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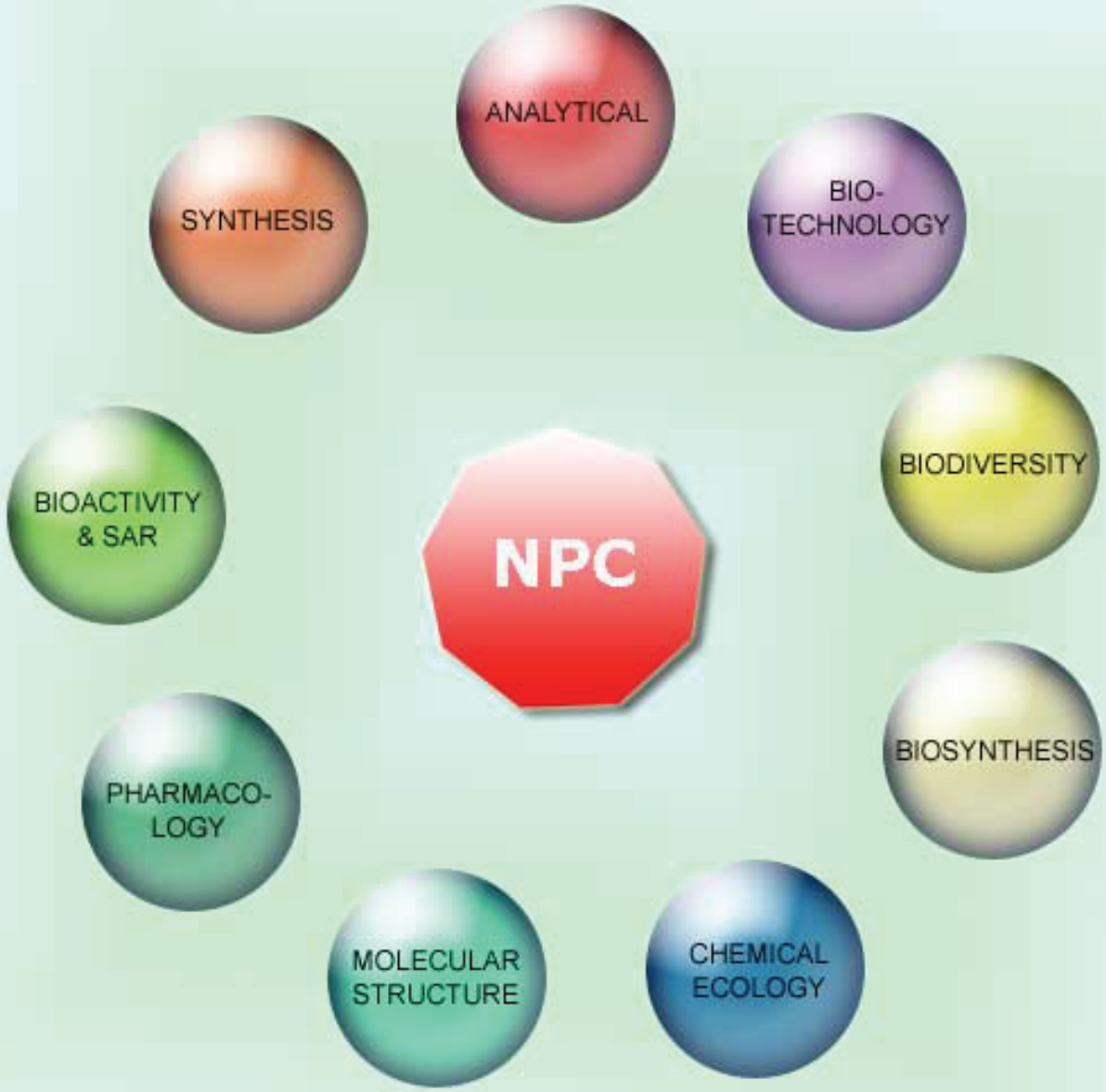

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Chemical Composition of Vietnamese Essential Oils of *Cinnamomum rigidifolium*, *Dasymaschalon longiusculum*, *Fissistigma maclurei* and *Goniothalamus albiflorus*

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Dedicated to Prof. Dr. Wilhelm Fleischhacker on account of his 85th Birthday.

