

# Enantiomeric Composition of Linalol in the Essential Oils of *Ocimum* Species and in Commercial Basil Oils\*

Uzi Ravid<sup>1\*\*</sup>, Eli Putievsky<sup>1</sup>, Irena Katzir<sup>1</sup> and Efraim Lewinsohn<sup>1</sup>

<sup>1</sup>Institute of Field Crops, Agricultural Research Organization, Neve Ya'ar Research Center, PO Box 90000, Haifa 31900, Israel

The amount and the enantiomeric composition of linalol were determined in the essential oils of seven chemotypes of *Ocimum basilicum* L., in the oils of *O. sanctum* L., *O. gratissimum* L. and *O. canum* Sims. of Thai origin, and in commercial basil oils. The linalol isolated from cultivars of *O. basilicum* L., of various origins, and from commercial basil oils consisted of (*R*)(–)-linalol and was proved to be optically pure in most cases. In essential oils of *O. sanctum* L. and *O. canum* Sims., (*S*)(+)-linalol was the main enantiomer. Thus, the enantiomeric differentiation of linalol may be helpful in interspecific taxonomy in the genus *Ocimum*. © 1997 by John Wiley & Sons, Ltd.

*Flavour Fragr. J.*, **12**, 293–296 (1997) (No. of Figures: 2 No. of Tables: 2 No. of Refs: 11)

KEY WORDS: (*R*)(–)-linalol; (*S*)(+)-linalol; enantiomeric composition; essential oils; *Ocimum basilicum* L.; *Ocimum gratissimum* L.; *Ocimum sanctum* L.; *Ocimum canum* Sims.; Lamiaceae; basil

## INTRODUCTION

The enantiomeric differentiation of linalol is useful in the quality control of essential oils and oleoresins, as it was found to provide an important indication of the authenticity of many herbs and spices. The enantiomeric composition of linalol has been determined in many essential oils including basil, bergamot, rosemary, lavandin, lavender, balm, coriander, mace, pelargonium, rose, *Cymbopogon*, lemon, mandarin, *Osmanthus*, davana, jasmin and orange, as well as in many fruit extracts.<sup>1–3</sup> As to their olfactory qualities, the Linalol enantiomers differ considerably. (*R*)(–)-Linalol was found to have an odour reminiscent of lavender and a woody note. The (*S*)(+)-enantiomer has a petitgrain odour with more of a citrus and fruity note, and its threshold value is higher than that of the (*R*)(–)-enantiomer.<sup>4</sup>

## EXPERIMENTAL

### Plant Material

Plants of 11 cultivars of *O. basilicum* L. var. *basilicum* were grown in an experimental field at the

\* Contribution from the Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel. No. 1923-E, 1996 series.

\*\* Correspondence to: Uzi Ravid, Institute of Field Crops, Agricultural Research Organization, Neve Ya'ar Research Center, PO Box 90000, Haifa 31900, Israel.

Neve Ya'ar Research Center. Commercial seeds of cultivar 68 were received from France. Commercial seeds of cultivars 88, 90, 107 and 150 were obtained from the USA. The other commercial seeds were received from Holland (160) and from Switzerland (161, 174 and 216). Plants of two cultivars (170 and 181) were transferred from private growers in Israel. Seeds of Moroccan *O. basilicum* were obtained from a private company in Morocco.

*O. canum* Sims. seeds were received from Dr S. Pimsamarn (Khon Kaen, Thailand). Plants of *O. basilicum* L., *O. sanctum* L. (white and red) and *O. gratissimum* L. of Thai origin were cultivated and hydrodistilled at Khon Kaen University.

### Isolation of the Essential Oils

The essential oils were hydrodistilled from the fresh aerial plant parts for 1 h in a modified Clevenger apparatus.

