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CEROALBOLINIC ACID*

D.D. Gadgil, A.V. Rama Rao and K. Venkataraman
National Chemical Laboratory, Poona, India.

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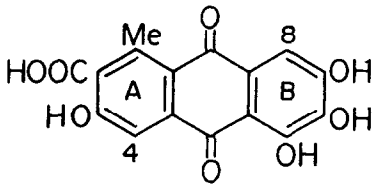
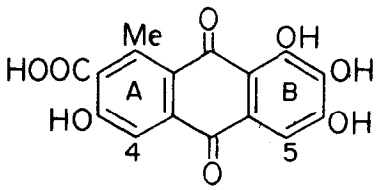
Structure (I) was assigned by Rios[1] to ceroalbolinic acid, a pigment produced by the insect Ceroplastes albolineatus. The isomeric structure (II) was considered less probable for a reason which does not appear to us to be valid: the two aromatic protons of the tetramethyl ether-ester showed up in the NMR spectrum as two separate signals at 2.34 and 2.67 (chemical shifts on the τ scale), and they should have appeared as a single signal for structure (II). The two aromatic protons in (I) or (II) are in different environments and may be expected to have different chemical shifts in either case. Biogenesis by the acetate route will in fact favour (II).



(I)



(II)

Condensation of pyrogallol trimethyl ether with the anhydride of cochinellic acid methyl ether in an aluminium chloride-sodium chloride melt at 180° for 20 minutes gave (I) which darkened at

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290-295° and did not melt below 320°. The tetramethyl ether-ester, m.p. 220-222°, obtained by treatment with ethereal diazomethane, and the pentamethyl ether-ester, m.p. 228-230°, obtained by the dimethyl sulphate-potassium carbonate method, differed in their m.ps. from the corresponding derivatives of ceroalbolinic acid (245-248° and 201-204° respectively). The R_f values (TLC on silica gel; benzene-acetone) of the two sets of ether-esters were also different. The NMR spectrum of the pentamethyl ether-ester of (I) in $CDCl_3$ shows five methoxyls (between 5.95 and 6.05), a methyl (7.30) and two singlet aromatic proton signals (2.26 and 2.37), assignable to the 8- and 4-protons. In the NMR spectrum of anthragallol trimethyl ether the 4-proton appears at 2.32.

The NMR spectrum of the tetramethyl ether-ester shows four methoxyl groups at 6.00, a methyl at 7.37, two aromatic protons at 2.38 and 2.67 as singlets, assignable to the 4- and 8-protons respectively, and a chelated hydroxyl at-2.6. Incidentally, the assignments by Rios of the signals at 2.67 and 2.34 to the aromatic protons in rings A & B of the tetramethyl ether-ester of ceroalbolinic acid should be reversed.

Ceroalbolinic acid consequently has structure (II), and its synthesis is in progress.

ACKNOWLEDGEMENT

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Reference

1. T. Rios, Tetrahedron 22, 1507 (1966).