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Chemical Fingerprinting of the Fragrant Volatiles of Nineteen Indian Cultivars of *Cymbopogon* Spreng. (Poaceae)

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Abstract: The essential oil compositions of total nineteen cultivars of *Cymbopogon* Spreng. (Poaceae) species viz. *C. martinii* (Roxb.) Wats. var. *motia* Burk., *C. flexuosus* Nees ex Steud, *C. winterinus* Jowitt., *C. pendulus* Nees ex Steud. and a hybrid of *C. khasianus* (Hack) Stapf. ex Bor and *C. pendulus* Nees ex Steud. were examined and compared using capillary GC and GC-MS. The analysis led to the identification of 48 constituents forming 90.1% to 99.7% of their total oil compositions with monoterpenoids (78.9% to 97.4%) as the most exclusive constituents. The comparative results showed considerable variation in the qualitative and quantitative compositions of essential oils from nineteen different cultivars of the studied *Cymbopogon* species. On the basis of chemical similarity the cultivars of genus *Cymbopogon* was divided into five chemical variants/groups within two series viz. *Citrati* and *Rusae*. The volatile profile of existing cultivars of *Cymbopogon* are useful for their commercial utilization as they possess range of essential oils and aroma chemicals used in perfumery, flavour, pharmaceutical and other allied industries. Moreover, the marker constituents in their essential oils may be utilized as an important tool in oil authentication.

Keywords: *Cymbopogon*; cultivars;, monoterpenoids; essential oils; citrals; geraniol.

1. Introduction

Cymbopogon is one of the most important essential oil yielding genera of the family Poaceae. The genus *Cymbopogon* comprised of about 140 species world wide, out of which 45 species have been reported to occur in India. The members of the genus *Cymbopogon* occur abundantly in tropics and sub tropics regions of Asia, Africa and America with a regular distribution ranging from mountains and grassland to arid zones [1-3]. *Cymbopogon* species display wide variation in morphological attributes and essential oil composition at inter and intra specific level and over the years different chemo cultivars varying in their aroma have been selected or breed by crossing with other cultivars or closely related species. The most common economic species viz., *C. winterianus, C. flexuosus, C. martinii* var. *motia* and *sofia, C. nardus* var. *nardus,C. citratus, C. pendulus, C. warancusa, C. khasianus* produces different types of essential oil, such as palmarosa oil, lemongrass oil, citronella oil, ginger grass or rusa oil of commercial interest [3-5].

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Three *Cymbopogon* grasses, namely, Java citronella (*C. winterinus*), lemongrass (*C. flexuosus* and *C. pendulus*) and palmarosa (*C. martinii* var. *motia*) are the most common species that are widely cultivated for their essential oils of commercial importance used in perfumes, soaps, cosmetics, toiletry, tobacco products and other related industrial products [5-7]. The unique characteristics of these aromatic grasses are that they have wide adaptability to grow in different types of soils in different agriclimatic conditions and cropping sequences. In India, total area under cultivation of these aromatic grasses is more than 40 thousands hectares, distributed mainly in Assam, Kerala, Madhya Pradesh, South Gujarat, Karnataka, Maharashtra, Andhra Pradesh and Uttar Pradesh [8-11]. The essential oils from *Cymbopogon* species contain a wide variety of terpenoids, some of which like geraniol and its ester, citronellol and citronellal are important perfume materials. Other constituent like citral is used in vitamin A and ionone synthesis. Several *Cymbopogon* species possessed significant anthelmintic, anti inflammatory, analgesic, antiageing, pesticidal, antimicrobial, mosquito repellant and larvicidal activities and thus, are used in native medicine for curing a number of diseases [4, 11-12]. Studies on the oil composition of various *Cymbopogon* species have been carried out time to time, which reports geraniol, geranyl acetate, citral, piperitone, limonene, elemecin, monoterpene alcohols and sesquiterpenes as the major constituents in their essential oils [12-26]. The commercial aspects of the essential oils of these aromatic grasses and their cultivars prompted us to carry out detailed comparative terpenoid composition of cultivated cultivars of genus *Cymbopogon* form northern plain of India.

