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To cite this article: N.K. Leela , T.M. Vipin , V. Priyanka , K.M. Shafeekh & J. Rema (2012) *Cinnamomum citriodorum* Thw. – new source of citronellol, Journal of Essential Oil Research, 24:6, 507-511, DOI: [10.1080/10412905.2012.728084](https://doi.org/10.1080/10412905.2012.728084)

To link to this article: <https://doi.org/10.1080/10412905.2012.728084>



Published online: 23 Oct 2012.



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## *Cinnamomum citriodorum* Thw. – new source of citronellol

N.K. Leela<sup>a\*</sup>, T.M. Vipin<sup>a</sup>, V. Priyanka<sup>a</sup>, K.M. Shafeekh<sup>a</sup> and J. Rema<sup>b</sup>

<sup>a</sup>Division of Crop Production & Post-Harvest Technology, Indian Institute of Spices Research, Calicut, India; <sup>b</sup>Division of Crop Improvement & Biotechnology, Indian Institute of Spices Research, Calicut, India

(Received 25 February 2011; final form 10 April 2012)

The essential oil composition of *Cinnamomum citriodorum* leaves and petioles was determined by gas chromatography (GC) and GC–mass spectrometry (GC–MS) analysis. Leaf and petioles yielded 0.11% and 0.42% essential oil respectively. In leaf oil, twenty-seven constituents representing 97.2% of the oil were identified. Major components of the oil were citronellol (66.5–71.1%), citronellal (10.8–10.9%) and *trans*-geraniol (5.9–6.5%). In the oil from the petiole, thirty-eight compounds contributing 91.3% of the oil were identified, of which citronellol (36.2–38.3%), citronellal (9.9–15.4%) and  $\alpha$ -copaene (8.7–10.3%) were the chief constituents. Although both oils were dominated by monoterpene alcohols, the oil from the petiole contained a higher level of sesquiterpenes (26.3–36.2%) compared with the leaf oil (5.0–9.9%).

**Keywords:** *Cinnamomum citriodorum*; essential oil composition; citronellol; citronellal; *trans*-geraniol

### Introduction

The genus *Cinnamomum* (Lauraceae) comprises over 300 species of trees and shrubs distributed in the tropical and subtropical regions of the world. Many of the species of *Cinnamomum* have medicinal and spice value, *C. verum* being the most important. Due to its economic importance and medicinal values, the genus has attracted the attention of phytochemists, and several terpenes, flavonoids, alkaloids and aliphatic compounds have been isolated (1–7). Even though several species have been subjected to phytochemical studies, there are some endemic species that are not explored for their chemical constituents. *Cinnamomum citriodorum* is one among them.

*Cinnamomum citriodorum* is a medium-size tree, which occurs in Sri Lanka and South western Ghats. *Cinnamomum citriodorum* has the aroma of lemongrass, and its leaf and bark are used by tribes as both spice and a medicinal plant. A decoction of its bark and leaves is used by local people in the treatment of stomach ailments (8). The only phytochemical study reported in this plant is the thin-layer chromatography analysis of volatile oils by Sritharan et al. (9). This prompted us to investigate the essential oil constituents of leaves of *C. citriodorum*.

### Experimental

#### Plant material

Fresh leaves of *C. citriodorum* were collected during July 2008–09, from the Experimental Farm,

Peruvannamuzhi, IISR, Calicut, where a voucher specimen is available.

#### Isolation of volatile components

Leaves and petioles (3 × 300 g each) collected during June 2008–09 were separately hydrodistilled in a Clevenger-type apparatus for 3 hours. The oil was dried over anhydrous sodium sulfate and stored at 4°C until the analysis was carried out.

#### Gas chromatography

Gas chromatography (GC) analysis was performed on a Shimadzu (GC-2010) gas chromatograph fitted with a flame ionization detector (FID) and RTX–5 column (30 m × 0.25 mm, film thickness 0.25  $\mu$ m). Nitrogen was used as carrier gas at a flow rate of 1 mL/minute. The oven was programmed as follows: 60°C, held for 5 minutes, up to 110°C at 5°C/minute, to 200°C at 3°C/minute, to 220°C at 5°C/minute, held for 5 minutes; injection port temperature: 260°C and detector temperature: 250°C. The split ratio was 1:40, and a 0.1- $\mu$ L sample was injected. The percentage composition of the oil was determined by area normalization.

