

THE SESQUITERPENE ALCOHOL OF *MYOPORUM CRASSIFOLIUM* FORST.

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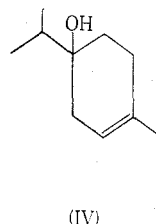
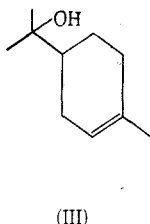
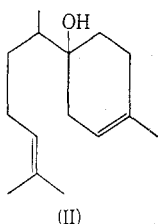
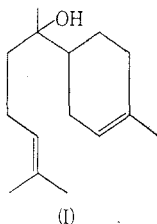
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Summary

The principal sesquiterpene alcohol (anymol) of the wood oil of *Myoporum crassifolium* Forst. is a stereoisomer of bisabolol. A convenient method of detecting methyl groups attached to the hydroxyl-bearing carbon of tertiary alcohols involves the infrared examination of the pyrolysate of the phenylazophenylurethane for bands due to $=CH_2$.

I. INTRODUCTION

A decision between formulae I and II put forward by O'Brien, Penfold, and Werner (1953) for the principal sesquiterpene alcohol (here called anymol) from the essential oil of the wood of *Myoporum crassifolium* Forst. was prevented by exhaustion of the original supply of oil and the apparent impossibility of



obtaining a further quantity. This difficulty has now been overcome by making use of the only crystalline derivative of anymol that had been obtained, namely, the phenylazophenylurethane, to determine the location of the hydroxyl thus leading to formula I for anymol.

α -Terpineol (III) and terpinen-4-ol (IV) may be regarded as model substances corresponding to the two possibilities (I and II) for the structure of anymol. The phenylazophenylurethanes ("azourethanes") (Davenport and Sutherland 1950) of III and IV decompose with vigorous gas evolution above 170 °C yielding a distillate of terpenes and a residue which is principally aminoazobenzene. This reaction is analogous to the pyrolysis of methyl xanthates (O'Connor and Nace 1952) and may well proceed by a similar mechanism with the resultant advantage of freedom from rearrangements. The advantage of phenylisocyanate as a dehydrating agent in this respect has been noted (Bacon and Farmer 1937).

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An alternative manner of decomposition is exhibited by phenylurethanes derived from phenols (Leuckart 1890; Hoshino, Mukaiyama, and Hoshino 1952) or primary alcohols (Schweitzer 1947). In the compounds under consideration, this reaction, which would lead to the regeneration of the alcohol and phenylazophenylisocyanate, occurs to a negligible extent, since the pyrolysate shows very weak absorption in the OH stretching region by infra-red examination.

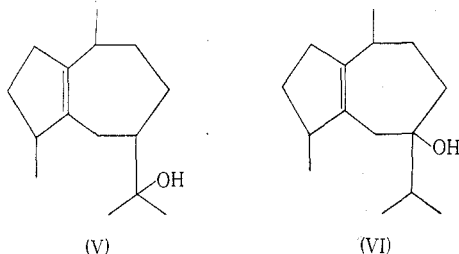


By pyrolysing about 50 mg of azourethane under reduced pressure at 200–210 °C in close proximity to a water cooled finger condenser, a yellow oily condensate is obtained which on cooling deposits crystals of aminoazobenzene but yields sufficient hydrocarbon for infra-red examination. The pyrolysate of the azourethane of III showed bands at 1644 and 887 cm^{-1} , positions expected for $\text{R}_2\text{C}=\text{CH}_2$ absorption (for references see O'Brien, Penfold, and Werner 1953). Also observed were bands at 836 cm^{-1} and another stronger band at 797 cm^{-1} (Werner and Lark 1954) presumably due to out-of-plane bending of the hydrogen attached to the double bond in the ring. On the other hand, the pyrolysate from the azourethane of IV showed the 1660 and 825 cm^{-1} bands derived from $\text{R}_2\text{C}=\text{CRH}$ and no absorption due to the $\text{R}_2\text{C}=\text{CH}_2$ arrangement. The technique thus appears suitable for discriminating between I and II. The pyrolysate from the azourethane of anymol showed distinct bands at 1640 and 888 cm^{-1} which indicates clearly the presence of $\text{R}_2\text{C}=\text{CH}_2$ in the hydrocarbons and establishes the α -terpineol-like structure I for anymol.