2. Materials and Methods

2.1. Plant Material

The fresh plant materials of different cultivars of *C. martinii* var. *motia*, *C. flexuosus, C. winterinus, C. pendulus* and hybrid (CKP-25) were collected from cultivated crops at experimental field of CIMAP Research Centers, Pantnagar. The experimental site is located at latitude of 29^0 N, longitude of 79.38^0E and at an altitude of 243.84 MSL and it experiences climate with hot summer and chilled winter. The maximum temperature ranges between 35°C-45°C and the minimum between 2°C-5°C with average rainfall 1350 mm. The soil was clay loam in texture with neutral in reaction (pH 7.1). Voucher specimens of all cultivars have been maintained in CIMAP Research Center, Pantnagar, Uttarakhand (India). The origin of all the cultivars and their essential oil yield are given in Table 1.

2.2 Isolation of Essential Oils

The fresh plant materials were subjected to hydro-distillation using Clevenger-type apparatus for 3 hours. The oils were dried over anhydrous Na_2SO_4 and were stored in sealed vials under refrigeration prior to analysis. The oil yields were calculated on the basis of fresh weight of the material (v/w).

2.3 GC and GC-MS Analysis

The GC analysis of the oil samples was carried out on Nucon 5765 gas chromatograph equipped with dual FID, using two different stationary phases Rtx-5 (30 m × 0.32 mm i.d., 0.25 µm film coating) and CP-Wax 52 CB (30 m × 0.32 i.d., 0.25 µm film thickness) fused silica columns, respectively. Nitrogen and Hydrogen were the carrier gas at 1.0 mL/ min in nonpolar and polar column, respectively. Temperature programming was from 70°C-230°C at 4°C/min (CP-Wax 52 CB) and from 60°C-210°C at 4°C/min (Rtx-5), respectively. The injector and detector temperatures were 210°C and 230°C, respectively. The injection volume was 0.02 µL neat and 0.1 µL in hexane, split ratio was 1: 40. The GC-MS analysis of the oils were carried out on PerkinElmer AutoSystem XL GC interfaced with a Turbomass Quadrupole mass spectrometer fitted with an Equity-5 fused silica capillary column (60 m × 0.32 mm i.d., film thickness 0.25 µm; Supelco Bellefonte, PA, USA). The oven column temperature ranged from 70°C–250°C, programmed at 3°C/min, with initial and final hold time of 2 min, using He as carrier gas at 10 psi constant pressure, a split ratio of 1:30, an injection size of 0.03 µL neat, injector, transfer line and source temperatures were 250°C; ionization energy 70 eV; mass scan range 40-450 amu.

2.4 Identification of Constituents

Identification of constituents were done on the basis of retention time, Retention Index (RI, determined with reference to homologous series of *n*-alkanes (C_9-C_{26}, Polyscience Corp., Niles IL) under identical experimental condition), coinjection with standards (Aldrich and Fluka), mass spectra library search (NIST/EPA/NIH version 2.1 and Wiley registry of mass spectral data 7th edition) and by comparing with the mass spectral literature data [27-28]. The relative amounts of individual components were calculated based on GC peak areas without using correction factors.

