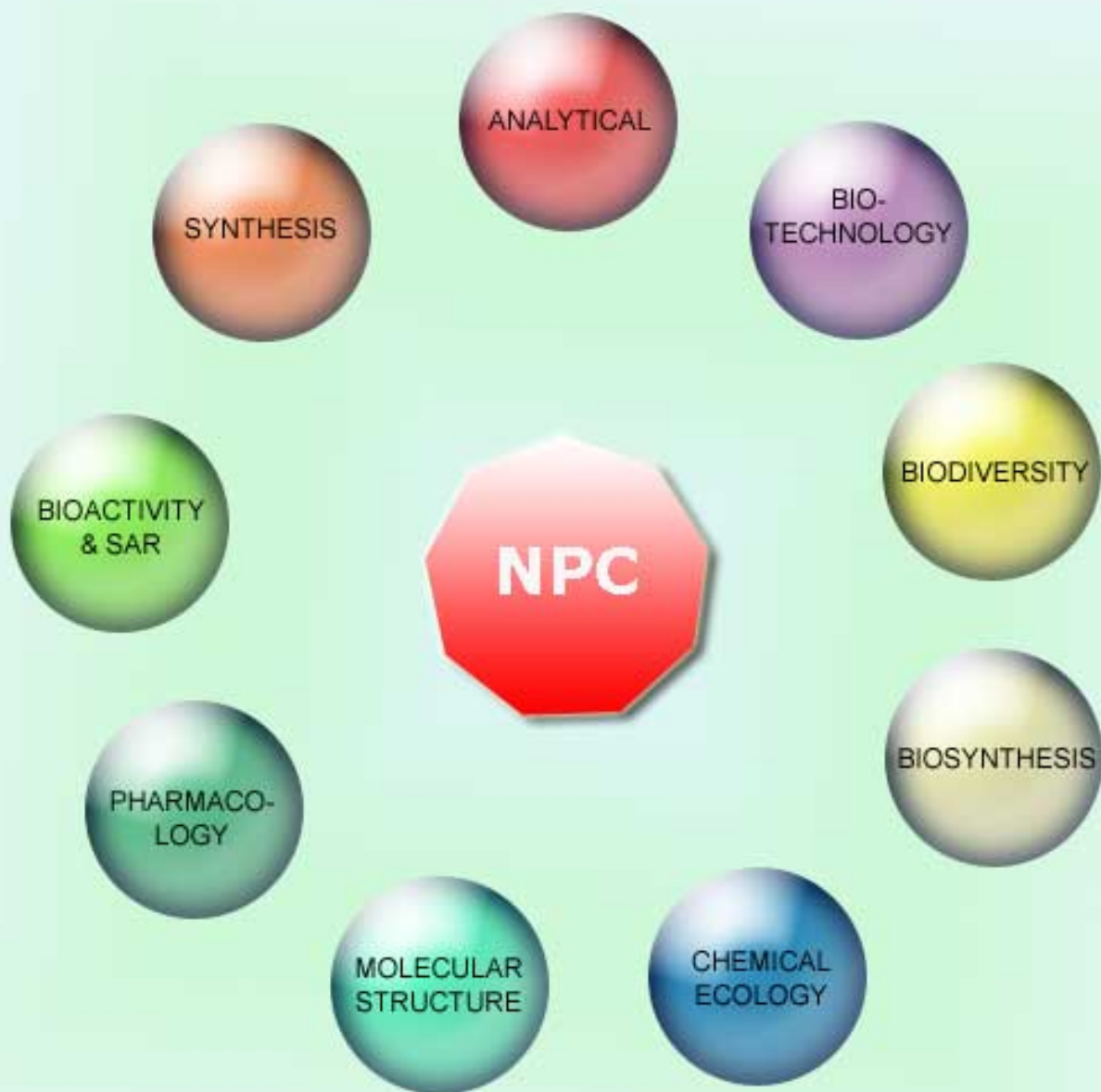


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Enantiomeric Composition of (3*R*)-(-)- and (3*S*)-(+)-Linalool in Various Essential Oils of Indian Origin by Enantioselective Capillary Gas Chromatography-Flame Ionization and Mass Spectrometry Detection Methods*

