	1270	1270	1.2	8.9	6.5	1.9
25	Bornyl acetate	1289	1289	-	0.3	0.9	1.0
26	α-Cubebene	1351	1347	2.5	tr	0.7	0.6
27	α-Copaene	1377	1374	14.2	1.4	7.5	7.1
28	α-Gurjunene	1412	1410	-	-	0.3	0.3
29	(*E*)-Cinnamyl acetate	1413	1415	-	0.7	-	-
30	β-Caryophyllene	1419	1417	2.5	0.5	3.4	3.1
31	Aromadendrene	1441	1439	1.7	tr	-	-
32	(*Z*)-β-Farnesene	1443	1441	tr	1.8	1.1	0.4
33	γ-Muurolene	1480	1480	0.3	2.4	-	-
34	Germacrene D	1480	1482	1.2	0.2	1.1	1.0
35	β-Vatirenene	1486	1488	1.1	tr	-	-
36	β-Bisabolene	1506	1505	tr	0.6	-	-
37	γ-Cadinene	1514	1513	-	0.7	-	-
38	β-Curcumene	1517	1519	0.7	0.9	1.0	0.7
39	δ-Cadinene	1525	1522	5.9	tr	tr	1.0
40	*trans*-Calamenene	1527	1527	1.2	tr	-	-
41	β-Calacorene	1546	1550	0.9	-	-	0.3
42	Nerolidol	1558	1553	0.2	-	-	-
43	Ledol	1564	1566	1.5	-	-	-
44	Spathulenol	1577	1577	1.2	tr	-	-
45	Caryophyllene oxide	1583	1581	1.0	-	-	-
46	*allo*-Aromadendrene oxide	1595	1597	tr	1.6	-	-
47	α-Guaiol	1600	1600	1.1	-	-	-
48	*trans*-Longipinocarveol	1618	1620	4.0	tr	-	-
49	Isoaromadendrene epoxide	1623	1623	0.4	-	-	-
50	Longiverbenone	1627	1628	2.1	-	-	-
51	β-Acorenol	1634	1634	2.0	-	-	-
52	τ-Cadinol	1639	1639	5.7	1.3	-	-
53	Cubenol	1642	1642	0.9	-	-	0.2
54	α-Cadinol	1654	1652	0.4	1.1	-	-
55	7(11)-Selinen-4α-ol	1662	1662	1.9	-	-	-
56	α-Santalol	1676	1674	5.7	tr	-	-
Total				93.7	95.8	94.8	95.3
Monoterpene hydrocarbons (Sr. No. 2-12,14-16)				17.3	61.2	46.4	40.6
Oxygenated monoterpenes (Sr. No. 13, 17-25, 29)				15.2	22.1	30.0	36.5
Sesquiterpene hydrocarbons (Sr. No. 26-28, 30-41)				31.2	8.5	15.1	14.5
Oxygenated sesquiterpenes (Sr. No. 42-56)				28.1	4.-0	-	0.2
Non-terpenes (Sr. No. 1)				-	-	3.3	3.5

[a] Elution order on HP-5MS column; [b] Retention indices on HP-5MS column; [c] Literature retention indices; tr Trace amount < 0.1%; - not identified

The low content of (*E*)-cinnamaldehyde in the *Cinnamomum* species is typical for majority of species already reported from Vietnam [2-5]. It could be seen that the compositional pattern of studied oil samples are quite different from data obtained from other species either from Vietnam or other parts of the world. It is known that different parts of plant accumulate different phytochemicals [2-5]. These differences in accumulated phytochemicals may be attributed to differences in ethnomedical uses and biological potentials of the different parts of the same plant. Other factors such as the nature of the plant, geographical areas, time of collection, method of extraction, plant parts and maturation of the harvested plant may be responsible for the varying compositional pattern between the studied samples and other *Cinnamomum* plants grown in Vietnam [9-11] and other parts of the world [12-14]. The chemical compositions of essential oils of *Cinnamomum* plants grown in Vietnam have been classified into seven groups [3]. The stem bark of *C. curvifolium* as well as the oils of *C. mairei* belongs to group with abundant of monoterpene hydrocarbon compounds. It could be postulated the essential oils of *C. mairei* exist in two chemical forms dominated by oxygenated monoterpenes [3] and monoterpene hydrocarbons (present study). Similarly, *C. curvifolium* consists of oil rich in aromatic esters [3] and monoterpene hydrocarbons (this study).

4. Conclusions

The paper reported the compounds identified in the essential oils of *C. curvifolium* and *C. mairei* grown in Vietnam. The significant compounds of the oil were α-pinene, β-pinene, sabinene, α-copaene and 1,8-cineole. In addition, a comparative analysis of the composition of the essential oils was performed with results from the same species reported elsewhere and other species reported from Vietnam as well as

Cinnamomum plants grown in other parts of the world. The results indicated differing compositional pattern with the same species and other species.

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