3. Results and discussion

The essential oil compositions of aerial parts of nineteen cultivars of *Cymbopogon* (four cultivars of *C. martinii* var. *motia*, seven cultivars of *C. flexuosus*, six cultivars of *C. winterinus*, one cultivar of *C. pendulus* and a hybrid (of *C. khasianus* and *C. pendulus*) cultivated in Pantnagar, a tarai area of Uttarakhand, India were analyzed and compared using capillary GC and GC-MS. The essential oil yield was found to vary from 1.0%-1.4% in leaves and 0.7%-1.1% in inflorescence of *C. martinii* var. *motia*. Similarly, the oil yields varied from 0.7% to 1.0% in different cultivars of *C. flexuosus*; while in cultivars of *C. winterinus,* it varied from 1.0% to 1.3%. The oil yield of cv. Praman (of *C. pendulus*) was found to be 0.8%; while in CKP-25 (hybrid of *C. khasianus* and *C. pendulus*) the oil yield was found 1.2% (*Table 1*). The GC and GC-MS analysis of the essential oils led to the identification of 48 constituents forming 90.1% to 99.7% of the total oil compositions (Table 2). Monoterpenoids (78.9% to 97.4%) constituted the major proportion of oil composition in different cultivars of the studied aromatic grasses. The leaf and inflorescence essential oils of *C. martinii* var. *motia* cvs. Vaishnavi, Trishna, Tripta and PRC-1 were dominated by oxygenated monoterpenoids (86.2%-96.1%, respectively) and represented mainly by geraniol (64.0%-92.6%), geranyl acetate (1.1%-23.3%) along with limonene (≤0.1%-4.4%) and *epi*-α-cadinol (≤0.1%-7.2%). The geraniol proportion was found to be higher in leaf essential oil (82.0% to 92.6%) as compared to inflorescence essential oil (64.0% to 84.0%). While inflorescence oil was found to be rich in geranyl acetate (9.9%-23.3%) as compared to leaf essential oil which contained upto 1.1%-4.5%. The present results are in good agreement with the earlier findings which showed leaf lamina and leaf sheath oils richer in geraniol; while inflorescence oil was richer in geranyl acetate [25]. Although the characteristics marker constituents in all studied oils were same however, there were considerable variations in the quantitative make up of the constituents.

The cultivars of *C. flexuosus* viz., Cauvery, Neema, OD-19, Krishna, Chirharit and Pragati were rich in citrals (comprised of neral and geranial) with highest proportion in cv. Krishna (84.4%; neral 32.9% and geranial 51.5%) followed by Chirharit (84.0%; neral 32.4% and geranial 51.6%), OD-19 (83.6%; neral 31.6% and geranial 52.0%), Pragati (82.9%; neral 31.6% and geranial 51.3%), Nima (82.7%; neral 31.5% and geranial 51.2%) and Cauvery (80.6%; neral 32.3% and geranial 48.3%). While the cultivar GRL-1 of *C. flexuosus* contained high geraniol (87.9%) proportion with only 4.7% citrals (1.9% neral and 2.8% geranial). Besides total citrals proportion, variability in geraniol content in Cauvery, Neema, OD-19, Krishna, Chirharit and Pragati cultivars was found, which vary from 0.4% to 4.5% with highest in cv. Krishna and lowest in cv. OD-19. Other constituents identified in significant amount were limonene (≤0.1%-1.8%), β-caryophyllene (≤0.1%-0.9%) and geranyl acetate (0.1%-0.8%). The cv. Praman of *C. pendulus* was also dominated by citrals (80.4%; neral 32.2% and geranial 48.2%) along with limonene (2.3%), geraniol (1.8%) and terpinen-4-ol (1.2%) as major constituents. The essential oil obtained from the leaves of CKP-25 (hybrid of *C. khasianus* and *C. pendulus*) was also found to be dominated by citral (75.9%; 31.5% neral and 44.4% geranial) along with limonene (5.5%), geranyl acetate (3.9%) and β-myrcene (2.4%). Thus, the essential oil composition of obtained from cv. CKP-25 was very close to the cultivars of *C. flexuosus.* Generally three species of *Cymbopogon* viz., *flexuosus*, *citratus* and *pendulus* yield lemongrass oil of commerce, with citrals as major constituents (> 75.0%). The qualitative and quantitative performance of all the cultivars of *C. flexuosus* except GRL-1; cv. Praman of *C. pendulus* and hybrid CKP-25 grown at tarai conditions produces essential oils of commercial interest rich in citrals (75.9% to 84.4%).

