Journal of Chromatography, 396 (1987) 378–381
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 486

Note

Gas chromatographic diastereomer separation of linalool derivatives

Application to the determination of the enantiomeric purity of linalool in essential oils

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(First received December 12th 1986; revised manuscript received January 24th, 1987)

Linalool (3,7-dimethyl-1,6-octadien-3-ol) is widely encountered in essential oils[1], and occurs in nature in both dextrorotatory [(*S*)-(+)-linalool or coriandrol] and laevorotatory [(*R*)-(−)-linalool or licareol] forms.

Current methods for the determination of enantiomeric compositions using gas chromatography (GC) on chiral stationary phases have recently been reviewed[2]. Enantiomer separation by complexation GC has been extended to various classes of compounds[3] and various underivatized terpenic alcohols have been separated into enantiomers by use of this technique[4–7]. On the other hand, several authors have obtained enantiomer separation of various terpenic alcohols or their derivatives using chiral stationary phases[8–12]. Koppenhoefer and Bayer[13,14] determined thermodynamic data and discussed mechanistic aspects of chiral recognition. The range of compounds separated by Chirasil-Val has been summarized by Bayer *et al.*[14–16].

Whereas several methods have been described for the determination of (±)-linalool in essential oils using GC[17] or proton NMR spectroscopy[18], we have not found a convenient chromatographic method for enantiomeric determination of this component. Since the influence of chirality on the odour quality of various aromatic compounds has been recognized[19–21], we described here a convenient procedure for the diastereomer separation of linalool by GC using phenylethyl urethane derivatives and a capillary column coated with Carbowax 20M as stationary phase; the latter phase is commonly used and recommended[17,22] for GC analyses of essential oils.

EXPERIMENTAL

Materials

Isopropyl isocyanate, *R*-(+)-1-phenylethyl isocyanate {purity > 98% (GC), $[\alpha]_D^{20}$ +12.0 ± 0.5° neat}, *S*-(−)-1-phenylethyl isocyanate {purity > 98% (GC), $[\alpha]_D^{20}$ −12.0 ± 0.5°} and racemic (±)-linalool were obtained from Fluka (Buchs, Switzerland). 3*R*-(−)-Linalool {purity > 98% (GC), $[\alpha]_D^{20}$ −17.5 ± 0.5° neat} was obtained by fractional distillation on a Nester-Faust NF-200 Perkin-Elmer spinning-band column from an authentic sample of ylang-ylang essential oil as described previously[23]. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

0021-9673/87/$03.50

Formation of derivatives

A racemic mixture of linalool (3 μl) was dissolved in 200 μl of dichloromethane and 200 μl of isopropyl isocyanate. The mixture was heated in a screw-capped vial at 100°C for 2 h. The excess of reagent was removed with a stream of dry nitrogen. In the case of diastereomeric urethane derivatives, the racemic mixture of linalool or 3*R*-(−)-linalool or essential oil (10 μl) was heated as described above with *R*-(+)- or *S*-(−)-1-phenylethyl isocyanate at 100°C for 1 h without dichloromethane. The reaction mixture was cooled and 50 μl of methanol were added.

Gas chromatography

For the separation of isopropyl urethanes of linalool a FID-type Delsi 30 gas chromatograph equipped with a fused-silica capillary column (50 m × 0.30 mm I.D.) coated with XE-60–*S*-valine-*S*-α-phenylethylamide (Chrompack, Middelburg, The Netherlands) was used at 110 or 120°C. For the separation of diastereomer derivatives of linalool with *R*-(+)- or *S*-(−)-1-phenylethyl isocyanate, a FID-type Delsi 30 gas chromatograph equipped with a glass capillary column (50 m × 0.30 mm I.D.) coated with Carbowax 20M (phase thickness 0.15 μm) was used at 180°C (isothermal).

RESULTS AND DISCUSSION

We did not succeed in analyzing the enantiomers of (±)-linalool by use of the procedure described by König *et al.*[8]. As shown in Table I, the differences in retention between the enantiomers, expressed as the separation coefficients, α, were only 1.006 at 120°C and 1.009 at 110°C. Furthermore the retention times were very long. Better results were obtained by derivatizing the linalool with *R*-(+)- or *S*-(−)-1-phenylethyl isocyanate in a similar approach to that described by several authors[24–26]. The separation coefficient of the resulting diastereomers was α = 1.015 and 180°C on a Carbowax 20M column, which allowed an optical purity determination of linalool with retention times of about 80 min. The order of emergence of enantiomers on the

TABLE I

GAS CHROMATOGRAPHIC SEPARATION OF LINALOOL ENANTIOMERS OR DIASTEREOMERS

Reagent	*Stationary phase*	*Column temp. (°C)*	*Retention time (min.)*		*Separation coefficient, α (2nd/1st)*
			First peak	*Second peak*	
Isopropyl Isocyanate	Chiral*	110	150.11[*S*-(+)]	151.45[*R*-(−)]	1.009
		120	93.34[*S*-(+)]	93.91[*R*-(−)]	1.006
R-(+)-1-Phenylethyl isocyanate	CW 20M	180	80.14[*R*-(−)]	81.34[*S*-(+)]	1.015
S-(−)-1-Phenylethyl isocyanate	CW 20M	180	81.48[*S*-(+)]	82.72[*R*-(−)]	1.015

* Chiral stationary phase XE-60–*S*- valine-*S*-α-phenylethylamide.

