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CONSTITUTION OF CAROTOL AND DAUCOL

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SEVERAL years ago, we, in these Laboratories, studied the sesquiterpenic alcohol carotol[1] of molecular formula $C_{15}H_{26}O$ and ascribed, on the basis of dehydrogenation which afforded 1,7-dimethyl-4-isopropylnaphtalene (II) as the main product, the carbon skeleton I to it. As the dehydrogenation was carried out in the presence of palladized charcoal under relatively drastic conditions and as it gave rise to the formation of a certain amount of azulenes which was not in accordance with the proposed formula for carotol, we re-investigated this sesquiterpenic alcohol.

On sulphur dehydrogenation, neither carotol nor the unsaturated hydrocarbon prepared by dehydration of dihydrocarotol afforded the naphtalenic hydrocarbon II but only a small amount of a mixture of azulenes. As the aromatization of hydrogenated naphtalenic systems usually proceeds without difficulties, the negative result, in our case, was contradictory

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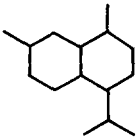
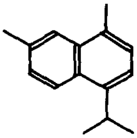
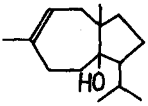
[1] F. Šorm and L. Urbanek, Coll. Czech. Chem. Comm. **13**, 49, 420 (1948).

to the isocadalene skeleton of carotol; the formation of II, on the other hand, was due obviously to the isomerization in the course of the reaction with palladized charcoal. On the basis of degradation reactions, we arrived at formula III for carotol; the correctness of this formula was verified, above all, by two independent proofs of the existence of a seven-membered ring in the molecule of carotol.


I


II



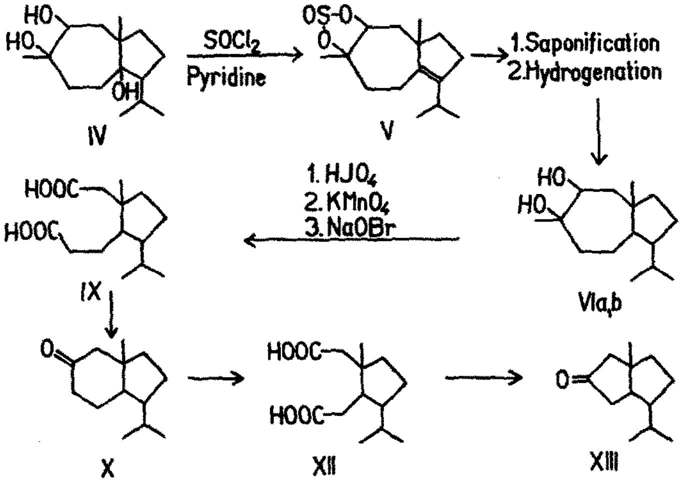
III

On treatment with thionyl chloride in pyridine, the triol[1] IV afforded an unsaturated cyclic sulphite (V) which on subsequent hydrolysis and hydrogenation yielded a mixture of two crystalline stereoisomeric diols (VI a, b,) (m.p. 116-117° and 91.5-93°; Found: C, 74.69; H, 11.57; C, 75.03; H, 11.89. $C_{15}H_{28}O_2$ requires: C, 74.95; H, 11.74). On oxidation with periodic acid, the diol VIb afforded the keto-aldehyde VII, which on further oxidation with potassium permanganate in acetic acid yielded keto-acid VIII. The latter, on treatment with hypobromite, was converted into dicarboxylic acid IX. Pyrolysis of its barium salt afforded ketone X (I.R. max. 1717 cm^{-1}, semicarbazone m.p. 184-186°; Found: C, 66.63; H, 9.96; N, 16.83. $C_{14}H_{25}N_3O$ requires: C, 66.89; H, 10.03; N, 16.72).