The major constituents in the essential oils of five cultivars of *C. winterinus* viz. Manjari, Manjusha, Jalpallavi, Bio-13 and Mandakani were citronellal (29.1%-35.4%), geraniol (22.5%-30.2%), citronellol (7.4%-11.0%), geranyl acetate (≤0.1%-4.6%), neral (≤0.1%-8.8%), geranial (1.1%-12.2%) elemol (1.0%-3.8%) and limonene (≤0.1%-2.7%). The cultivar Medini contained high geraniol (50.1%) proportion followed by geranial (12.9%), citronellal (11.8%), neral (8.9%) and citronellol (7.5%). The comparative results showed considerable variation in the quantitative compositions of essential oils obtained from different cultivars of *C. winterinus.* In present study, citronellal was found to be lesser than the cultivars grown in the region of Karnataka (37.8%-38.2%), Andhra Pradesh (50.93%), Jammu & Kashmir (41.6%), West Bengal (36.0%-44.6%) and Assam (40.7%-45.5%) of India [26]. While geraniol showed a reverse trend. This might be due to the agriclimatic conditions, and more appropriately, the time of sample collection which revealed decrease in citronellal content during winter. Further, the differences in chemical compositions could also be due to a number of other factors including stage of developments & processing of plant materials before extraction of oil. The characteristics organoleptic nature of these aromatic grasses were thus due to their high proportion of: total alcohol viz., geraniol and citronellol (in cvs. of palmarosa, citronella and cv. GRL-1 of lemongrass); aldehydes viz., geranial, neral and citronellal (in cvs. of lemongrass, CKP-25 and citronella grass) and less but varying amount of esters such as geranyl acetate, geranyl butyrate, geranyl hexanoate and geranyl propanoate, citronellyl acetate, citronellyl butyrate (in palmarosa and citronella). The trace constituents present are also responsible for the characteristics olfactory note of the oils of these aromatic grasses and their cultivars.

In *Cymbopogon,* the essential oil composition showed significant qualitative and quantitative commonality across the species/cultivars. On the basis of chemical similarity the cultivars of genus *Cymbopogon* were divided into three series viz. *Citrati*, *Rusae* and *Scheonanthi* [29]. Considering the presence or absence of the major components in 18 cultivars belonging to four species and a hybrid, it was possible to classify them in to 5 groups. The group I comprised of all four cultivars of *C. martinii* (Vaishnavi, Trishna, Tripta and PRC-1) with geraniol and geranyl acetate as principal components and it belongs to the series *Rusae*. Similarly, the cultivars of *C. flexuosus* except GRL-1, could be put together in series *Citrati* (group II) due to presence of citrals. The cv. Praman (of *C. pendulus*) and one hybrid CKP-25 (of *C. khasianus* and *C. pendulus*) was also placed in group II (series *Citrati*) as their oil composition was very close to the cultivars of *C. flexuosus* with citrals (80.4%, 75.9% respectively) as major constituents. On the other hand, *C. flexuosus* cultivar GRL-1 was chemically dissimilar from other cultivars of lemongrass and thus, finds a separate group III with very much similarity to series *Rusae* of *C. martinii*. In *C. winterinus*, the major components in the oils of cultivars Manjari, Jalpallavi, Manjusha, BIO-13 and Mandakini were citronellal, geraniol and citronellol and assigned as group IV. The remaining cv. Medini was dominated by geraniol followed by citrals and citronellal and it could be placed in group V. Therefore, classification based on morphological characters is not fully supported by their volatile profile or more appropriately by chemotaxonomy. Moreover, the three *Cymbopogon* species belong to five chemical variants. This is because of the environmental and geographical features which have a strong influence on their morphological traits. The cultivars of *C. martinii* var. *motia* were the prospective source of essential oil rich in geraniol contents used in high grade perfume. GRL-1 (cv. of *C. flexuosus*) and Medini (cv. of *C. winterianus*) are excellent supplement or substitute to palmarosa oil. All other cultivars of citronella Java, yield oils whose ingredients citronellal, citronellol and geraniol are widely used in soap, pharmaceutical, perfumery, cosmetics and flavoring agents. While other six cultivars of *C. flexuosus*, cv. Praman of *C. pendulus* and hybrid CKP-25 were very good source of citrals (75.9% to 84.4%) used for various industrial purposes.