Cinnamomum rigidifolium, *Dasymaschalon longiusculum*, *Fissistigma maclurei* and *Goniothalamus albiflorus* were collected from different landscapes in Vietnam and hydro distilled to produce essential oils with yields from 0.15 – 0.35%. The oils were analyzed by GC-MS-FID and rechecked by measurements on two different instrumentation configurations. The main components of the studied essential oils were for *Cinnamomum rigidifolium* linalool (19.4%), α-pinene (13.8%), verbenone (9.9%) and *cis*-verbenol (8.9%), total identified 90.5%; for *Dasymaschalon longiusculum* spathulenol (21.4%), caryophyllene oxide (17.6%), α-pinene (5.5%) and β-pinene (5.2%), total identified 70.1%; for *Fissistigma maclurei* spathulenol (17.8%), guaia-6,10(14)-diene-4β-ol (10.3%), *(E)*-β-caryophyllene (7.3%) and caryophyllene oxide (7.0%), total identified 75.3% and for *Goniothalamus albiflorus* 1,8-cineole (13.2%), α-pinene (10.6%), ledol (7.5%) and caryophyllene oxide (7.3%), total identified 78.0%.

Keywords: Vietnam, Essential oils, GC-MS-FID, *Cinnamomum rigidifolium*, *Dasymaschalon longiusculum*, *Fissistigma maclurei*, *Goniothalamus albiflorus*.

Due to its very diverse landscapes and climates Vietnam boasts a realm of plants and spices, some of which are used to produce commercial essential oils like ginger, curcuma, galangal, pepper, and anis [1]. Even the rare and very valuable agar wood oil is being produced commercially from *Aquilaria crassna* grown in plantations [2]. However, there are many other oil bearing plants that have not yet been fully characterized or even discovered, although they are often used as healing remedies in folk medicine and possess biological activities. These activities can be due to the volatile, more apolar low molecular substances produced in the plant or the more polar extractable compounds. The plant volatiles are usually gained by hydro or steam distillation, either on a small scale in the laboratory or on a larger scale on the field or in a plant.

In the present study the chemical compositions of four essential oils of the rare plants *Cinnamomum rigidifolium* [3], *Dasymaschalon longiusculum* [4], *Fissistigma maclurei* [5], and *Goniothalamus albiflorus* [6] are reported and shown in Tables 1 - 4.

The essential oil of *C. rigidifolium* consists mainly of monoterpenes, with the main components α-pinene and linalool, whereas in [3] the sesquiterpene hydrocarbons α-selinene, β-caryophyllene and α-copaene were found to be the major components.

F. maclurei is composed of the sesquiterpene alcohols spathulenol and guaia-6,10(14)-diene-4β-ol, which is different from the analysis in [5], where germacrene D, α-terpinene, spathulenol and bicyclogermacrene were reported as the vital ingredients.

G. albiflorus is comprised of α-pinene, 1,8-cineole, caryophyllene oxide, ledol and mustakone; here the quantities of monoterpenes and sesquiterpenes were roughly equal.

For confirmation, the oils were reanalysed on different GC-MS and GC-MS-FID instruments. No significant differences were detected and the above shown compositions remained unchanged. In conclusion, it can be stated that all four oils were quite different from previous findings [3-6], which might be due to divergent geographical position, microclimate and condition of the soil.

Experimental

Plant material: Leaves of *Cinnamomum rigidifolium* Kosterm. and *Fissistigma maclurei* Merr. were collected in Pù Mát National park, Nghệ An Province and hydro distillation provided a yield of 0.35% for the former and 0.15% for the latter. Leaves of *Dasymaschalon longiusculum* Bân were gathered in Pu Hoat Nature Reserve, Nghệ An Province; essential oil yield 0.15%. Leaves of *Goniothalamus albiflorus* Bân came from Pù Mát National Park, Nghệ An Province (yield 0.2%). Botanical identification was performed by Dr Do N. Dai. Voucher specimens DND 882, DND 890, DND 892 and DND 899, respectively were deposited at the Botany Museum, Vinh University, Vietnam.

Extraction of the oils: About 500 g of air-dried leaves of each plant sample were shredded and their oils obtained by hydro distillation for 3 h at normal pressure, according to the Vietnamese Pharmacopoeia [7]. Analysis was made in triplicate.

Table 1: Chemical composition of *Cinnamomum rigidifolium* essential oil.