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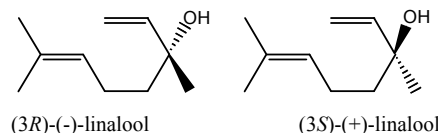
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Enantiomeric ratios of linalool have been determined in various authentic essential oils of Indian origin using 10% heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)- β -cyclodextrin as a chiral stationary phase. A complete enantiomeric excess (ee) for (3*S*)-(+)-linalool was characteristic of *Lippia alba* and *Cinnamomum tamala* leaf oils while less than 90% excess was noticed in *Zanthoxylum armatum* leaf, *Zingiber roseum* root/rhizome and *Citrus sinensis* leaf oils. On the contrary, an enantiomeric excess of (3*R*)-(-)-linalool characterizes essential oils of basil (100% for *Ocimum basilicum*) and bergamot mint (72 to 75% for *Mentha citrata*). Notably, some essential oils containing both enantiomers in equal ratios or in racemic forms are rose, geranium, lemongrass and *Origanum*. The enantiomeric composition studies are discussed as indicators of origin authenticity and quality of essential oil of Indian origin.

Keywords: Cyclodextrins, chiral terpenoid, essential oil, (3*R*)-(-)-linalool, (3*S*)-(+)-linalool, enantiomeric excess.

Linalool (3,7-dimethyl-1,6-octadien-3-ol) is an important oxygenated monoterpene in industrial flavor preparation [1]. It occurs naturally in two isomeric optical forms viz., (3*R*)-(-)- and (3*S*)-(+)-linalool, each having quite distinctive odors.

Extensive studies by various authors have led to the evaluation of the enantiomeric ratio and enantiomeric excess of chiral terpenes including hydrocarbons and their oxygenated derivatives in various essential oils [2-10]. The monoterpene hydrocarbons have a characteristic enantiomeric composition that can be utilized as a 'fingerprint' for chemotaxonomic assignments and for detecting adulteration [3]. Moreover, chirality determination has been adopted for quality assurance as an indicator of genuineness. (*R*)-Linalool has been reported from natural bergamot oil [3,4]. However, a large number of commercial bergamot samples showed adulteration with synthetic or racemic linalool and linalyl acetate [3]. Enantiomeric distribution of linalool and linalyl acetate enantiomers in various aromatic plants have been reported [4].



Ocimum basilicum essential oil was reported to contain (*R*)-(-)-linalool and was proved optically pure in many other samples [7]. Linalool has been reported in the essential oils of *Zingiber roseum* [11], *Pelargonium graveolens* [12] and *Origanum vulgare* [13]. In continuation of our investigations on enantiomeric separation of terpenoids [14], we now report compositional studies of enantiomeric linalool in indigenous essential oils using enantioselective GC-FI/MS methods.

The enantiomeric distribution of linalool isomers is presented in Tables 1-3. Plants possessing higher levels of (3*R*)-(-)-linalool are listed in Table 1. Some of our results confirm previous published work, especially for basil [7] and bergamot mint [4]. Pure (3*R*)-(-)-linalool was noticed in Indian basil, *O. basilicum*, and indicated a complete excess. In bergamot mint, the enantiomeric ratio for

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Table 1: Linalool: enantiomeric ratio and excess (%) in favor of (3R) isomer in different plants.

Species	Origin	Extraction method	Ratio		Enantiomeric excess for (3R)
			(3R)	(3S)	
<i>Ocimum basilicum</i>	Cultivated -1	HD	100	0	100
	Cultivated -2	HD	100	0	100
	Cultivated -3	HD	100	0	100
<i>Mentha citrata</i>	Cultivated-1	HD	86.1	13.9	72.2
	Cultivated -2	HD	87.9	12.1	75.7

Table 2: Linalool: enantiomeric ratio and excess (%) in favor of (3S) isomer in different plants. For details, see Experimental.

Species	Origin	Extraction method	Ratio		Enantiomeric excess for (3S)
			(3R)	(3S)	
<i>Zingiber roseum</i>	Wild	HD	9.1	90.9	81.8
<i>Cinnamomum tamala</i>	Cultivated-1	HD	0	100	100
	Cultivated-2	HD	0	100	100
	Cultivated -3	HD	0	100	100
	Cultivated-4	HD	0	100	100
<i>Citrus sinensis</i>	Cultivated	HD	16.2	83.8	67.6
<i>Coriandrum sativum</i>	Reference sample	HD	11.8	88.2	76.4
<i>Lippia alba</i>	Cultivated	HD	0	100	100
<i>Zanthoxylum armatum</i>	Wild	HD	8	92	84

Table 3: Low linalool enantiomeric ratio and excess in different plants.

