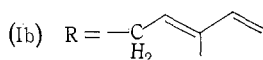
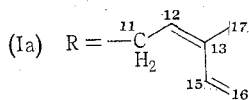
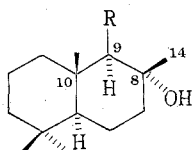


DITERPENOIDS*

XV.† TRANS-ABIENOL

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cis-Abienol (Ia)¹ occurs widely in *Abies* oleoresins² and in particular in the oleoresin of *A. balsamea* (L.) Mill. (Canada balsam),³ but the isomeric *trans*-abienol (Ib) has not been reported. In view of the known co-occurrence of *cis*- and *trans*-communic acid in *Agathis australis*⁴ (Lamb. ex D. Don) Stend., and *cis*- and *trans*-biformene in *Dacrydium biforme*,⁵ it seemed biogenetically reasonable to expect *trans*-abienol to co-occur with *cis*-abienol. A preliminary investigation of Canada balsam did not afford a compound corresponding to *trans*-abienol, and so we synthesized an authentic sample.



The *cis,trans*-isomerization of non-conjugated olefins by irradiation in the presence of a photosensitizer is well documented.⁶ *cis*-Abienol hydrate in acetone as solvent and photosensitizer was irradiated with a naked Hanovia ultraviolet lamp to give a mixture of double-bond isomers. Gas chromatography showed two components in equal amounts. The first had a retention time identical with that of authentic *cis*-abienol. Chromatography over alumina impregnated with silver nitrate gave unchanged crystalline *cis*-abienol together with the second component, *trans*-labda-12,15-dien-8*R*-ol (Ib; *trans*-abienol).

The use of spectral evidence in the determination of *cis/trans* isomerism in conjugated dienes has previously been reported.³ The proton magnetic resonance spectrum of *trans*-abienol confirms the gross structure (Ib) and provides evidence concerning the *trans* nature of the Δ^{12} double bond. The C12 proton occurs as a broad triplet at 4.57τ ($J \simeq 6.5$ c/s) and the C15 and C16 protons occur as a seven-line ABX system (four X lines, three broad AB lines). The *trans* assignment (Ib) is also

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¹ Carman, R. M., *Aust. J. Chem.*, 1966, **19**, 629.

² Gray, P. S., and Mills, J. S., *J. chem. Soc.*, 1964, 5822.

³ Carman, R. M., *Aust. J. Chem.*, 1966, **19**, 1535.

⁴ Thomas, B. R., *Acta chem. scand.*, 1966, **20**, 1074.

⁵ Carman, R. M., and Dennis, N., *Aust. J. Chem.*, 1967, **20**, 157.

⁶ Moussebois, C., and Dale, J., *J. chem. Soc. (C)*, 1966, 260.

supported by the peak position and intensity of the ultraviolet absorption of *trans*-abienol. These results are in agreement with those obtained previously^{5,7} for *trans*-dienes.

With authentic *trans*-abienol in hand, Canada balsam was reinvestigated for the presence of this isomer. Gas chromatographic analysis of the neutral components of the balsam showed *trans*-abienol to be present to an extent of about 0.25% of the total balsam. Chromatography of the neutral fraction over alumina impregnated with silver nitrate gave *trans*-abienol.

Experimental

Melting points were uncorrected. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer 237 spectrophotometer. Optical rotations were recorded in chloroform solutions on a Perkin-Elmer 141 polarimeter. P.m.r. spectra were recorded at 60 Mc/s on a Varian A60 spectrometer in carbon tetrachloride solutions with tetramethylsilane as internal reference. All gas chromatograms were obtained on an Aerograph Hi-Fi 600-B with flame-ionization detector using stainless-steel columns, 5 ft long and $\frac{1}{8}$ in. o.d. The solid support was acid-washed Chrom. W 60/80 (5% SF 96) and 80/100 (5% E.G.S. and 5% SE 30) mesh. Retention times for the diterpenoids are listed in Table 1.

