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DESOXYERYTHROLACCIN AND LACCAIC ACID D*

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Erythrolaccin,[1] the main pigment of seed lac (stick-lac from which the water-soluble dye has been removed), is accompanied by desoxyerythrolaccin which we have now isolated from jalari stick lac (host tree Shorea tellura) in a yield of 0.02%. The seed lac was extracted with cold ethanol and the extract concentrated and poured into 5% hydrochloric acid. The spongy mass that separated was mixed with Hyflo Super-Cel and extracted with ether. The residue from the ether extract was again mixed with the filter aid and successively extracted with hexane and benzene to remove waxes. The residue was shaken with cold ethanol, the ethanol extract concentrated and diluted with water when erythrolaccin separated. The filtrate was evaporated and the residue submitted to column chromatography on polycaprolactam powder, using ethanol-formic acid-water (8.5:0.5:1.0) as solvent. The fast moving band gave desoxyerythrolaccin, orange needles (dec. above 300°) from methanol; molecular formula $C_{15}H_{10}O_5$ (mass spectral M and elemental analysis); ν_{max} 1665 and 1631 cm^{-1}, corresponding to non-bonded and bonded carbonyl groups. Colour reactions showed that it is an anthraquinone derivative not containing hydroxyls in 1,2- or 1,4-positions. It contains three

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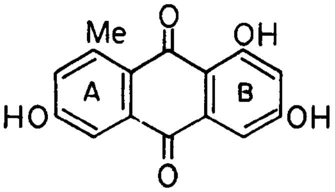
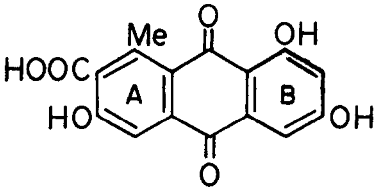
hydroxyl groups, yielding a triacetate, m.p. 172°, and a trimethyl ether, m.p. 205°. Methylation with diazomethane in dry ether gave a dimethyl ether, m.p. 208°, indicating that two hydroxyl groups are in β-positions. The NMR spectrum of the trimethyl ether in $CDCl_3$ (chemical shifts on the τ scale) shows three methoxyl groups at 6.03, 6.08 and 6.09 and an α-methyl group at 7.23. In the aromatic region there are four protons; two doublets (J= 3 cps) at 3.26 and 2.68 show that two methoxyl groups are in the 1,3-positions in one ring; two other doublets (J= 3 cps) at 2.47 and 3.08 correspond to α- and β-protons in the second ring of anthraquinone, the latter signal being in the right position if it is flanked by a methyl and a methoxyl group. These data lead to structure (I or the isomer with the B-ring hydroxyl groups in the 5,7-positions) for desoxyerythrolaccin; (I), more probable by the acetate pathway of biogenesis, was confirmed by synthesis. Condensation of 3,5-dimethoxyphthalic anhydride from the acid (prepared by oxidation of 3,5-dimethoxytoluene-2-carboxylic acid)[2] with *m*-cresol methyl ether in aluminium chloride-sodium chloride melt at 180° for 30 minutes gave emodin as the major product, together with desoxyerythrolaccin (5%). Separation was effected by TLC on oxalated silica gel plates and benzene-alcohol (9:1). The trimethyl ethers of the synthetic and natural products were identical in all respects.



(I)



(II)

Evidence for the structures of laccaic acids A and B have been presented earlier.[3] From Rangini stick lac (host trees *Butea monosperma* and *Zizyphus mauritiana*) we have now isolated laccaic acid D. An acetone solution of crude laccaic acid isolated as described earlier[3] was passed through a short column of silica gel, and a fast moving yellow band was eluted with the same solvent. Removal of the solvent and crystallization from water gave yellow needles (*dec.* above 300°). Laccaic acid D, $C_{16}H_{10}O_7$ (*M* 314, mass spectrum), exhibits colour reactions and other properties characteristic of hydroxyanthraquinone carboxylic acids. Methylation by the usual method yielded an ether-ester, m.p. 226°, with the molecular formula $C_{20}H_{18}O_7$ (*M* 370). The NMR spectrum in $CDCl_3$ shows three aromatic protons, four methoxyl groups (at 6.0) and a *C*-methyl group. Two doublets at 2.69 and 3.23 with the same coupling constant (J = 3 cps) correspond to two aromatic protons in 1,3-positions in one ring of anthraquinone, the 2,4-positions being occupied by two methoxyl groups. A singlet at 2.37 can be assigned to an α-proton with an adjacent methoxyl group. The position of the methyl singlet at 7.30 suggests that it is in an α-position and is probably sandwiched between a quinone carbonyl and a carbomethoxy group. In the pentamethyl ether-esters of carminic acid and kermesic acid, both of which possess an α-methyl group sandwiched between a quinone carbonyl and a carbomethoxy group, the methyl signal appears at 7.38 and 7.35 respectively.

Two possible structures (II or the isomer with the B-ring hydroxyl groups in the 5,7-positions) can be suggested from the available data, but II is supported by the acetate route of biosynthesis, and has been confirmed by unequivocal chemical evidence. Decarboxylation by refluxing with diethylaniline for two hours gave a compound identical in all properties with desoxyerythrolaccin; the two trimethyl ethers were also identical.

Laccaic acid D is identical in all its properties with xanthokermesic acid.

ACKNOWLEDGEMENT

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References

1. N.S. Bhide, A.V. Rama Rao and K. Venkataraman, Tetrahedron Letters 33 (1965); P. Yates, A.C. Mackay, L.M. Pande and M. Amin, Chem. & Ind. 1991 (1964).
2. A. Robertson and R. Robinson, J. Chem. Soc. 2200 (1927); Cf. G.D. Graves and R. Adams, J.Amer.Chem.Soc. 45, 2439 (1923).
3. E.D. Pandhare, A.V. Rama Rao, R. Srinivasan and K. Venkataraman, Tetrahedron Suppl. 8, Part I, 229 (1966); E.D. Pandhare, A.V. Rama Rao, I.N. Shaikh and K. Venkataraman, Tetrahedron Letters 2437 (1967).