Table 1. Origin of different cultivars of *Cymbopogon* species and their essential oil yield

Plants	Cultivars	Abbreviations	Oil Yield* (%, v/w)	Development/Origin
Cymbopogon martinii var. *motia* (Palmarosa)	Vaihnavi	I	1.2 (1.0)	Selection in OPSPs [30]
	Trishna	II	1.0 (1.1)	Synthetic population breeding [31]
	Tripta	III	1.0 (0.7)	Mass selection [32]
	PRC-1	IV	1.4 (1.1)	Composite population breeding [33]
Cymbopogon flexuosus (Lemongrass)	Caveri	V	0.8	Phenotypic recurrent selection [33]
	Nima	VI	0.7	Clonal selection in OPSPs [34]
	Krishna	VII	1.0	Phenotypic recurrent selection [35]
	Chirharit	VIII	0.7	Clonal selection in OPSPs [36]
	OD-19	IX	0.7	Clonal selection [4]
	Pragati	X	0.7	Clonal selection in OPSPs [33]
	GRL-1	XI	0.8	Selection in OPSPs of OD-19 [4]
Cymbopogon pendulus (Lemongrass)	Praman	XII	0.8	Clonal selection [37]
Hybrid of *C. khasianus* × *C. pendulus*	CKP-25	XIII	1.2	Hybridization [38]
Cymbopogon winterinus (Java Citronella)	Manjari	XIV	1.3	Induced mutagenesis [39]
	Jal Pallavi	XV	1.2	Clonal selection [40]
	Medini	XVI	1.2	Clonal selection [40]
	Manjusha	XVII	1.0	Clonal selection [33]
	Bio-13	XVIII	1.2	*In-vitro* somaclonal selection [33]
	Mandakani	XIX	1.1	Clonal selection [33]

* The oil yields in parentheses are for inflorescence; OPSPs: Open Pollinated Seed Progenies

Table 2. Comparative chemical composition of the commercially grown cultivars of *Cymbopogon* Spreng.