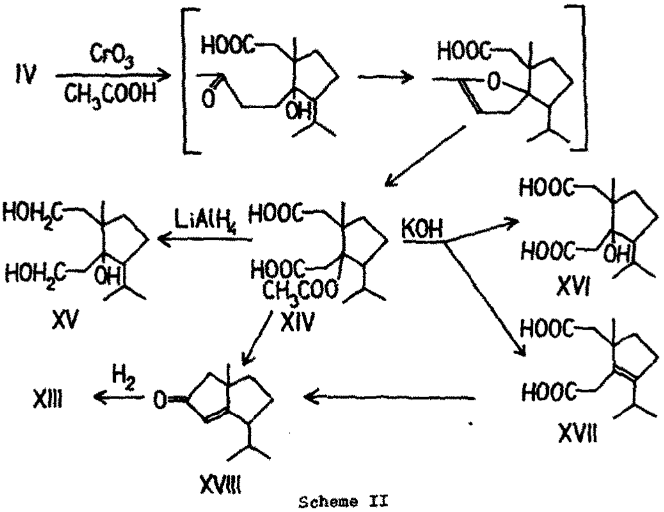
Its monobenzylidene derivative XI when ozonized yielded dicarboxylic acid XII (dimethyl ester b.p. (bath temperature) 128-135°/0.3 mm; Found: C, 66.38; H, 9.48. $C_{15}H_{26}O_4$ requires: C, 66.63; H, 9.69), which on pyrolysis of its barium salt again converted into a ketone XIII (I.R. max. 1741 cm^{-1}, semicarbazone m.p. 197.5-199°. Found: C, 65.52; H, 10.03; N, 17.89. $C_{13}H_{23}N_3O$ requires: C, 65.78; H, 9.77; N, 17.71). All these reactions are outlined in Scheme I.

On treatment with chromic acid in acetic acid, the triol IV afforded acetoxydicarboxylic acid XIV as the main product (I.R. max. 1708 cm^{-1}, 1735 cm^{-1}; m.p. 169-172°; Found: C, 60.01; H, 8.16. $C_{15}H_{24}O_6$ requires: C, 59.98; H, 8.05; dimethyl ester b.p. (bath temperature) 155-160°/0.06 mm; Found: C, 62.17; H, 8.61. $C_{17}H_{28}O_6$ requires: C, 62.17; H, 8.59). The presence in the acid XIV of an acetoxy group was verified, besides the infra-red spectrum, by the course of pyrolysis of XIV which affords acetic acid in almost quantitative yield, further by the reduction with lithium aluminium hydride which leads to the triol XV (b.p. (bath temperature) 175-190°/0.1 mm; Found: C, 67.54; H, 11.38; 1.42 H act. $C_{13}H_{26}O_3$ requires: C, 67.78; H, 11.38; H act. 1.31) and finally by alkaline hydrolysis which affords, besides acetic acid, hydroxydicarboxylic acid XVI (m.p. 147°; Found: C, 60.31; H, 8.77; $C_{13}H_{22}O_5$ requires: C, 60.44; H, 8.59) and the unsaturated dicarboxylic acid XVII (dimethyl ester b.p. (bath temperature) 140°/0.3 mm; Found: C, 66.91; H, 9.01. $C_{15}H_{24}O_4$ requires: C, 67.13; H, 9.02. Pyrolysis of the barium salt of XVII or better directly of the acid XIV gave rise to the ketone XVIII (I.R. max. 1715 cm^{-1}, 1623 cm^{-1}) which on hydrogenation afforded a ketone (I.R. max. 1742 cm^{-1}); its semicarbazone (m.p. 199-200°; Found: C, 65.55; H, 9.98;

N, 17.58; $C_{13}H_{23}N_3O$ requires: C, 65.78; H, 9.77; N, 17.71) according to the mixed melting point appeared to be identical with the semicarbazone of XIII. All these reactions are outlined in Scheme II.



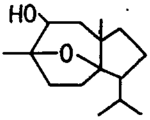
Scheme I



Scheme II

On treatment with nitric acid, the triol IV yielded, besides other products, also isobutyric and succinic acid. These findings together with the above mentioned course of alkaline hydrolysis of the acid XIV corroborate the position of functional groups in carotol in the course of formula III.

The alcohol daucol[2] (XIX) from the oil of Daucus carota L. seeds which was prepared also from carotol on oxidation with peracids[3] or from IV on treatment with benzoic anhydride as well was considered to be the epoxide of carotol. As daucol may be oxidized by means of chromic acid in pyridine to the keto-ether XX (I.R. max. 1719 cm^{-1} m.p. 44-45°; Found: C, 76.56; H, 10.41. $C_{15}H_{24}O_2$ requires: C, 76.22; H, 10.24) it evidently is not an epoxide but a hydroxy-ether of formula XIX.



XIX

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[2] E. Richter, Arch. Pharm. 247, 391 (1909).

[3] Y. Asahina and T. Tsukamoto, J. Pharm. Soc. Japan 525, 961 (1925); Chem. Abstr. 20, 284 (1926).