CLXXIV.—*Methylation of* dl-*Glyceraldehyde.*

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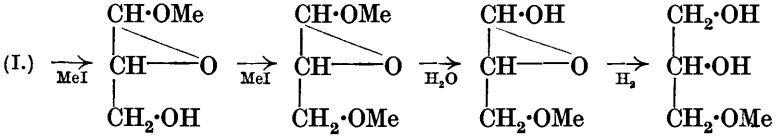
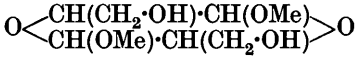
ALTHOUGH *dl*-glyceraldehyde usually reacts in the bimolecular form (Reeves, J., 1927, 2477), there are two possible structures for the unimolecular form, *viz.*,

It seemed that complete methylation, hydrolysis, and reduction would determine which of these represents the unimolecular form, for (I) should give α-methyl glycerol,

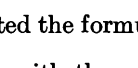


and (II) should give β-methyl glycerol, $OMe{\cdot}CH(CH_2{\cdot}OH)_2$.

Unfortunately, it has as yet been found impossible to obtain a completely methylated derivative. A bimolecular *monomethyl* compound has been isolated for which the formula



is suggested, the secondary hydroxyl groups apparently being methylated with more ease than the primary ones.

Fischer and Taube (*Ber.*, 1927, **60**, 1704) obtained in good yield from the diacetyl derivative of glyceraldehyde a bimolecular methyl *cyclo*acetal, m. p. 158·5—159·5°, crystallising in needles, for which they suggested the formula  . It does not agree in properties with the *compound* that has now been obtained by the methylation of glyceraldehyde at the ordinary temperature.

EXPERIMENTAL.

Methylation of Glyceraldehyde with Methyl Sulphate and Sodium Hydroxide.—In the apparatus described by Haworth (J., 1915, **107**, 11), a solution of 2 g. of glyceraldehyde in 90 c.c. of water was warmed to 35°, 1·6 c.c. of methyl sulphate were added, and 3·2 c.c. of methyl sulphate and 2·6 c.c. of 30% sodium hydroxide solution were simultaneously introduced during 3 hours. Thereafter the

following additions of methyl sulphate and the alkali solution were made: at 45°, 0·8 c.c. and 1·3 c.c.; after 12 hours, 0·8 c.c. and 1·3 c.c. at 55°; after 2 hours, 0 c.c. and 2·7 c.c., causing slight alkalinity; at 70°, 2·7 c.c. and 4·2 c.c. during 1 hour. The water-bath was finally boiled for ½ hour. After 48 hours, the reaction mixture had become brown and did not reduce Fehling's solution. A chloroform extract of it, after being dried with anhydrous magnesium sulphate and evaporated in a vacuum, gave a 10% yield of a pale yellow oil, which was soluble in water and did not reduce Fehling's solution [Found: OMe, 21·9; *M*, cryoscopic in water, 220. $(C_4H_8O_3)_2$ requires OMe, 29·8%; *M*, 209]. Refluxing with methyl iodide and silver oxide failed to augment the methoxyl content.

Formation of the Glucoside (Fischer, *Ber.*, 1893, **26**, 2400; 1895, **28**, 1145).—Glyceraldehyde (1·8 g.) was suspended in 5 g. of pure, acetone-free methyl alcohol and heated in a Carius tube at 100° for 24 hours. Next day, the yellowish-brown mixture was neutralised with silver carbonate and concentrated in a vacuum, a 50% yield of a non-reducing brown oil being obtained (Found: OMe, 22·3%; *M*, cryoscopic in water, 216). It was found impossible to methylate this oil further.

Methylation at Room Temperature (Haworth and Baker, J., 1925, **127**, 365).—A suspension of 5 g. of glyceraldehyde in 100 c.c. of pure methyl alcohol containing 4 g. of hydrogen chloride was shaken for 24 hours: the colourless solution obtained after 2 hours became yellow towards the end of the reaction. The excess of acid was neutralised (litmus) with silver carbonate, the filtrate evaporated to dryness in a vacuum, the crystalline product refluxed for 10 minutes in 50 c.c. of ethyl acetate, and the solution filtered. Next day, short colourless prismatic needles of a *monomethyl* derivative had been deposited (average yield in ten experiments, 5%), m. p. 204·5° after drying for a week over calcium chloride [* Found: C, 46·2; H, 7·7; OMe, 29·5; *M*, cryoscopic in water, 215. $(C_4H_8O_3)_2$ requires C, 46·2; H, 7·7; OMe, 29·8%; *M*, 209]. The monomethyl derivative is readily soluble in water and benzene, sparingly in chloroform and ligroin, and insoluble in ether. It does not reduce Fehling's or Benedict's solution even when hot, whereas the aldehyde is strongly reducing even in the cold. Attempts to methylate it further or acetylate it have been unsuccessful.

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* These figures have been verified by micro-analyses.

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