CCCXII.—*The Preparation of 2 : 5-Dihydroxybenzaldehyde (Gentisaldehyde).*

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Neubauer and Flatow (*Z. physiol. Chem.*, 1907, **52**, 375) prepared 2 : 5-dihydroxybenzaldehyde by the oxidation of salicylaldehyde, but the present method with *m*-hydroxybenzaldehyde as initial material gives an improved yield of a less crude product.

A solution of *m*-hydroxybenzaldehyde (61 g.) and sodium hydroxide (25 g.) in water (400 c.c.), while being vigorously stirred and kept at 30—35°, is treated simultaneously from separate dropping-funnels with aqueous solutions of potassium persulphate (150 g. in 1500 c.c.) and sodium hydroxide (200 c.c.; 40%), the additions being made during 90 minutes at such rates that the mixture is always alkaline. After 36 hours' standing, the deep brown solution is rendered faintly acidic (Congo paper) with concentrated hydrochloric acid, and unchanged *m*-hydroxybenzaldehyde (31 g.) is extracted by ether. The solution is then strongly acidified (350 c.c. of concentrated hydrochloric acid) and heated slowly to 70°, the dark brown, amorphous precipitate (5 g.), which forms gradually, being filtered off. (This substance, which chars above 330°, is almost insoluble in all organic solvents except boiling glacial acetic acid, but readily soluble in aqueous sodium carbonate; it contains the aldehyde group, as shown by formation of a p-*nitrophenylhydrazone* which gives the characteristic magenta colour with alkalis, and invariably constitutes about 40% of the yield.) The 2 : 5-dihydroxybenzaldehyde is extracted from the filtrate by ether, the ether is removed by evaporation, and the residue extracted by benzene; yield 13 g. (m. p. 89—92°). The substance crystallises from benzene in bright yellow needles, containing solvent of crystallisation, which rapidly effloresce at the ordinary temperature, leaving yellow needles, m. p. 98—99° (Tiemann and Müller, *Ber.*, 1881, **14**, 1986, give m. p. 99°). The aqueous solution gives a green colour with ferric chloride and red with sodium hydroxide. Identity was established with 2 : 5-dihydroxybenzaldehyde prepared by Neubauer and Flatow's method (*loc. cit.*), in which the corresponding yield of crude product was 12 g. (m. p. 83—90°). Substitution of ammonium for potassium persulphate, reduction in time of keeping, and oxidation at higher temperatures all produced lower yields.

2 : 5-Dihydroxybenzaldehyde could not be obtained from 2-nitro-5-hydroxybenzaldehyde by reduction, diazotisation, and any variation of decomposition procedure, although Sandmeyer treatment of the diazo-solution afforded 30% yields of 2-chloro- or 2-bromo-5-hydroxybenzaldehyde.

Derivatives. The p-*nitrophenylhydrazone* crystallises from glacial acetic acid in brick-red needles, m. p. 256—257° (decomp.) (Found : N, 15·6. $C_{13}H_{11}O_4N_3$ requires N, 15·4%). The *dibenzoate* separates from alcohol in slender, colourless needles, m. p. 106—107° (Found : C, 72·5; H, 4·1. $C_{21}H_{14}O_5$ requires C, 72·8; H, 4·0%), and is readily hydrolysed by cold 20% aqueous sodium hydroxide. The p-*nitrophenylhydrazone* of the dibenzoate crystallises from glacial acetic acid in fine, orange needles, m. p. 272° (Found : N, 9·0. $C_{27}H_{19}O_6N_3$ requires N, 8·7%).

Methylation in 10% aqueous sodium hydroxide solution with methyl sulphate (2 mols.) gives the dimethyl ether, which crystallises from dilute alcohol in colourless needles, m. p. 51° (Tiemann and Müller, *loc. cit.*, give m. p. 51°), and forms a p-*nitrophenylhydrazone*, red needles, m. p. 216° (Found : N, 14·7. $C_{14}H_{14}O_4N_3$ requires N, 14·6%), from glacial acetic acid. In this methylation a monomethyl ether may be isolated, after extraction of the dimethyl ether, by acidification and steam-distillation; it passes over and remains as a colourless oil with a vanillin-like odour, and gives a blue-black colour with ferric chloride and a bright yellow solution with aqueous sodium hydroxide, both tests being characteristic of 5-methoxysalicylaldehyde (Tiemann and Müller, *loc. cit.*); the p-*nitrophenylhydrazone* crystallises from glacial acetic acid in bright orange needles, m. p. 206° (Found : N, 15·4. $C_{13}H_{12}O_4N_3$ requires N, 15·3%).

The authors thank the Department of Scientific and Industrial Research for a grant to one of them (H. G. B.), and the British Dyestuffs Corporation for gifts of chemicals.

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