Tetrahedron. Vol. 28, pp. 3439 to 3440. Pergamon Press 1972 Printed in Great Britain

STRUCTURE AND SYNTHESIS OF A NEWLY DISCOVERED TERPENOID ISOLATED FROM LAVANDIN OIL

TRANS-5-HYDROXY-2-ISOPROPENYL-5-METHYLHEX-3-ENYL ACETATE

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(*Received in the UK* 27 *March* 1972; *Accepted for publication* 11 *April* 1972)

Abstract—A newly discovered component of the oil of *Lavandin abrialis* has been shown by spectroscopic data to be *trans*-5-hydroxy-2-isopropenyl-5-methylhex-3-enyl acetate (I). A synthesis of this material is described.

DURING an investigation of the composition of the oil of Lavandin a component was isolated which has not been previously described in the literature. The compound occurs only as a trace component (less than 0·001%) and was found in the high boiling (b.p. 85–90°/5 mm) fractions of the oil. It was isolated in the pure state by means of preparative scale GLC using FFAP as the stationary phase.

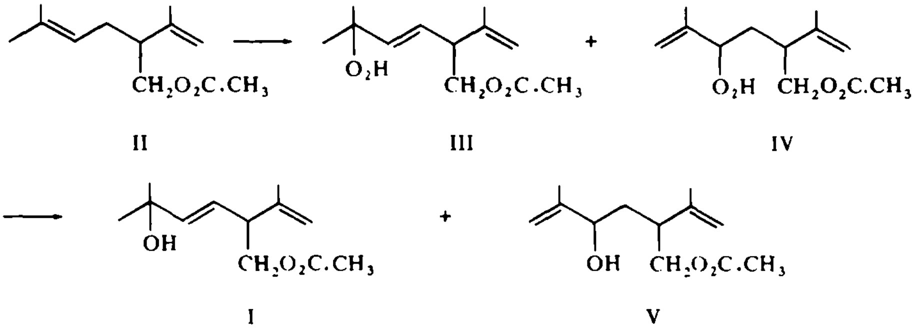
The isolated compound had a mass spectrum consistent with the molecular formula $C_{12}H_{20}O_3$. The IR spectrum (liq. film) had the following characteristic absorption bands: hydroxy-OH str at 3445 cm^{-1} (s), OH def at 1157 cm^{-1} (tert), an acetate group C=O str at 1737 cm^{-1} (s), C—O def at 1240 cm^{-1} (s), a terminal methylene C—H str at 3080 cm^{-1} (w), C—H def at 898 cm^{-1} (s), and a *trans* double bond C—H str at 3020 cm^{-1} (w) and CH def at 980 cm^{-1} (s).

In confirmation of the IR data, the NMR spectrum of the lavandin component shows signals for the two terminal methylene protons and three acetate methyl protons at δ 4·75, δ 4·80 and δ 1·98 respectively, while the OH signal is observed as a broad singlet whose shift is dependent on concentration and temperature. The presence in the molecule of a further, disubstituted, double bond is revealed by the signals from two protons between δ 5 and 6 ppm. Together with the molecular formula this information indicates an acyclic structure.

The remaining features of the spectrum are as follows: (i) a distorted —CH_2— doublet at δ ca 4·08 attributable to the methylene protons of the grouping $CHCH_2OCOCH_3$. (At 220 MHz, however, this feature appeared clearly as two overlapped quartets due to the non-equivalence of the two methylene protons, demonstrating the asymmetric substitution of the adjacent carbon atom). (ii) a signal at δ 1·72 due to a Me group situated on a double bond. Evidence of allylic coupling, as shown by the splittings of this signal and of the terminal methylene signals at δ 4·75 and 4·80, serves to define an isopropenyl group. (iii) a six proton Me singlet situated at δ 1·26, attributable to a hydroxyisopropyl group.

In the region of the spectrum between δ 5·0 and 6·0 ppm the protons of the disubstituted double bond give rise to signals corresponding to the AB part of an ABX spectrum, defining the further grouping $R_1CH{=}CHCH(R_2)CH_2OCOCH_3$, and a value of 15·8 Hz for J_{AB} confirms *trans* substitution of the double bond.[1]

Structure I can be seen to be closely related to lavandulyl acetate (II) from which it can be readily synthesized. Photosensitized oxygenation of lavandulyl acetate using methylene blue as a photosensitizer according to the method of Schenck[2] gave a mixture of hydroperoxides (III and IV) which on reduction with aqueous sodium sulphite gave the corresponding alcohols by the following scheme.



Separation of the pure compound (I) was effected by means of preparative scale GLC. The product was found to have identical IR and NMR spectra with those of the material isolated from Lavandin oil.

EXPERIMENTAL

The NMR spectra were obtained from Varian Associates A-60A and HR-220 spectrometers. Data are reported for CCl_4 solution with TMS internal standard. The IR spectra were obtained from a Unicam SP 100, and the mass spectrum from an AEI-MS 902 instrument. Pye 104 instruments were used for gas-chromatographic analyses.

trans-5-*Hydroxy*-2-*isopropenyl*-5-*methylhex*-3-*enyl acetate* (I). A soln of lavandulyl acetate (50 g) and methylene blue (0·6 g) in EtOH (400 ml) was irradiated in a Hanovia photochemical reactor for 24 hr at 18 to 22°. During this period a stream of O_2 was passed through the soln at the rate of 300 ml/min. The resulting soln of hydroperoxides was concentrated under reduced pressure (maximum temp of 40°). The concentrate was added dropwise over a period of 1 hr to a stirred soln of sodium sulphite heptahydrate (19·5 g) in water (100 ml). During this addition the temp of the mixture rose from 20° to 35°. The mixture was stirred for a further 8 hr at 40°, after which time the mixture was cooled and the product was isolated with ether in the usual manner. Distillation of the product gave a fraction b.p. 112–118°/1·5 mm (18 g) which contained a 1 : 1 mixture of I and V. The separation of these two was effected by means of preparative scale GLC using a 6 m × 7 mm column packed with 7% FFAP on Chromosorb G. The structure of the component which eluted first was shown by IR to be identical with the Lavandin component. The IR and NMR spectra of the second component were consistent with the expected structure.

Acknowledgement—The authors wish to thank P. Sherrington for the preparation of the compounds and R. A. Lucas for the Mass spectrum.

REFERENCES

[1] L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* (2nd Edition) Pergamon Press, Oxford (1969)

[2] G. O. Schenck, *Angew. Chem.* **69**, 579 (1957)