Compds	substance	RRT	%
1	1,2,4,4-Tetramethyl-cyclopentene	840	tr.
2	Tricyclene	931	0.1
3	α-Pinene	942	13.8
4	α-Fenchene	956	0.1
5	Camphene	959	1.4
6	Thuja-2,4(10)-diene	963	0.6
7	β-Pinene	987	2.9
8	Verbenene	1000	0.1
9	Verbenene (isomer?)	1012	0.2
10	*o*-Cymene	1020	tr.
11	*p*-Cymene	1032	0.3
12	Limonene	1037	0.1
13	1,8-Cineole	1041	4.7
14	Lavender lactone	1044	0.3
15	*cis*-Linalool oxide furanoid	1079	4.7
16	*trans*-Linalool oxide furanoid	1095	4.8
18	Linalool	1102	19.4
19	α-Fenchol	1126	0.1
20	Dehydrosabinaketon	1132	0.1
21	α-Campholenal	1136	0.7
22	Nopinone	1151	0.5
23	*trans*-Pinocarveol	1154	4.0
24	*cis*-Verbenol	1156	8.9
25	Pinocamphone	1175	0.2
26	*cis*-Linalool oxide pyranoid	1178	0.8
27	*trans*-Linalool oxide pyranoid	1181	0.7
28	*cis*-3-Hexenyl butanoate	1191	1.1
29	*p*-Cymen-8-ol	1194	1.2
30	α-Terpineol	1202	0.5
31	Myrtenol	1209	0.8
32	*trans*-Carveol	1229	1.07
33	Carvone	1255	0.61
34	Bornyl acetate	1297	0.11
35	Spathulenol	1608	0.38
36	Caryophyllene oxide	1617	1.27
37	Globulol	1627	0.23
38	Ledol	1639	0.5
39	Humulene epoxide II	1644	0.84
40	Cadalene	1703	0.19
41	Mustakone	1710	1.16
	Sum		90.5

tr. = trace < 0.05%.

Table 2: Chemical composition of *Dasymaschalon longiusculum* essential oil.

Compds	substance	RRT	%
1	α-Pinene	943	5.5
2	Camphene	961	0.1
3	Thuja-2,4(10)-diene	965	0.2
4	β-Pinene	990	5.2
5	α-Fenchol	1131	0.3
6	α-Campholenal	1141	0.3
7	Nopinone	1156	0.6
8	*trans*-Pinocarveol	1159	2.4
9	*cis*-Verbenol	1161	0.6
10	Pinocarvone	1182	0.4
11	Borneol	1186	0.2
12	*p*-Cymen-8-ol	1200	0.3
13	α-Terpineol	1207	1.4
14	Myrtenol	1215	0.8
15	Myrtenal	1216	1.0
16	Verbenone	1229	1.2
18	Bornyl acetate	1304	0.4
19	*cis*-Pinocarvyl acetate	1317	0.3
20	Myrtenyl acetate	1342	0.1
21	δ-Elemene	1360	0.1
22	β-Elemene	1416	0.4
23	Aromadendrene	1473	1.1
24	Elemol	1577	0.5
25	Spathulenol	1614	21.4
26	Caryophyllene oxide	1623	17.6
27	Globulol	1632	2.2
28	Viridiflorol	1636	0.2
29	Humulene epoxide II	1650	0.8
30	alismol	1661	0.8
31	Caryophylla-3(15),7(14)-dien-6-ol	1675	1.9
32	δ-Cadinol	1678	0.8
33	14-Hydroxy-β-caryophyllene	1705	1.5
	sum		70.1

Table 3: Chemical composition of *Fissistigma maclurei* essential oil.

Compds	substance	RRT	%
1	α-Pinene	942	1.6
2	β-Pinene	987	0.3
3	*p*-Cymene	1031	0.3
4	Limonene	1036	0.4
5	δ-Elemene	1353	2.8
6	α-Ylangene	1392	0.5
7	α-Copaene	1397	1.1
8	β-Elemene	1409	3.9
9	β-Ylangene	1443	0.3
10	*(E)*-β-Caryophyllene	1447	7.3
11	γ-Elemene	1451	0.3
12	β-Copaene	1454	0.4
13	Aromadendrene	1467	0.8
14	α-Humulene	1481	3.5
15	γ-Muurolene	1497	1.1
16	α-Amorphene	1501	1.6
18	Germacrene D	1507	0.3
19	β-Selinene	1515	1.3
20	α-Muurolene	1520	0.7
21	α-Selinene	1523	0.9
22	γ-Cadinene	1538	0.6
23	δ-Cadinene	1543	0.9
24	α-Calacorene	1568	0.3
25	Elemol	1570	0.5
26	Salviadienol	1577	0.5
27	Mintoxide	1598	0.9
28	Spathulenol	1607	17.8
29	Caryophyllene oxide	1616	7.0
30	Globulol	1625	0.6
31	Torilenol	1639	0.7
32	Humulene oxide II	1643	0.8
33	Guaia-6,10(14)-diene-4β-ol	1654	10.3
34	Alismol	1666	1.2
35	Isospathulenol	1668	0.8
36	τ-Muurol	1671	0.7
37	Cubenol	1678	0.3
38	α-Cadinol	1681	2.1
	Sum		75.3

Table 4: Chemical composition of *Goniothalamus albiflorus* essential oil.