#### Gas chromatography–mass spectrometry

GC–mass spectrometry (GC–MS) analysis was carried out by means of a Shimadzu GCMS QP 2010 system equipped with RTX–5 column (30 m × 0.25 mm, film thickness 0.25  $\mu$ m). Helium was used as the carrier gas at a flow rate of 1 mL/minute. The injection port was maintained at 250°C, the detector temperature was

\*Corresponding author. Email: leela@spices.res.in

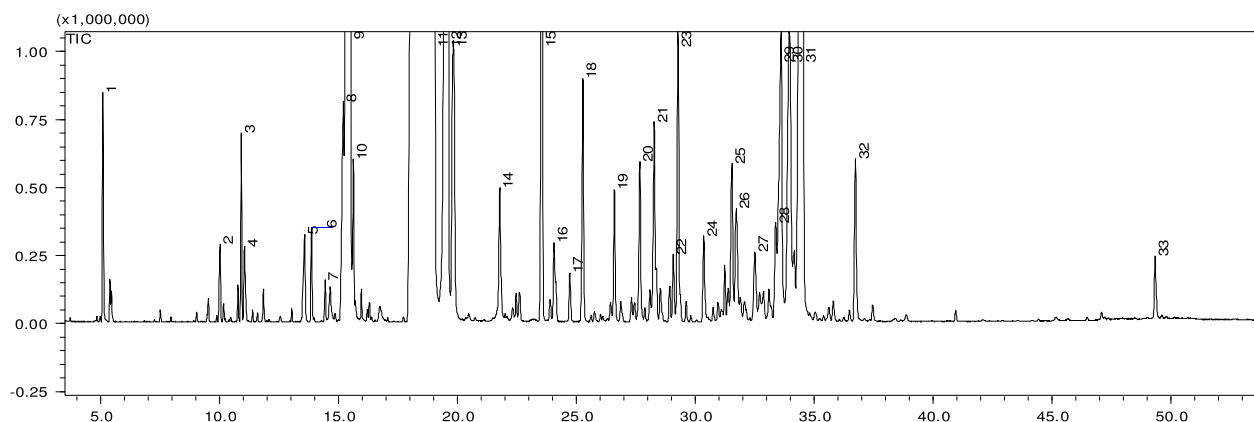


Figure 1. Gas chromatography (GC) profile of essential oil of *Cinnamomum citriodorum* leaf. 1: (*Z*)-3-Hexen-1-ol, 2:  $\alpha$ -phellandrene, 3: limonene, 4: 1,8-cineole, 5: linalool, 6: 2-methyl butyl-2-methyl butyrate, 7: *trans*-rose oxide, 8: isopulegol, 9: citronellal, 11:  $\beta$ -citronellol, 12: geraniol, 13: geranial, 14:  $\alpha$ -terpinyl acetate, 15:  $\alpha$ -copaene, 16:  $\beta$ -bourbonene +  $\beta$ -cubebene, 17: dodecanal, 18: *trans*-caryophyllene, 19:  $\alpha$ -humulene; 20: germacrene d, 23:  $\delta$ -cadinene, 24: elemol, 25: spathulenol, 29: epi- $\alpha$ -cadinol, 30:  $\beta$ -eudesmol, 31:  $\alpha$ -cadinol, 32: (*2Z,6E*)-farnesol, 33: phytol.

