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COMPOSITION OF ESSENTIAL OIL OF *Cinnamomum tetragonum*

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In this paper we report the volatile oil composition of *Cinnamomum tetragonum* A. Chev., growing in Vietnam. A compound of plant extracts containing extract of *C. tetragonum* was effective for suppressing 15-hydroxyprostaglandin dehydrogenase (15-PGDH), which is a core material for inactivation of PGE2 with low cytotoxicity [1]. The leaves of *C. tetragonum* are made into a stimulating drink. Even though the genus *Cinnamomum* is a large family of evergreen aromatic trees and shrubs, the authors have found no literature information on the oil components of *C. tetragonum*. Moreover, there are literature reports on the volatile constituents of *Cinnamomum* species grown in Vietnam [2–8] and other parts of the world [9–11]. The volatile contents are usually monoterpenes, sesquiterpenoids, and non-terpene compounds of diverse structural pattern. For example, *C. sericans* leaf consists mainly of the sesquiterpenes spathulenol (14.5%) and caryophyllene oxide (9.3%), while the leaf oil of *C. magnificum* contains the sesquiterpenes bicyclogermacrene (33.9%) and β-caryophyllene (25.5%) [2]. The monoterpenes ρ-cymene (15.6%) and limonene (13.9%) dominated in *C. durifolium* [2]. The present report is part of an extensive research aimed at the characterization of volatile compounds from Vietnamese flora as they are made available [12].

Leaves and stem bark of *C. tetragonum* were collected from Pu Huong Natural Reserve, Nghean Province, Vietnam, in August 2013. A voucher specimen PHM13 was deposited at the Botany Museum, Vinh University, Vietnam. Aliquots of air-dried and pulverized samples (0.5 kg each) were subjected to hydrodistillation for 3 h at normal pressure, according to the Vietnamese Pharmacopoeia [13]. The volatile oils distilled over water and were collected separately into clean weighed sample bottles. The oils were kept under refrigeration (4°C) until the moment of analysis as described previously [2–8, 12].

Gas chromatography (GC) analysis was performed on an Agilent Technologies HP 6890 Plus Gas chromatograph equipped with an FID and fitted with an HP-5MS column (30 m × 0.25 mm, film thickness 0.25 μm, Agilent Technology). The analytical conditions were: carrier gas He (1 mL^{-1} min), injector temperature (PTV) 250°C, detector temperature 260°C, and column temperature programmed from 40°C (2 min hold) to 220°C (10 min hold) at $4°C^{-1}$ 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. Each analysis was performed in triplicate. The relative amounts of individual components were calculated based on the volume injected by splitting, and the split ratio was 10:1. The relative amounts of individual components were calculated based on the GC peak area (FID response). An Agilent Technologies HP 6890N Plus Chromatograph fitted with a fused silica capillary HP-5 MS column (30 m × 0.25 mm, film thickness 0.25 μm) and interfaced with a mass spectrometer HP 5973 MSD was used for the gas chromatography/mass spectrometry experiment, under the same conditions as those used for gas chromatography analysis as described previously [2–10]. The GC conditions were the same as described above with He (1 mL^{-1} min) as carrier gas. The MS conditions were as follows: ionization voltage 70 eV; emission current 40 mA; acquisitions scan mass range 35–550 amu at a sampling rate of 1.0 scan s^{-1}.

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TABLE 1. Constituents of *C. tetragonum* Essential Oils