### Packed Column Preparative GC

Linalol was collected from the essential oils by preparative gas chromatography on a Varian 3700 gas chromatograph equipped with FID, a 1:50 effluent splitter and a modified Brownlee–Silverstein thermal-gradient collector. A glass column (3 m × 4 mm i.d.) with 5% Carbowax

Table 1. The content (%) and the enantiomeric composition (%) of linalol in laboratory-produced essential oils of *Ocimum* species of various origins or cultivars

Origin/species and variety (cultivar)	Content (%)	(S)(+)-linalol (%)	(R)(-)-linalol (%)
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,f</sup> (68)	59.3	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,f</sup> (88)	54.6	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,f</sup> (white) (90)	48.7	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,d</sup> (107)	43.8	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,e</sup> (150)	3.9	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,c</sup> (160)	52.6	—	100
<i>O. basilicum</i> L. cv. Dark Opal <sup>a,f</sup> (161)	67.6	—	100
<i>O. basilicum</i> L. var. <i>basilicum</i> <sup>a,d</sup> (170)	45.8	8	92
<i>O. basilicum</i> L. var. <i>basilicum/purpurascens</i> intermediate <sup>a,g</sup> (174)	46.5	—	100
<i>O. basilicum</i> L. var. <i>purpurascens</i> <sup>a,e</sup> (181)	0.3	—	100
<i>O. basilicum</i> L. cv. Dark Opal/var. <i>basilicum</i> intermediate <sup>a,f</sup> (216)	61.5	—	100
<i>O. basilicum</i> L. <sup>a,c</sup> Morocco	48.6	—	100
<i>O. basilicum</i> L. <sup>b,e</sup> Thailand	0.2	9	91
<i>O. gratissimum</i> L. <sup>b,h</sup> Thailand	2.5	—	100
<i>O. sanctum</i> L. (white) <sup>b,h</sup> Thailand	0.2	85	15
<i>O. sanctum</i> L. (red) <sup>b,i</sup> Thailand	1.3	95	5
<i>O. canum</i> Sims. <sup>a,i</sup> Thailand	0.6	93.5	6.5

<sup>a</sup> Cultivated at the Newe Ya'ar Research Center. <sup>b</sup> Cultivated and hydrodistilled at Khon Kaen University, Thailand. <sup>c</sup> Linalol and eugenol type. <sup>d</sup> Linalol and methyl chavicol type. <sup>e</sup> Methyl chavicol type. <sup>f</sup> Linalol type. <sup>g</sup> Linalol and *trans*-methyl cinnamate type. <sup>h</sup> Eugenol type. <sup>i</sup> Methyl eugenol type.

20M on 100/120 Supelcoport was used for collecting the linalol fractions. The temperature programme was 80°C for 2 min, 80 to 200°C at 5°C/min; the carrier gas was N<sub>2</sub> (30 ml/min).

#### Capillary GC Analysis

The purified linalol sample was identified on a Supelcowax 10 (30 m × 0.25 mm i.d.) fused silica column, with the temperature programme, 80°C for 2 min and 80 to 200°C at 4°C/min; carrier gas N<sub>2</sub>, 2 ml/min.

#### Chiral Analysis

Chiral separations were performed on a Varian 3300 gas chromatograph equipped with FID and a Varian 4400 integrator. Diluted samples (in hexane) were injected on to a heptakis(2,3,6-tri-*O*-methyl)- $\beta$ -cyclodextrin on a DB 1701 (permethylated  $\beta$ -cyclodextrin, Cyclodex B, J&W) fused silica column (30 m × 0.25 mm i.d.; 0.25  $\mu$ m film thickness). Temperature programme: 70°C for 2 min, 70 to 150°C at 1°C/min; carrier gas H<sub>2</sub>, 40 cm/s; split ratio 1 : 50.