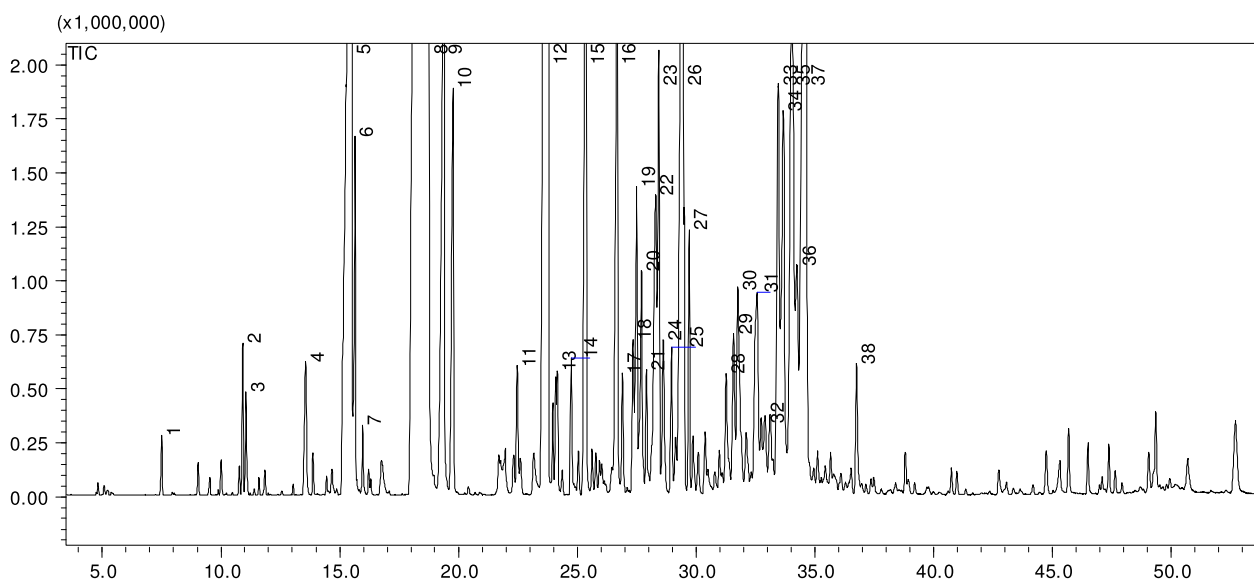


Figure 2. Gas chromatography (GC) profile of essential oil of *Cinnamomum citriodorum* petiole. 1: (*Z*)-3-Hexen-1-ol, 2: limonene, 3: 1,8-cineole, 4: linalool, 5: citronellal, 6: isopulegol, 8:  $\beta$ -citronellol, 9: geraniol, 10: geranial, 11:  $\alpha$ -terpinyl acetate,  $\alpha$ -cubebene, cyclosativene, 12:  $\alpha$ -copaene, 13:  $\beta$ -bourbonene +  $\beta$ -cubebene, 14: dodecanal, 15: *trans*-caryophyllene, 16:  $\alpha$ -humulene, 17: alloaromadendrene, 19:  $\gamma$ -muurolene, 20: germacrene d, 22:  $\beta$ -selinene, 23:  $\alpha$ -selinene 25:  $\gamma$ -cadinene, 26:  $\delta$ -cadinene, 27: *trans*-cadin-1(2),4-diene, 29: caryophyllene alcohol, 30: spathulenol, 32: globulol, 33: tetradecanal, 34: epi- $\alpha$ -cadinol, 36:  $\beta$ -eudesmol, 37:  $\alpha$ -cadinol, 38: (*2Z,6E*)-farnesol.

220°C, ion source temperature 250°C, interface temperature 250°C, oven temperature programmed as stated above. The split ratio was 1:40 and ionization energy 70 eV. The retention indices were calculated relative to C<sub>8</sub>–C<sub>20</sub> *n*-alkanes (Fluka Chemicals). The constituents of the oil were identified by comparison of retention indices with those reported in literature (10), by matching the mass spectral data with those stored in NIST and Wiley libraries, and wherever possible, by co-injec-

tion with authentic standards purchased from Fluka Chemicals.

#### Quantification

A known concentration (20–60  $\mu$ g/mL) of citronellol in toluene containing 10  $\mu$ g/mL of *n*-decane (internal standard) was used for preparing calibration curves. The ratio of the peak area of analyte and that of the internal standard was plotted against the analyte

Table 1. Composition of *Cinnamomum citriodorum* essential oils.