Compds	Substance	RRT	%
1	Tricyclene	931	0.1
2	α-Pinene	942	10.6
3	Camphene	959	1.4
4	Thuja-2,4(19)-diene	963	0.3
5	β-Pinene	987	1.0
6	Verbenene	999	0.0
7	Verbenene (isomer?)	1012	0.1
8	*p*-Cymene	1031	0.1
9	Limonene	1034	0.1
10	1,8-Cineole	1040	13.2
11	*cis*-Linalool oxide	1079	0.1
12	Linalool	1101	0.1
13	α-Fenchol	1125	0.2
14	α-Campholenal	1135	0.8
15	*trans*-Pinocarveol	1153	2.3
16	*trans*-Verbenol	1156	3.1
18	Camphor	1159	0.3
19	Camphene hydrate	1165	0.1
20	Pinocamphone	1174	0.1
21	Pinocarvone	1176	0.4
22	Borneol	1180	0.8
23	*p*-Cymen-8-ol	1193	1.1
24	α-Terpineol	1201	0.6
25	Myrtenol	1209	0.3
26	Myrtenal	1210	0.6
27	Verbenone	1223	3.2
28	*trans*-Carveol	1228	0.7
29	*trans*-Verbenyl acetate	1233	0.9
30	Bornyl formate	1243	0.2
31	*trans*-Pinocarvyl acetate	1254	0.5
32	Bornyl acetate	1297	0.8
33	α-Cubebene	1366	0.2
34	α-Ylangene	1397	0.3
35	Aromadendrene	1489	0.7
36	1,11-Oxidocalamenene	1511	0.4
37	*epi*-Cubebol	1518	0.8
38	Cubebol	1540	0.7
39	δ-Cadinene	1543	0.2
40	Calamenene	1545	0.7
41	Spathulenol	1607	2.7
42	Caryophyllene oxide	1616	7.3
43	Globulol	1625	1.3
44	Ledol	1637	7.5
45	Humulene epoxide II	1643	1.7
46	1-*epi*-Cubenol	1656	1.6
47	Cadalene	1702	2.3
48	Mustakone	1709	5.5
	Sum		78.0

Gas chromatography-mass spectrometry: GC-FID and GC-MS analyses were performed in one run and one GC with the help of a MS-FID-splitter consisting of a quartz Y-splitter and a short (ca. 20 cm) 0.1 mm ID fused silica restrictor column as an inlet to the GC-MS interface and a ca. 1 m x 0.25 mm deactivated fused silica column serving as a transfer line to the FID detector. The restriction column limits the flow into the MS vacuum and prevents entering combustion gases from the FID, which is operated at atmospheric pressure. The flow in the analytical column must be greater than the inflow to the MS detector, which is limited to about 1 mL/min by means of the restriction line. The GC column flow must be held

constant otherwise the split ratio changes with temperature. This configuration yields a FID and a MS chromatogram with almost identical retention times, thus facilitating substance assignment of the FID peaks. The following instrumentation was used:

A Thermo Fisher Scientific Trace GC Ultra with a split/splitless injector heated at 230°C and connected to a 50 m x 0.25 mm x 1.0 µm SE-52 (95% Polydimethyl-, 5% Polydiphenylsiloxan) capillary column, a FID detector operated at 250°C and a TriPlus RSH autosampler. Essential oil samples (0.1 µL) were injected neat with a 0.5 µL plunger-in-needle syringe at a split ratio of 1:100.

For substance identification, a Thermo Fisher Scientific ISQ mass spectrometer was used with GC-MS interface heating at 250°C, ion source 230°C, EI mode @ 70 eV, filament 50 µA, and scan range 40 - 500 amu. The following oven temperature program was used: 60°C for 1 min. then heated to 230°C at a rate of 3°C/Min, and 230°C isotherm for 12.3 Min. The carrier gas was helium 5.0, with a constant flow rate of 1.5 mL/min.

ThermoXcalibur 2.2 software was used for identifying the compounds by correlating mass spectra to databases of NIST 08 [8], Wiley 8th ed. [9], Adams Library [10], MassFinder terpenoids library [11] and our own library. Retention indices were determined with the use of the measured retention times of a series of *n*-alkanes that elute over the whole span of the chromatogram and calculated according to the method of van den Dool and Kratz [12,13].

Quantification was performed using normalized peak area calculations of the FID chromatogram without (by first approximation) relative FID-response factors.

For confirmation of the above analysis, the same oils were also run on a ThermoQuest Trace GC – ThermoQuest Finnigan Automass Solo GC-MS-FID system equipped with the same column and operated with the same temperature program as above and once more analysed on a Varian GC 3700 – Finnigan MAT ITS40 GC-Ion Trap-MS provided with a 60 m x 0.25 mm x 0.25 µm DB-1701 column and run with the identical temperature program.

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