Species	Origin	Extraction method	Ratio		Enantiomeric excess
			(3R)	(3S)	
<i>Origanum vulgare</i>	Wild	HD	44.5	55.5	11.0 (3S)
<i>Rosa damascena</i>	Reference	SD	56.2	43.8	12.4 (3R)
Linalool mixture	Reference	SD	48.5	51.5	3.0 (3S)
<i>Cymbopogon flexuosus</i>	Cultivated	HD	41.6	58.4	16.8 (3S)
<i>Pelargonium graveolens</i>	Cultivated-1	HD	50.7	49.3	1.4 (3R)
	Cultivated-2	HD	50.4	49.6	0.8 (3R)
	Cultivated-3	HD	56.2	43.8	12.4 (3R)
	Cultivated-4	HD	63.6	36.4	27.2 (3R)
	Cultivated-5	HD	49.1	50.9	1.8 (3S)
	Cultivated-6	HD	49.2	50.8	1.6 (3S)

(3R)-(-)-linalool varied from 86-88% while the enantiomeric excess falls within the range 72-76%. Notably, the observed ratios for our oil samples were well within the limit [4].

The essential oils that contained (3S)-(+)-linalool in high proportions are given in Table 2. *Zingiber roseum* contained more than 80% linalool in the essential oil of the roots/rhizomes. On chiral examination, a higher enantiomeric ratio (90.9%) for (3S)-(+)-linalool was noticed leading to an excess of more than 81%. The leaf oil of *C. sinensis* contained (3S)-(+)-linalool with 84% optical purity equivalent to 67% excess. There are two publications reporting the chiral discrimination of *C. sinensis* peel oil; 95.1% (3S)-(+)-linalool and 4.9% (3R)-(-)-linalool [8,15] and 85-91% (3S)-(+)-linalool and 9-15% (3R)-(-)-linalool [4]. The leaf essential oil of *Zanthoxylum armatum*, a highly valued medicinal plant used as a remedy for toothache in the Himalayan region, was characterized by 92% (3S)-(+)-linalool along with 8% (3R)-(-)-linalool and indicates a (3S)-(+)-linalool excess of more than 84%. Optically pure (3S)-(+)-

linalool with complete excess was identified in *Cinnamomum tamala* leaf essential oil. (3R)-(-)-Linalool was not noticed, even in trace amount. (3R)-(-)-Linalool has been reported in *C. zeylanicum* essential oil from Madagascar [9], while Sri Lankan cinnamon showed vast variation; 64% (3R)-(-)- and 36% (3S)-(+)-linalool [4]. Therefore, based on the enantiomeric ratio determination, we concluded that *C. tamala* essential oil could not be treated in a similar way to that of *C. zeylanicum*. *Lippia alba* essential oil was comprised of enantioenriched (3S)-(+)-linalool, which is confirmed by a previous work [6]. It is a well known fact that orange and coriander essential oils have specific chiral distributions. *Coriandrum sativum* revealed a high proportion of (3S)-(+)-linalool (88% purity and 76% ee) as compared to earlier work (85.5-90%) [4]. Hence, our results confirm the published reports, especially for *L. alba* and *C. sativum*. However, it is also important to mention here that the coriander sample, having less than an 81% ratio, indicates an abnormal enantiomeric distribution and should be considered as an adulterated sample [4].

Plants having low enantiomeric ratios are grouped in Table 3. *Origanum vulgare* showed almost a racemic distribution: 55.5% (3*S*)-(+)-linalool and 44.5% (3*R*)-(-)-linalool. *Rosa damascena* contained a slightly lower enantiomeric ratio of about 56% for (3*R*)-(-)-linalool as compared with 60-62% in a published report [4]. (3*S*)-(+)-Linalool with the enantiomeric ratio of 58.4% was noticed in *Cymbopogon flexuosus*, which was a slightly lower value in comparison with *C. winterianus* (61.3%; (3*S*)-(+)-linalool) from southern Brazil [10]. Geranium oils have been characterized by sharp inversion in both the optical forms. Out of the six cultivated samples, four have been marked by (3*R*)-(-)-linalool (50.4-63.6%), while the others showed (3*S*)-(+)-linalool (50.8-50.9%) in slight excess. The conversion mechanism is beyond the scope of the present study. Hence, in general, it has been emphasized that linalyl acetate is hydrolyzed; petitgrain oil showed a sharp decrease in (*R*)-linalyl acetate during steam distillation [4]. This is contrary to the work of Kreis et al [2]; genuine lavender oils always had a ratio of (3*S*)-(+)-linalool between 2% and up to 5%, while (3*R*)-(-)-linalyl acetate was a minimum of 99%. It is well known that petitgrain oil can have up to 6.6% of (3*S*)-(+)-linalyl acetate [4] but it cannot be generalized for all distilled essential oils bearing linalyl acetate. In a previous publication, it has been established that geranium leaves contains an acid matrix of approx. pH 3.0. Similar conditions prevail for rose, sage and lavender when the distillation process is of long duration [4]. Furthermore, under such conditions, geraniol produces linalool via rearrangement of the geranyl carbocation and subsequent hydration leads to linalool formation.