Compound	RI <sub>lit.</sub>	RI <sub>calc.</sub>	% Composition				Method of identification
			Leaf		Petiole		
			Plant1	Plant 2	Plant 1	Plant 2	
(Z)-3-Hexen-1-ol	859	857	0.4	0.3	0.4	–	RI, MS
α-Pinene	939	935	–	t	0.1	–	RI, MS
α-Phellandrene	1002	1001	–	0.1	0.1	0.1	RI, MS
Limonene	1029	1031	0.1	0.2	0.3	0.4	RI, MS
1,8-Cineole	1031	1033	–	0.4	0.2	–	RI, MS
Linalool	1096	1104	0.1	0.4	0.5	0.2	RI, MS, Co
2-Methyl butyl-2-methyl butyrate	1100	1108	–	0.2	–	0.1	RI, MS
trans-Rose oxide	1125	1127	0.1	0.2	0.1	0.1	RI, MS
Isopulegol	1149	1150	0.6	0.2	–	2.7	RI, MS
Citronellal	1153	1151	10.8	10.9	9.9	15.4	RI, MS, Co
β-Citronellol	1225	1231	71.1	66.5	36.2	38.3	RI, MS, Co
Neral	1238	1241	0.7	–	–	1.4	RI, MS
Geraniol	1252	1251	5.9	6.5	3.1	3.7	RI, MS, Co
Geranial	1267	1271	0.9	1.0	1.4	2.2	RI, MS, Co
α-Terpinyl acetate	1349	1344	–	0.3	–	0.4	RI, MS
α-Cubebene	1348	1345	–	t	0.3	0.3	RI, MS
Cyclosativene	1371	1371	–	–	–	0.1	RI, MS
α-Copaene	1376	1382	1.3	1.1	10.3	8.7	RI, MS
β-Bourbonene	1388	1384	–	0.1	0.1	0.1	RI, MS
β-Cubebene	1388	1386	0.2	0.3	0.2	–	RI, MS
Dodecanal	1408	1404	0.1	0.1	0.4	0.3	RI, MS
trans-Caryophyllene	1419	1416	0.4	0.5	3.0	1.6	RI, MS, Co
α-Humulene	1454	1450	0.2	0.2	2.4	1.2	RI, MS, Co
Alloaromadendrene	1460	1456	–	–	0.3	0.2	RI, MS
trans-Cadina-1(6), 4-diene	1476	1472	–	–	–	0.1	RI, MS
γ-Murolene	1479	1476	–	–	1.2	0.4	RI, MS
Germacrene D	1485	1488	0.3	0.3	0.6	0.4	RI, MS
β-Selinene	1490	1490	–	–	0.3	0.1	RI, MS
α-Selinene	1498	1497	–	–	2.7	–	RI, MS
α-Murolene	1500	1499	–	–	–	0.7	RI, MS
trans-β-Guaiene	1502	1503	–	–	–	0.1	RI, MS
γ-Cadinene	1513	1512	–	–	0.4	0.2	RI, MS
δ-Cadinene	1523	1521	0.5	0.6	4.8	2.9	RI, MS
trans-Cadina-1(2),4-diene	1534	1531	–	t	0.6	0.2	RI, MS
Elemol	1549	1546	0.1	0.2	–	0.2	RI, MS
Caryophyllene alcohol	1572	1569	–	–	0.4	0.2	RI, MS
Spathulenol	1578	1576	0.2	0.4	0.4	0.4	RI, MS
Caryophyllene oxide	1583	1583	0.2	–	–	–	RI, MS
Globulol	1590	1593	–	–	0.2	0.6	RI, MS
Tetradecanal	1612	1613	–	–	1.0	0.8	RI, MS
epi-α-Cadinol	1638	1643	–	2.2	2.6	1.9	RI, MS
β-Eudesmol	1650	1650	0.8	1.7	1.7	2.0	RI, MS
α-Cadinol	1654	1654	0.8	1.9	3.3	2.3	RI, MS
(2Z,6E)-Farnesol	1716	1725	–	0.4	0.4	0.3	RI, MS
Phytol	1943	1944	0.2	–	0.3	–	MS
Total (%)			96	97.2	90.2	91.3	
Monoterpenes (%)			90.3	86.7	51.9	65.0	
Sesquiterpenes (%)			5.0	9.9	36.2	26.3	

Notes: RI<sub>lit.</sub>, retention indices from the literature (10); RI<sub>calc.</sub>, experimental retention indices calculated against a C<sub>8</sub>–C<sub>20</sub> n-alkanes mixture on the RTX-5 column; MS, mass spectrometry; Co, co-injection with standards.

concentration. The calibration curve was linear over the concentrations tested, for the regression equation,  $Y=1.4825X-0.1587$ . The content of citronellol in the oil was determined by comparing the ratio of the peak area of the analyte and that of the internal standard in the sample with that of the standard.