Compound[a]	RI[b]	Barks	Leaves	Compound[a]	RI[b]	Barks	Leaves
α-Pinene	939	0.8	2.1	α-Copaene	1377	Tr.	0.3
Camphene	953	1.0	0.6	Geranyl acetate	1381	14.8	0.2
β-Thujene	968	0.4	0.2	Caryophyllene	1419	1.5	1.6
Benzaldehyde	978	Tr.	0.7	α-Humulene	1454	0.4	Tr.
β-Pinene	980	1.6	1.1	Cinnamyl acetate	1455	Tr.	3.5
β-Myrcene	987	0.1	0.3	(*E*)-β-Farnesene	1460	3.7	0.3
α-Phellandrene	1006	0.2	–	γ-Muurolene	1480	0.2	–
δ-2-Carene	1008	–	1.1	Germacrene D	1480	1.1	Tr.
δ-3-Carene	1011	Tr.	0.6	δ-Cadinene	1525	–	0.4
p-Cymene	1028	1.5	Tr.	*trans*-Calamenene	1527	0.1	0.1
Limonene	1032	0.7	1.2	(*E*)-Nerolidol	1558	–	0.2
1,8-Cineole	1034	Tr.	2.1	Ledol	1564	0.2	–
α-Terpinolene	1090	–	0.2	Spathulenol	1577	Tr.	0.4
Linalool	1100	0.5	1.0	Isoaromadendrene epoxide	1595	0.3	0.3
Camphor	1145	–	0.6	β-Acorenol	1634	0.4	Tr.
Hydrocinnamaldehyde	1150	Tr.	2.1	Cubenol	1642	Tr.	0.2
β-Terpineol	1154	Tr.	0.1	7(11)-Selinen-4α-ol	1662	0.2	–
Terpinen-4-ol	1177	0.7	0.6	Total		98.7	99.9
α-Terpineol	1189	Tr.	1.5	Monoterpene hydrocarbons		6.3	9.4
cis-Geraniol	1239	65.1	33.8	Oxygenated monoterpenes		84.3	86.0
trans-Geraniol	1268	0.6	0.2	Sesquiterpene hydrocarbons		7.0	2.7
(*E*)-Cinnamaldehyde	1270	2.6	41.0	Oxygenated sesquiterpenes		1.1	1.1
Cinnamyl alcohol	1303	Tr.	0.2	Non-terpenes		–	0.7

[a] Elution order on HP-5MS column; [b] Retention indices on HP-5MS column; Tr.: trace < 0.1%; – not identified.

Most constituents were identified by gas chromatography by comparison of their retention indices with those in the literature or with those of available authentic compounds. The retention indices were determined in relation to a homologous series of *n*-alkanes (C_6–C_{32}) obtained under the same operating conditions. Further identification was made by comparison of their mass spectra with those stored in the library [14], peak enrichment on co-injection with authentic standard where possible as described previously [2–5].

The volatile compounds are displayed in Table 1, along with their percentages and retention indices calculated on a HP-5MS column. The hydrodistillation of *C. tetragonum* afforded yellow oils in yields of 0.53% and 0.21% (v/w, stem barks and leaves, respectively). The stem bark and leaf oils consist mainly of oxygenated monoterpene compounds (84.3% and 86.0%, respectively). The main constituents of the bark oil were *cis*-geraniol (65.1%) and geranyl acetate (14.8%). However, (*E*)-cinnamaldehyde (41.0%) and *cis*-geraniol (33.8%) were present in the leaf oil.

This is the first report on the volatile oils of *C. tetragonum*.

The high content of (*E*)-cinnamaldehyde in the essential oil of *C. tetragonum* species is noteworthy. It was noted previously that the volatile constituents of several species of *Cinnamomum* plants already reported from Vietnam contained low amounts of (*E*)-cinnamaldehyde [2–8, 12] or none. It can 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. The differences may be attributed to differences in the nature of the plant, geographical areas, time of collection, method of extraction, plant parts, and maturation of the harvested plants. The chemical compositions of essential oils of *Cinnamomum* plants grown in Vietnam have been classified into seven groups [3]. Therefore, the oils of *C. tetragonum* fall into a group containing oxygenated monoterpenes, but the main components of the individual species differ from one another. For example, linalool occurs in *C. doederleinii* var. *raoanensis* [12] while methyl eugenol, terpinen-4-ol, and 1,8-cineole are the main compounds of *C. kunstleri* [3]. The leaf oil of *C. mairei* consist mainly of eugenol, neryl acetate, eugenol acetate, and 1,8-cineole, while linalool, 1,8-cineole, and myrtenal are the main compounds of *C. damhaensis* [3]. Similarly, linalool and terpinen-4-ol occur in *C. cambodianum*, while 1,8-cineole dominates in the oil of *C. caryophyllus* [3]. The significant compounds of *C. glaucescens* are geraniol and terpinen-4-ol, while *C. verum* consists of linalool [5]. The existence of common compounds in the essential oils of *Cinnamomum* plants could be of chemotaxonomic significance. For example, the essential oils of *C. doederleinii* var. *raoanensis* [12],

C. cambodianum [3], and *C. verum* [5] from Vietnam may be classified as being of the linalool chemotype. Various authors from all parts of the world have described different main monoterpene compounds (chemotypes) of essential oils of *C. verum*. These include eugenol type [15–18], safrole type [19], cinnamaldehyde isomers type [5], (*E*)-cinnamaldehyde–eugenol–linalool type [20], and cinnamyl acetate type [21].

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