In conclusion, enantiomeric ratio determination is a powerful tool in authenticity establishment, especially when the enantiomeric forms are unchanged by the extraction processes and the acid index. We have noticed that a low enantiomeric ratio for linalool isomers in some samples of Indian origin might be due to the acidic media, which induce very poor excess. However, low enantiomeric excess should not be considered as evidence of adulteration until or unless proper experimentation is carried out.

Experimental

General: All the oils were analyzed on a Varian CP-3800 GC (Varian Associates, USA) apparatus using a BETA DEX 110 fused-silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Supelco) equipped with a Flame-Ionization Detector (FID).

The oven temperature program was 60°C (isothermal for 2 min) to 180°C (isothermal for 2 min) at 3°/min, than 180° to 220° at 3.5°/min with a final hold time of 5 min, with hydrogen as carrier gas at 1.8 mL/min constant flow; the injector and detector temperatures were 220°C and 250°C, respectively. Injection vol. was 0.04 μL prepared in diethyl ether with a split ratio of 1:200. For GC-MS studies, a Perkin Elmer AutoSystem XL GC (Perkin Elmer, USA) coupled with a Turbomass Quadrupole mass spectrometer was used. The column and oven temperature program was the same as that used in GC while the injector, transfer line and source temperatures were 250°C. The injection size was 0.02 μL prepared in diethyl ether and a split ratio of 1:30 was used with He as carrier gas at 10 psi constant pressure. Mass spectra were recorded in the EI mode at 70 eV in the range *m/z* 40-450. Enantiomeric excess for all the samples was calculated based on the results recorded in triplicate. Both the enantiomers were identified based on their elution order in a β DEX 110 capillary column, by co-injection with pure (3*R*)-(-)-linalool and (±)-linalool (Fluka) and by comparison of their mass spectra with those of the NIST/EPA/NIH version 2.1 and Wiley registry of mass spectral data, 7th edition, and literature data [16].

Plant material: *C. tamala*, *Z. roseum*, *P. graveolens*, *O. vulgare*, *Z. armatum* and *C. sinensis* were compared with herbarium records and identified by a renowned taxonomist Prof. YPS Pangtey at the Botany Department, Kumaun University, Nainital. The roots/rhizomes of *Z. roseum*, leaves of *C. sinensis*, *Z. armatum* and *C. tamala* and aerial parts of *P. graveolens* were collected from Jones Estate, 1500 m above sea level while aerial parts of *O. vulgare* at the flowering stage were collected from Bhowali (1700 m). Plant materials of *O. basilicum*, *P. graveolens*, *L. alba*, *C. flexuosus* and *M. citrata* were collected from our research farm at Lucknow. The plant herbarium and germplasm are maintained in the CIMAP gene bank repository.

Table 4: Linalool percentage in different aromatic plants under study.

Plant species	Plant part	GC-FID
<i>Zingiber roseum</i>	rhizomes	81.9
<i>Cinnamomum tamala</i>	leaves	17.8-30.2
<i>Zanthoxylum armatum</i>	leaves	9.7-23.6
<i>Origanum vulgare</i>	aerial	11.0-14.7
<i>Ocimum basilicum</i>	aerial	30.5-52.9
<i>Mentha citrata</i>	aerial	48.7
<i>Citrus sinensis</i>	leaves	18.9
<i>Lippia alba</i>	aerial	69.4
<i>Cymbopogon flexuosus</i>	aerial	2.2
<i>Pelargonium graveolens</i>	aerial	9.2-10.9

Extraction and isolation of oils: The fresh materials: roots/rhizomes of *Z. roseum*, leaves of *C. tamala*, *Z. armatum*, *C. sinensis* and aerial parts of *O. vulgare*, *O. basilicum*, *P. graveolens*, *L. alba*, *C. flexuosus* and *M. citrata* (0.1 kg each) were distilled in a Clevenger-type apparatus while *P. graveolens* (0.5 kg; cultivated-6) was distilled using a copper still fitted with a spiral glass condenser for 3 h. The distillate was saturated with NaCl then extracted with HPLC grade *n*-hexane and dichloromethane. The organic layer was dried over Na₂SO₄ and concentrated to yield the pure essential oil.

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