Compounds[*]	**RI**[a]	**RI**[b]	**I**		**II**		**III**		**IV**		**V**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**	**XII**	**XIII**	**XIV**	**XV**	**XVI**	**XVII**	**XVIII**	**XIX**
			LO	**FO**	**LO**	**FO**	**LO**	**FO**	**LO**	**FO**															
α-pinene	1026	942	t	t	0.2	-	t	-	t	t	0.1	-	-	0.1	t	t	-	0.1	0.1	-	-	-	-	-	-
β-pinene	1105	980	-	-	-	-	-	-	-	-	-	t	0.1	0.1	t	t	t	t	t	0.2	1.8	t	0.1	t	-
myrcene	1153	991	-	-	t	t	0.2	0.1	t	0.2	-	-	-	-	-	-	-	-	2.4	-	-	-	-	-	-
limonene	1194	1034	t	t	0.2	2.4	0.7	4.4	0.3	3.6	1.8	0.8	1.2	t	t	1.2	1.0	2.3	5.5	t	2.2	t	2.7	2.4	2.3
(*Z*)-β-ocimene	1234	1043	t	t	t	t	-	-	0.8	-	t	0.8	t	t	-	t	0.1	0.2	t	t	t	-	-	-	-
(*E*)-β-ocimene	1246	1052	t	t	0.1	-	-	-	0.2	t	-	-	t	t	-	0.2	0.5	0.3	t	t	0.1	-	t	-	t
p-cymene	1271	1028	-	-	-	-	-	-	-	-	-	0.2	t	0.1	-	-	t	0.1	t	t	-	0.1	t	t	t
terpinolene	1278	1090	t	0.1	t	-	0.6	-	-	t	0.2	-	0.5	t	-	t	-	t	t	t	-	-	t	-	t
6-methyl hept-5-en-2-one	1343	987	-	-	-	-	-	-	-	-	0.3	0.7	0.5	0.1	0.6	t	t	0.5	0.6	0.1	t	t	0.1	-	-
(*Z*)-rose oxide	1344	1112	-	-	-	-	-	-	-	-	-	*0.3*	-	-	*0.3*	-	-	0.4	-	0.1	0.1	t	0.1	t	t
(*E*)-sabinene hydrate	1463	1069	-	-	-	-	-	-	-	-	0.1	0.9	t	0.2	0.8	0.2	0.1	0.5	t	t	-	t	-	t	t
citronellal	1474	1154	**t**	**t**	**-**	**0.2**	**-**	**-**	**-**	**t**	**0.1**	**0.3**	**0.5**	**t**	**t**	**t**	**t**	**0.3**	**0.4**	**35.4**	**29.1**	**11.8**	**31.4**	**32.3**	**33.6**
camphor	1507	1148	-	-	-	-	-	-	-	-	0.5	-	t	0.2	0.8	-	-	t	0.1	0.3	-	-	t	-	t
β-bourbonene	1516	1384	-	-	-	-	-	-	-	-	0.6	-	0.3	0.1	-	0.1	-	t	0.4	0.1	-	-	t	-	-
linalool	1534	1098	0.4	0.5	0.2	t	0.8	0.2	0.2	0.3	t	0.8	0.6	0.8	0.8	t	-	0.8	0.8	0.1	t	0.3	t	0.3	0.4
linalyl acetate	1546	1256	-	-	-	-	-	-	-	-	-	0.4	-	-	0.5	-	-	t	-	0.6	t	t	0.5	t	0.1
iso-pulegol	1574	1213	-	-	-	-	-	-	-	-	t	0.3	-	0.3	0.2	t	-	0.2	-	0.1	0.3	-	0.3	t	-
β-elemene	1589	1392	-	-	-	-	-	-	-	-	-	-	t	0.1	-	0.3	-	t	-	0.2	t	t	0.3	-	t
β-caryophyllene	1594	1418	0.3	0.4	0.5	0.5	1.0	0.2	0.2	0.3	0.5	0.9	0.6	0.3	0.4	t	0.3	0.1	1.5	0.1	0.4	0.2	0.3	0.1	t
terpinen-4-ol	1606	1181	-	-	-	-	-	-	-	-	t	0.9	t	0.8	0.7	t	t	1.2	0.4	0.1	0.1	t	0.1	t	-
citronellyl acetate	1655	1356	t	t	0.3	-	-	-	-	0.2	t	0.4	t	0.1	0.3	0.3	t	0.6	0.3	0.5	0.1	0.2	3.5	4.4	2.9
(*E*)-β-farnesene	1662	1458	-	-	-	-	-	-	-	-	-	-	-	0.1	-	t	-	0.2	t	t	t	t	-	0.1	-
α-humulene	1675	1454	-	-	-	-	-	-	-	-	-	-	-	t	-	1.2	-	0.3	t	t	0.1	t	t	0.5	-
neral	1678	1241	**t**	**0.1**	**0.2**	**t**	**0.4**	**t**	**0.8**	**-**	**32.3**	**31.5**	**32.9**	**32.4**	**31.6**	**31.6**	**1.9**	**32.2**	**31.5**	**8.8**	**2.7**	**8.9**	**0.3**	**t**	**0.3**
γ-muurolene	1680	1477	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	t	-	-	0.2	-	0.8	0.3	-
α-terpineol	1682	1191	t	-	-	-	0.2	-	-	-	0.1	0.9	0.1	0.2	0.4	t	-	0.6	t	0.3	0.6	0.1	t	-	-
borneol	1695	1168	-	-	-	-	-	-	-	-	t	0.8	-	0.5	-	0.1	-	0.7	-	0.1	0.2	t	0.3	1.0	0.3
germacrene d	1701	1480	t	-	-	-	0.1	-	-	-	t	-	-	0.1	-	0.1	-	t	t	-	0.8	-	0.5	t	t