## RESULTS AND DISCUSSION

The amount and the enantiomeric composition of linalol was determined in essential oils of

*Ocimum* species (Table 1) and in commercial samples of basil oils (Table 2). Linalol was the main component (43.8–67.6%) in laboratory-produced *O. basilicum* oils, while methyl chavicol was the main component (68.1–77.3%) in seven commercial basil oils. Five more chemotypes were found in the samples of the *Ocimum* species: linalol and eugenol type, linalol and methyl chavicol type, linalol and *trans*-methyl cinnamate type, eugenol type and methyl eugenol type. Low quantities of linalol (0.2–2.5%) were detected in all the *Ocimum* species from Thailand. While eugenol was the main component (54.8% and 33.4%, respectively) in the white variety of *O. sanctum* and in *O. gratissimum*, methyl eugenol (52.1% and 47.0%, respectively) was the main component in *O. sanctum* (red variety) and *O. canum*. Grayer *et al.*<sup>5</sup> described the essential oil composition of 16 cultivars of *O. basilicum* of different origins (linalol content: 0.5–85.6%) to see whether they could be used as infraspecific taxonomic characters. Lawrence *et al.*<sup>6,7</sup> examined the chemotypes *O. basilicum* (0.5% linalol), *O. sanctum* (0.2–1.5% linalol), *O. canum* (0.3–69.3% linalol) and *O. gratissimum* (0.1–46.1% linalol) from Thailand and from other sources.

In an earlier publication<sup>8</sup> we reported on the enantiomeric composition of linalol in the essential oil from fresh leaves of *O. basilicum*, Mediterranean type. <sup>1</sup>H-NMR 'polarimetry' with the chiral

Table 2. The content (%) and the enantiomeric composition (%) of linalol in samples of basil oils from commercial sources

Origin	Content (%)	(S)(+)-linalol (%)	(R)(-)-linalol (%)
Basil oil; <sup>e</sup> Local market, Delhi, India	21.4	—	100
Basil oil; <sup>f</sup> Local market, Cairo, Egypt	57.7	—	100
Basil oil; <sup>f</sup> dried, hydrodiffused, Egypt; Schmid Hydrodiffusion, Switzerland	42.9	—	100
Sweet basil oil; <sup>d</sup> Givaudan, Switzerland	29.8	—	100
<i>Ocimum basilicum</i> oil; <sup>e</sup> Dragoco, Germany	4.0	—	100
Basil oil; <sup>e</sup> J. D. Schloss, Israel	1.4	—	100
Basil oil; <sup>e</sup> H&R, Germany	45.2	—	100
Basil oil; <sup>e</sup> Carl Roth, Germany	0.9	11	89
Basil oil; <sup>e</sup> Naarden, The Netherlands	7.4	t	> 99
Basil oil; <sup>e</sup> IFF, USA	1.5	t	> 99
Basil oil; <sup>e</sup> Akko	1.6	1	99

<sup>c,d,e,f</sup> See footnote to Table 1.

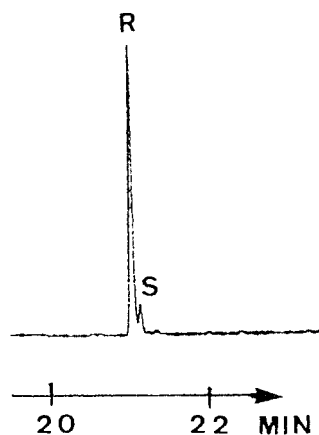


Fig. 1. Enantiomer separation of linalol isolated from *Ocimum basilicum* L. oil of Thai origin; for further details see 'Experimental' section.

shift reagent  $\text{Eu}(\text{hfc})_3$  showed that (*R*)(-)-linalol isolated from sweet basil oil was enantiomerically pure. In the present investigation we determined the enantiomeric differentiation of linalol from various *Ocimum* oils, by means of GLC on a permethylated  $\beta$ -cyclodextrin phase. The order of elution of linalol enantiomers was (*R*)(-), (*S*)(+). Linalol isolated from various cultivars of *O. basilicum*, of various origins, and from commercial basil oils was shown to consist of the (*R*)(-)-enantiomer and was optically pure in most cases. Linalol of three commercial basil oils showed also a very high enantiomeric purity (>99%). Lower enantiomeric purities of (-)-linalol were detected in two laboratory-produced *O. basilicum* oils and in one commercial basil oil (89–92%). The enantiomeric separation of linalol isolated from *O. basilicum* oil of Thai origin is shown in