TABLE II

CONTENT AND OPTICAL PURITY OF LINALOOL IN SOME ESSENTIAL OILS

Essential oil		*Linalool** (%)	*Coriandrol (%)*		*Licareol (%)*	
No.	*Name*		*R***	*S***	R**	*S****
1	Lavandin oil	41.5	0.0	2.0	100	98.0
2	Coriander oil	77.2	84.1	86.7	15.9	13.3
3	Rosewood oil	86.2	50.2	49.7	49.8	50.3

* Quantitative presence in oils determined by the method of peak-area normalization on a Carbowax 20M column, without the application of response-factor corrections.

** Using *R*-(+)-1-phenylethyl isocyanate.

*** Using *S*-(−)-1-phenylethyl isocyanate.

Carbowax 20M column was determined using 3*R*-(−)-linalool isolated from ylang-ylang essential oil[23] and is indicated in Table I.

This procedure was applied to three essential oils known to contain large amounts of linalool. The results obtained are given in Table II and typical chromatograms are shown in Fig. 1. Since different chemical behaviours (rates and product distributions) of an enantiomerically pure compound and of the corresponding racemic mixture in the absence of chiral reagents are possible [27–29], we have determined the contents of these three essential oils in coriandrol and licareol using either *R*-(+)- or *S*-(−)-1-phenylethyl isocyanate. As shown in Table II the results using the two reagents are in good agreement, therefore there is a linear relationship in the asymmetric synthesis of linalyl phenylethyl urethanes. Lavandin oil contains almost exclusively 3*R*-(−)-linalool or licareol (99 ± 1%). The coriander oil investigated contains 3*S*-(+)-linalool or coriandrol (85.4 ± 1.3%) as the major enantiomer. The linalool contained in rosewood oil is a racemic mixture probably formed during the hydrodistillation of this essential oil.

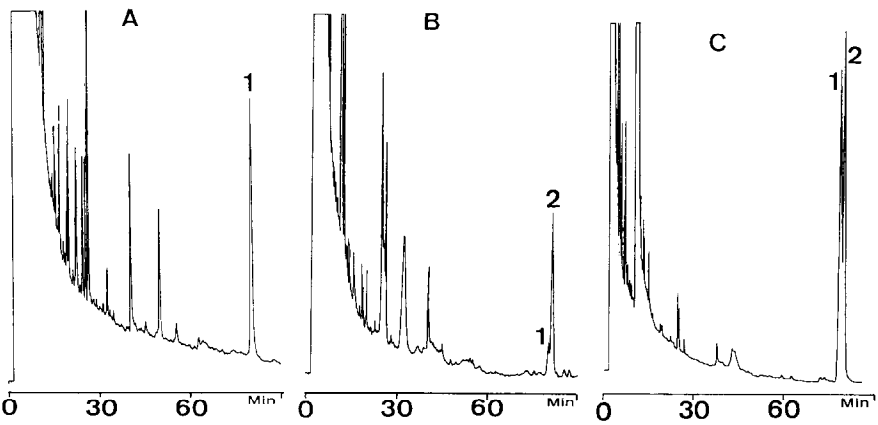

Fig. 1. Separation of 3*R*-(−)- and 3*S*-(+)-linalyl diastereomers contained in essential oils obtained by using *R*-(+)-1-phenylethyl isocyanate on a 50-m glass capillary column coated with Carbowax 20M (column temperature 180°C): (A) lavandin oil; (B) coriander oil; (C) rosewood oil. Peaks: 1 = 3*R*-(−)-linalyl derivative; 2 = 3*S*(+)-linalyl derivative.

CONCLUSION

Gas chromatographic resolution of (±)-linalool via diastereomeric urethanes was achieved, demonstrating therefore the possibility of analytical determination of the enantiomeric composition of this chiral component widely encountered in essential oils. It is now easy to check the optical purity of this component in order to identify asymmetric biosynthesis in plants or to control the racemization during the hydrodistillations of essential oils.

ACKNOWLEDGEMENTS

This work was supported by the Fonds d'Aide et de Coopération (France). We are very grateful to J. Touche, Centre Expérimentation Agriculture Montagne Sèche (CEAMS), for providing a lavandin oil sample and to J. P. Le Vanda, Adrian Society, for providing the rosewood (Brasil) and the coriander oil samples.

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