TABLE 1
RETENTION TIMES OF *cis*- AND *trans*-ABIENOLS RELATIVE TO MANOOL (\equiv 1)

Alcohols	5% Ethylene Glycol Succinate	5% SF96 at 165°	5% SE30 at 185°
<i>cis</i> -Abienol (Ia)	1.75 at 140° 1.58 at 165° 1.06 at 204°	1.41	1.21
<i>trans</i> -Abienol (Ib)	2.13 at 140° 1.89 at 165° 1.58 at 170°	1.57	1.41

cis-Abienol (Ia)

cis-Abienol was isolated from Commercial Canada balsam (F. W. Berk, London) essentially as described by Gray and Mills,² m.p. 40–41°, $[\alpha]_D +22^\circ$ (c, 1.05). Crystallization from aqueous acetone gave long needles of abienol hydrate, m.p. 65°, $[\alpha]_D +23^\circ$ (c, 1.2). λ_{\max} 238 m μ (ϵ 19800 in absolute ethanol).

trans-Abienol (Ib)

cis-Abienol hydrate (5 g) in acetone (200 ml) was irradiated in a silica flask with a naked Hanovia ultraviolet lamp for 20 hr. The neutral product was isolated with ether, chromatographed on neutral alumina (100 g), and eluted with ether-hexane (1:1) to give a colourless viscous oil (4.8 g) (gas chromatography showed two components in ratio 1:1). Further chromatography on silver nitrate-alumina (5%; 200 g) and elution with ether-hexane (1:9) gave *cis*- λ -12,15-dien-8*R*-ol (0.12 g) as a colourless viscous oil which crystallized from aqueous acetone as colourless needles of the hydrate, m.p. 65–66°, $[\alpha]_D +23^\circ$ (c, 0.83). Further elution with ether-hexane (2:3) gave, as a colourless viscous oil, *trans*- λ -12,15-dien-8*R*-ol (0.3 g), $[\alpha]_D +20^\circ$ (c, 0.085) (gas chromatography showed only one peak; see Table 1) (Found: C, 82.7; H, 11.9. C₂₀H₃₄O requires C, 82.7; H, 11.8%). λ_{\max} 232 m μ (ϵ 27100 in absolute ethanol). ν_{\max} (film): 3425s,

⁷ Norin, T., *Acta chem. scand.*, 1965, **19**, 1020.

3090w, 2940vs, 2870vs, 1720w, 1660w, 1640m, 1607m, 1461vs, 1350vs, 1367s, 1155s, 1120s, 1081s, 1067s, 906–883s, 831w cm^{-1} . P.m.r. spectrum: 3.74 (C15; quartet), 4.57 (C12; broadened triplet, $J_{11,12}$ 6.5 c/s), 5.06, 5.18 (C16, C16'; eight lines; $J_{15,16}$ 10.15, $J_{15,16'}$ 17.25, $J_{16,16'}$ 1.2 c/s), 7.85 (C11; complex), 8.30 (C17 methyl; fine doublet; J 1 c/s), 8.94 (C14 methyl), 9.18, 9.24, 9.27 (C18, C19, C20 methyls) τ .

trans-Abienol from Canada Balsam

The neutrals from commercial balsam were chromatographed in the vapour phase. Besides peaks for *cis*-biformene (0.3%), manool (0.4%), and *cis*-abienol (98.7%), a peak (0.5%) with retention time identical to authentic *trans*-abienol was observed on all columns used. Canada balsam (300 g) in ether was extracted with aqueous sodium hydroxide solution (2%). The neutral fraction (80 g) was dissolved in hexane and chromatographed on neutral alumina. Elution with hexane-ether (1:1) gave an alcohol fraction from which *cis*-abienol crystallized, m.p. 65°. The mother liquors were chromatographed on silver nitrate-alumina (5%; 10 g) and elution with hexane-ether (3:2) gave *trans*-labda-12,15-dien-8*R*-ol as a colourless viscous oil (0.19 g) with physical properties identical with those recorded above.