## Results and discussion

Hydrodistillation of fresh leaves and petioles afforded 0.11% and 0.42% colorless pleasant-smelling essential oils respectively. Table 1 shows the constituents identified in these oils, in the order of elution on the RTX-5

Table 2. Quantification of citronellol.

Compound	Leaf ( $\mu\text{g/mL}$ )		Petiole ( $\mu\text{g/mL}$ )	
	Plant 1	Plant 2	Plant 1	Plant 2
Citronellol	68.9	64.5	30.1	31.7

column. Citronellol content in  $\mu\text{g/mL}$  is given in Table 2.

In the leaf oil, twenty-seven constituents representing 97.2% of the oil were identified. The leaf oil contained 86.7–90.3% monoterpenes and 5.0–9.9% sesquiterpenes. Among the monoterpenes, 86.4–90.2% was represented by oxygenated monoterpenes with 73.6–77.4% monoterpene alcohols and 11.9–12.4% monoterpene aldehydes. Among monoterpene alcohols, citronellol alone represented 66.5–71.1%, and the aldehydes citronellal, geranial and neral together contributed 11.9–12.4% of the oil. Sritharan et al. (9) reported citronellal as the chief constituent of leaf oil, but our oil was rich in citronellol. Citronellol occurs naturally in several plant oils, black tea and in certain fruits (11, 12). (+) Citronellol dominates in oils from *Boronia citriodora* (80%) and *Eucalyptus citriodora* (15–20%); (–) citronellol is the predominant isomer (50%) in geranium and rose oils (11). It is reported as a minor constituent from *Cinnamomum camphora* leaf oil of Australian origin (5). To the best of our knowledge, this is the first report of a *Cinnamomum* species rich in citronellol.

Thirty-eight compounds representing 90.2–91.3% were identified in the petiole oil, in which monoterpenes and sesquiterpenes contributed 51.9–65.0% and 25.2–36.2%, respectively. Among the monoterpenes, alcohols and aldehydes represented 39.8–44.9% and 11.3–19.0%, respectively. Although the chief component of the oil was citronellol, its percentage contribution (36.2–38.3%) was comparatively less in petiole oil. Sesquiterpene hydrocarbons and sesquiterpene alcohols constituted 17.3–27.2% and 7.9–9.0% respectively with  $\alpha$ -copaene (8.7–10.3%) being the dominant component.

The oil from petiole contained higher proportions of sesquiterpenes and monoterpene aldehydes when compared with the leaf oil. The compounds, namely cyclosativene, alloaromadendrene, *trans*-cadinane-1(6),4-diene,  $\gamma$ -muurolene,  $\beta$ -selinene,  $\alpha$ -selinene,  $\alpha$ -muurolene, *trans*- $\beta$ -guaiene,  $\gamma$ -cadinene, globulol and tetradecanal, were present in the petiole oil only. Limonene was the only monoterpene hydrocarbon detected in both the oils. The essential oil from the leaf contained two oxides, namely rose oxide and caryophyllene oxide.

Citronellol is extensively used in cosmetics, flavoring and fragrance materials, particularly for rose notes

and floral compositions (11). It possesses potent antimicrobial, antifungal, acaricidal, insect repellent and mite attractant properties (13–16). A pesticide product containing citronellol as an active ingredient, registered as 'Biomite', is used for controlling mites, aphids and jassids in the USA (17). It is a logical choice for organic production in conventional crops. In this context, *C. citriodorum* offers a new natural source of the versatile chemical, citronellol.

#### Acknowledgements

The authors are thankful to the Director, Indian Institute of Spices Research, Calicut, for providing facilities and Indian Council of Agricultural Research for the financial support.

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