Table 2 continued…

Compounds	RI[a]	RI[b]	I		II		III		IV		V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
			LO	FO	LO	FO	LO	FO	LO	FO															
geranial	1728	1270	**t**	**t**	-	-	-	**t**	**t**	**t**	**48.3**	**51.2**	**51.5**	**51.6**	**52.0**	**51.3**	**2.8**	**48.2**	**44.4**	**12.2**	**1.7**	**12.9**	**1.1**	**6.3**	**0.9**
geranyl acetate	1751	1384	**1.1**	**9.9**	**2.7**	**10.0**	**4.5**	**23.3**	**2.4**	**14.1**	**0.5**	**0.7**	**0.4**	**0.6**	**0.1**	**0.8**	**0.8**	**0.9**	**3.9**	**1.4**	**3.6**	**1.1**	**4.6**	**t**	**4.0**
δ-cadinene	1758	1529	-	-	-	-	-	-	-	-	0.2	t	t	0.1	t	0.1	t	0.5	0.6	t	-	t	t	t	t
citronellol	1776	1226	**t**	-	-	**t**	**t**	-	**t**	-	**0.1**	**0.3**	**0.2**	**0.1**	**0.2**	**t**	-	**t**	**t**	**7.4**	**9.3**	**7.5**	**9.6**	**9.5**	**11.0**
nerol	1814	1229	t	-	0.2	t	0.3	-	t	t	0.1	0.5	t	0.1	t	0.5	t	0.2	0.2	0.3	0.1	0.1	0.3	t	0.1
geranyl propanoate	1821	1476	t	t	0.1	t	0.1	-	-	t	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
citronellyl butyrate	1830	1530	-	-	-	-	-	-	-	-	0.2	-	-	-	-	-	-	-	-	0.1	0.5	t	0.1	t	t
geraniol	1856	1257	**88.6**	**83.9**	**86.0**	**84.0**	**82.0**	**64.0**	**92.6**	**71.4**	**2.9**	**3.0**	**4.5**	**3.5**	**0.4**	**1.3**	**87.9**	**1.8**	**1.5**	**22.4**	**25.9**	**50.1**	**24.0**	**25.5**	**30.2**
geranyl butyrate	1896	1563	0.4	0.2	0.3	t	0.4	0.1	t	t	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
caryophyllene oxide	2004	1584	0.3	0.1	0.6	t	t	t	0.1	0.8	0.2	0.6	t	0.4	0.1	0.9	0.1	0.2	t	0.1	0.2	0.1	t	2.8	2.3
geranyl hexanoate	2069	1726	0.8	0.4	0.1	0.2	0.2	0.1	0.1	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
germacrene D-4-ol	2070	1578	-	-	-	-	-	-	-	-	0.3	t	0.1	t	0.1	-	-	-	t	0.1	2.5	t	2.6	t	-
elemol	2096	1550	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.0	3.8	0.8	3.8	3.7	3.8
10-*epi*-γ-eudesmol	2112	1622	t	0.2	0.2	-	0.2	0.1	0.4	0.4	t	0.1	0.6	0.5	0.1	t	0.2	0.2	2.5	0.1	1.2	t	2.0	1.3	0.5
spathulenol	2137	1576	-	-	-	-	-	-	-	-	0.2	t	t	t	0.1	0.1	0.4	-	-	0.1	0.7	0.4	1.0	1.5	0.5
geranyl heptanoate	2185	1830	0.2	0.2	0.1	t	0.1	t	t	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
epi-α-cadinol	2187	1642	1.0	1.7	t	2.4	0.8	7.2	1.5	5.2	0.1	t	t	t	t	-	0.3	0.2	t	0.3	1.6	0.2	1.9	1.7	1.0
α-cadinol	2254	1653	0.3	0.2	0.5	t	0.2	-	t	t	0.3	t	t	0.2	0.1	0.3	-	-	0.2	0.2	t	0.1	0.1	0.2	-
β-eudesmol	2258	1651	-	-	-	-	-	-	-	-	0.1	t	t	t	0.2	t	-	t	t	0.1	0.2	t	0.3	-	0.2
Monoterpene hydrocarbons			t	0.1	0.5	2.4	1.5	4.5	1.3	3.8	2.1	1.8	1.8	0.3	t	1.4	t	3.0	8.0	-	-	0.1	2.8	2.4	2.3
Oxygenated monoterpenes			91.3	95.0	90.1	94.4	88.9	87.7	96.1	86.2	85.2	93.6	90.7	91.4	89.1	86.1	89.1	89.1	83.5	90.2	89.1	92.9	76.2	79.3	83.8
Sesquiterpene hydrocarbons			0.3	0.4	0.5	0.5	1.1	0.2	0.2	0.3	1.3	0.9	0.9	0.8	0.6	2.1	0.6	1.2	2.5	0.6	1.2	0.2	1.9	1.1	t
Oxygenated sesquiterpenes			1.8	2.4	1.4	2.4	1.3	7.3	2.0	6.7	1.2	0.7	0.7	1.1	0.7	1.3	0.7	0.6	2.7	2.0	0.6	1.7	11.7	11.2	8.3
Others			-	-	-	-	-	-	-	-	0.3	0.3	0.5	0.1	0.6	t	0.6	t	0.6	0.1	t	t	0.1	-	-
Total Identified			**93.4**	**97.9**	**92.5**	**99.7**	**92.8**	**99.7**	**99.6**	**97.0**	**90.1**	**97.3**	**94.6**	**93.7**	**91.0**	**90.9**	**91.0**	**93.9**	**97.3**	**93.1**	**93.9**	**94.9**	**92.7**	**94.0**	**94.4**