The data recorded in Table 4 of the earlier paper shows that the anyme oil fractionated in an effective type of still yielded six consecutive fractions of the sesquiterpene alcohol of almost constant boiling point, refractive index, density, and optical rotation. It is probable, therefore, that this alcohol is only one of the two diastereoisomers represented by formula I, whereas the bisabolols of Ruzicka and Liguori (1932) and Ruzicka and Capato (1925) must be regarded as mixtures of diastereoisomers which were neither separated nor characterized. Naves has shown the presence of a bisabolol in aqueous layer from neroli oil (Naves 1934) and in cabreuva oil (Naves 1947) by isolating bisabolene trihydrochloride in each case. Similarly Seidel, Müller, and Schinz (1944) have obtained evidence for a bisabolol in French lavender oil. Only in the present instance has an apparently pure compound been isolated and the name anymol is thus appropriate to the particular diastereoisomer isolated from anyme oil and characterized by physical constants and the phenylazophenylurethane of m.p. 103–103.5 °C.

The technique described for detecting the grouping $\text{CH}_3-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{OH}$ has been applied also to the sesquiterpene alcohol guaiol and bands at 1643 and 887 cm^{-1} were observed in the pyrolysate. This supports V proposed by Plattner and Lemay (1940).

Structure VI, which accommodates more satisfactorily the products of ozonolysis and of chromic acid oxidation (Plattner and Magyar 1942) of crude dihydroguaiane, is excluded.



II. EXPERIMENTAL

(a) *Pyrolysis*.—Terpinen-4-ol phenylazophenylurethane (50.7 mg) was placed in a side-arm test tube fitted with a water cooled finger condenser reaching to within 1 cm of the sample. The pyrolysis was carried out under a pressure of 100 mm by immersing the bottom of the test tube in an oil-bath at 200–210 °C. Bubbling ceased after about 2 min and the apparatus was then withdrawn from the oil-bath. When the crystallization of the aminoazobenzene on the condenser appeared to be complete, the drop of yellow oil hanging from the tip of the condenser was collected and sealed into a capillary tube. The yield of aminoazobenzene saturated hydrocarbons was 10.5 mg, 57% of the theoretical yield, not allowing for dissolved aminoazobenzene.

α -Terpineol phenylazophenylurethane (87.2 mg) similarly pyrolysed for 4 min yielded 8.5 mg of yellow oil.

Guaiol phenylazophenylurethane (56 mg) (G. Lahey and M. D. Sutherland, unpublished data) pyrolysed under 50 mm pressure at 200–220 °C for 5 min gave an oily sludge from which sufficient oil for infra-red examination was obtained by touching with a capillary.

The phenylazophenylurethane (m.p. 100–102 °C; 55 mg) of the sesquiterpene alcohol from *M. crassifolium* similarly treated gave an oily sludge from which the oil could not be drawn off into the capillary. The difficulty was overcome by washing the oil from the sludge with about 2 ml of light petroleum (b.p. <40 °C) into a clean side-arm test tube. After removal of the solvent, the residue was partially distilled at 170 °C and 50 mm pressure onto a clean finger condenser as a drop of clear yellow oil.

(b) *Infra-red Spectrum Analysis*.—The infra-red spectrum was obtained on a Perkin Elmer model 12C spectrometer equipped with 13 cycles amplifier and NaCl optics. Calibration was effected in the usual manner against the data for water vapour and ammonia tabulated by Oetjen, Kao, and Randall (1942).

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