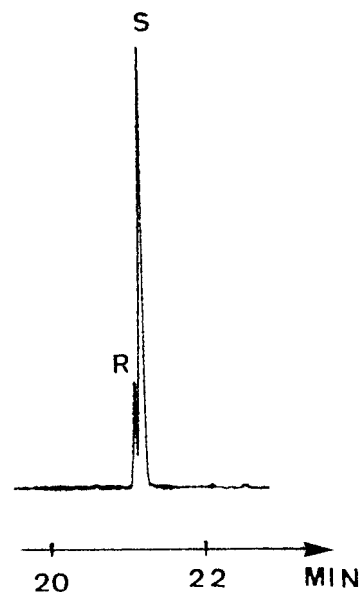


Fig. 2. Enantiomer separation of linalol isolated from *Ocimum sanctum* L. (white variety) oil; for details, see Figure 1.

Figure 1. Our findings were similar to those of Bernreuther and Schreier,<sup>9</sup> who found optically pure (-)-linalol in basil oils from authentic plant material and from a commercial sample. In another commercial sample they detected linalol with 90.7% of the (-)-enantiomer. Werkhoff *et al.*<sup>10</sup> also detected almost optically pure (ee = 99.8%) (-)-linalol in a sample of basil oil. In contrast, Schubert and Mosandl<sup>11</sup> reported that (-)-linalol isolated from two samples of sweet basil oil, was not enantiomerically pure (83.5% and 88.0%).

Surprisingly, (*S*)(+)-linalol was the main enantiomer in the oils of white (Figure 2) and red

*O. sanctum* (85 and 95%, respectively) and in the oil of *O. canum* (93.5%) of Thai origin. Thus, besides the chemical character of a specific cultivar, the enantiomer composition of linalol can be used for the interspecific differentiation in the genus *Ocimum*, and to assess the quality of commercial basil oils.

Comparison between new hydrodistilled oils and 1–2-year-old oils did not show any racemization of linalol, but its relative quantity was always lower in the old oils.

#### REFERENCES

1. C. Bicchi, V. Manzin, A. D'Amato and P. Rubiolo, *Flavour Fragr. J.*, **10**, 127 (1995).
2. P. Werkhoff, S. Brennecke, W. Bretschneider, M. Guntert, R. Hopp and H. Surburg, *Z. Lebensm. Unters. Forsch.*, **196**, 307 (1993).
3. A. Mosandl, *J. Chromatogr.*, **624**, 267 (1992).
4. M. H. Boelens, H. Boelens and L. J. van Gemert, *Perfum. Flavor.*, **18**, 1 (1993).
5. R. J. Grayer, G. C. Kite, F. J. Goldstone, S. E. Bryan, A. Paton and E. Putievsky, *Phytochemistry*, **43**, 1033 (1996).
6. B. M. Lawrence, J. W. Hogg, S. J. Terhune and N. Pichitakul, *The Flavour Industry*, Jan., 47 (1972).
7. B. M. Lawrence, *Essential Oils 1988–1991*, p. 199, Allured Publ., Carol Stream, IL (1993).
8. U. Ravid, E. Putievsky, V. Weinstein and R. Ikan, in *Essential Oils and Aromatic Plants*, ed. A. Baerheim Svendsen and J. J. C. Scheffer, p. 135, Martinus Nijhoff/Dr W. Junk Publ., Dordrecht, The Netherlands (1985).
9. A. Bernreuther and P. Schreier, *Phytochem. Anal.*, **2**, 167 (1991).
10. P. Werkhoff, S. Brennecke and W. Bretschneider, *Chem. Mikrobiol. Technol. Lebensm.*, **13**, 129 (1991).
11. V. Schubert and A. Mosandl, *Phytochem. Anal.*, **2**, 171 (1991).