*Mode of identification: Linear Retention Index (LRI, Based on homologous series of n-alkanes; C8-C24), coinjection with standards/Peak enrichment with known oil constituents, MS (GC-MS); [a]RI: Retention index on CP Wax 52 CB (30 m × 0.32 mm); [b]RI: Retention index on Equity-5 (60 m × 0.32 mm); t= trace (<0.1%); (-) = absent; For plant abbreviations, see Table 1.

Table 3. Classification of *Cymbopogon* cultivars based on their chemical markers/chemotaxonomy and their distribution

Group	Species	Major distribution	Cultivar	Marker constituents	Series
I	*C. martinii*	Throughout in India	Vaishnavi, Trishna, Tripta, PRC-1	Geraniol (64.0%-92.6%), geranyl acetate (1.1-23.3%)	*Rusae*
II	*C. flexuosus*	Southern and northern part of India	Cauvery, Nima, OD-19, Krishna, Chirharit, Praman, Pragati	Citral (80.6%-84.4%)	*Citrati*
	Hybrid *C. pendulus* × *C. khasianus*	Some part of Northern India	CKP-25	Citral (75.9%), limonene (5.5%)	
	C. pendulus	Southern and northern part of India	Praman	Citral (80.4%)	
III	*C. flexuosus*	Southern and northern part of India	GRL-1	Geraniol (87.9%), Citral (4.7%)	Very close to *Rusae*
IV	*C. winterinus*	Andhra Pradesh, Assam, Gujarat, Jammu & Kashmir, Tamilnadu, Uttar Pradesh and Uttarakhand	Manjari, Jalpalavi, Manjusha, BIO-13, Mandakini	Citronellal (31.1-35.4%), Geraniol (22.4-30.2%), Citronellol (7.4-11.0%)	*Citrati*
V	*C. winterinus*	Southern and northern sub Himalayan region of India	Medini	Gernaiol (50.1%), Citral (21.8%), Citronellal (11.8%)	-

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