C-ALKYL RESORCINOLS.

Part III. A Direct Synthesis of Rhizonaldehyde.

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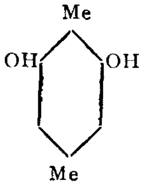
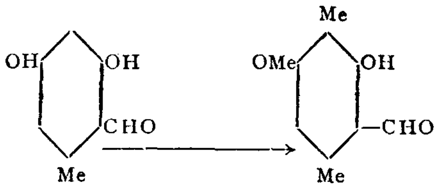
Rhizonic acid, 3 : 6-dimethyl-4-methoxy-2-hydroxy-benzoic acid, one of the more important lichen acids, has been obtained as a degradation product of a number of lichen depsides like barbatic acid, atranorin, soloric acid and dirhizonic acid. The acid, and the corresponding aldehyde, rhizonaldehyde, 3 : 6-dimethyl-4-methoxy-2-hydroxy benzaldehyde (III), both of which contain the β-orcinol (2 : 5-dimethyl resorcinol) nucleus, have been synthesised by various workers by indirect methods which are long and cumbersome. The essential intermediate for the synthesis of rhizonaldehyde (III), has been β-orcinol (I), which is obtained either from *p*-xylene or *p*-xylidene through a number of stages,[1,2,3] or from ethyl 5-methyl-dihydroresorcylate, through 5-methyl-dihydroresorcinol, by successive stages of methylation, bromination and catalytic debromination in the presence of palladised calcium carbonate.[4] The β-orcinol is then converted by methylation and formylation by the Gattermann method into rhizonaldehyde.

We find that rhizonaldehyde can be conveniently synthesised in a remarkably simple manner directly from orcinol. Orcinol was converted into orcylaldehyde (II) and this on nuclear methylation by methyl alcoholic caustic potash and methyl iodide, readily afforded rhizonaldehyde (III) in fair yield (*cf.* Robinson and Shah[6]).



(I)



(II) (III)

Experimental.

3 : 6-*Dimethyl-4-methoxy-2-hydroxy-benzaldehyde* (*Rhizonaldehyde*) (*III*).—The nuclear methylation of orcylaldehyde was carried out under conditions similar to those used by Robinson and Shah.[6] KOH (38 g., 6 mols.) was dissolved in hot methyl alcohol (170 c.c.) and orcylaldehyde (17 g., 1 mol.) added, which readily dissolved to a deep red solution. The mixture was cooled in ice water, and methyl iodide (42 c.c., 6 mols.) was added in one lot. After about 10 minutes, the separation of KI began to take place, after which it was kept at 0° for further three hours. The mixture was then taken out of the cooling bath, and after leaving overnight, refluxed gently for three hours, some more methyl iodide (25 c.c.) being added in two portions at intervals of one hour. Most of the methyl alcohol was then distilled off, on the water-bath, and the liquid concentrated at 100° in a porcelain basin. The residue was diluted with water and extracted with ether. The ether extract was washed with 50 c.c. of dilute NaOH (1N) five times. The first washing was rejected, and the remaining four washings, when acidified with hydrochloric acid, gave impure rhizonaldehyde (0·7 g.). The ethereal layer on evaporation gave crude rhizonaldehyde (2·5 g.) which was partially purified from a little alkali-insoluble matter by solution in alkali and reprecipitation by hydrochloric acid. The combined yield of the aldehyde was then crystallised twice from dilute alcohol, when it was obtained in fine colourless prisms, m.p. 136°. Robertson and Stephenson[3] and St. Pfau[5] give m.p. 136°. Yield 2·7 g. (Found: C, 66·4; H, 6·8; Calc. for $C_{10}H_{12}O_3$: C, 66·7 H, 6·7 per cent.). It gave a reddish brown coloration with alcoholic ferric chloride, and dissolved in dilute alkali only moderately easily.

The normal methylation production, the 4-methyl ether of orcylaldehyde, an expected bye-product in the reaction, was not isolated.

The Oxime.—A mixture of rhizonaldehyde (0·2 g.), KOH (0·03 g.), and hydroxylamine hydrochloride (0·1 g.) was refluxed in aqueous-alcoholic solution for three hours. The cooled mixture on dilution deposited the oxime as a whitish precipitate. It was collected and crystallised twice from alcohol and then from much water in small crystals, m.p. 187–89°. St. Pfau[5] gives m.p. 188–89°. (Found: C, 61·3; H, 6·5; N, 7·5. Calc. for $C_{10}H_{13}O_3N$: C, 61·5; H, 6·7; N, 7·2 per cent.)

Summary.

Rhizonaldehyde, 3 : 6-dimethyl-4-methoxy-2-hydroxy benzaldehyde, has been synthesised directly from orcinol. Orcinol was converted into

orcylaldehyde, and this on nuclear methylation by methyl-alcoholic KOH and MeI, afforded rhizonaldehyde.

REFERENCES.

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4. Sonn, Reisz and Fischer, *Ber.*, 1931, **64**, 1847.
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