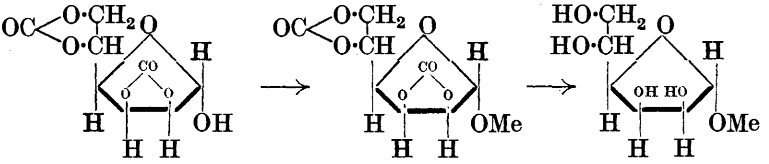
LXXXVI.—*Crystalline α-Methylmannofuranoside (γ-Methylmannoside). Part I.*

By Walter Norman Haworth and Charles Raymond Porter.

Until very recently the synthesis of homogeneous forms of the γ-alkylhexosides had not been possible owing to the lack of appropriate experimental methods. Latterly it has been shown, however, that the crystalline α- and β-forms of ethylglucofuranosides (γ-ethylglucosides) are obtainable through the sugar carbonates (Haworth and Porter, J., 1929, 2796). A further example of this mode of synthesis is now communicated from which it is seen that crystalline *α-methylmannofuranoside* (the α-form of γ-methylmannoside) is derivable from mannose dicarbonate (Haworth and Porter, this vol., p. 151). The mannose dicarbonate (mannofuranose dicarbonate) (I) undergoes methylation with either diazomethane or methyl iodide and silver oxide and yields the crystalline *methylmannofuranoside dicarbonate* (II). Elimination of the carbonate residue from the latter by the agency of barium hydroxide leads to the formation of the desired crystalline α-methylmannofuranoside (III).



(I.) (II.) (III.)

This substance is hydrolysed with much greater rapidity than the normal α-methylmannopyranoside, although it is slightly more stable towards $N/100$-hydrochloric acid than the corresponding glucofuranoside. The physical properties of this new five-atom ring form of methylmannoside are compared with those of the pre-existing six-atom ring form which was prepared by Fischer and Beensch (*Ber.*, 1896, **29**, 2927).

	M. p.	$[\alpha]^{20^\circ}$.
α-Methylmannofuranoside	118—119°	+113°
α-Methylmannopyranoside	190—191	+ 79

In the following paper by Haworth, Hirst, and Webb the chemical properties of the new methylmannoside are described and the proof of its constitution (III) is adduced. It is expected that further experiments which are being conducted will lead to the isolation of the stereoisomeric β-methylmannofuranoside.

EXPERIMENTAL.

Methylation of Mannofuranose Dicarbonate.—(a) *With diazomethane.* Diazomethane obtained from 0·5 c.c. of nitrosomethylurethane was distilled together with 4 c.c. of dry ether into 0·5 g. of mannose dicarbonate dissolved in 4 c.c. of dry dioxan (containing a trace of ether) which had been cooled to 0°. The cooling was continued during 2 hours. The solution acquired a yellow colour, gas was evolved, and a small amount of yellow syrup separated. By pouring off the solution and allowing it to evaporate at the ordinary temperature, about 0·1 g. of a crystalline material was obtained, m. p. 170—172°, identical with the methylmannofuranoside dicarbonate obtained in the following way.

(b) *With methyl iodide and silver oxide.* Mannose dicarbonate (0·4 g.) was dissolved in methyl iodide containing a little acetone and small amounts of silver oxide were added at intervals during ½ hour, whilst the solution was heated below the boiling point. Prolonged contact with large excesses of silver oxide is harmful. The solution was filtered and the residue was extracted with boiling acetone. The original filtrate and the acetone extracts were evaporated and the residue was again treated with the methylating agents as before. The filtrate from the second treatment yielded on evaporation 0·15 g. of a crystalline product, sparingly soluble in ethyl acetate and obtainable from this solvent as colourless crystals, m. p. 172—173° (decomp.) (Found : C, 43·75; H, 4·3; OMe, 12·2. $C_9H_{10}O_8$ requires C, 43·9; H, 4·1; OMe, 12·6%).

The *methylmannofuranoside dicarbonate* did not reduce Fehling's solution, but gave a precipitate of barium carbonate on being warmed with barium hydroxide solution. It did not undergo rapid hydrolysis with *N*/10-hydrochloric acid; but after being heated with *N*-hydrochloric acid at 90°, it gave a product which rapidly reduced Fehling's solution. It showed $[\alpha]_{5780}^{22^\circ}$ + 87°; $[\alpha]_{5461}^{22^\circ}$ + 98° (*c*, 2·45 in acetone).

α-*Methylmannofuranoside.*—The above dicarbonate, dissolved in a little acetone, was warmed gently with excess of barium hydroxide solution. Barium carbonate was precipitated, and after removal of the excess of barium hydroxide by means of carbon dioxide the filtrate was evaporated at 45°; the residue was extracted with ethyl acetate and then with methyl alcohol. Evaporation of either of these extracts gave crystals (yield, 95% of the theoretical). This product, recrystallised from methyl alcohol containing ether, formed colourless needles, m. p. 118—119°, showing $[\alpha]_{D}^{20^\circ}$ + 113° (*c*, 1·1 in water); $[\alpha]_{D}^{25^\circ}$ + 117°; $[\alpha]_{5780}^{25^\circ}$ + 123°; $[\alpha]_{5461}^{25^\circ}$ + 137° (*c*, 0·8 in methyl alcohol) (Found : C, 43·25; H, 7·5; OMe, 16·1. $C_7H_{14}O_6$ requires C, 43·25; H, 7·2; OMe, 16·0%).

α-*Methylmannofuranoside* is readily soluble in water or alcohol but sparingly soluble in ethyl acetate. It undergoes hydrolysis with $N/100$-hydrochloric acid during a period of 2 hours. Its m. p. is depressed on admixture with α-methylmannopyranoside.

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