73. *Maltal and 4-α-Glucosidomannose.*

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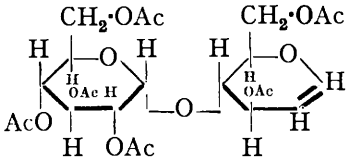
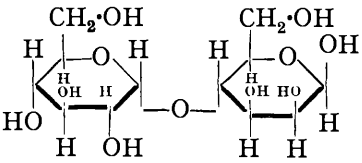
The properties of lactal and cellobial have been studied in detail, but little information had been available hitherto concerning maltal and its transformation products. The isolation of a penta-acetyl maltal hydrate, m. p. 173—174°, and of a hexa-acetyl maltal hydrate, m. p. 155—157°, has been described by Bergmann and Kobel (*Annalen*, 1923, **434**, 109). In the course of the present work we have found that these substances are respectively hepta-acetyl and octa-acetyl maltose and the analytical figures given by Bergmann and Kobel are in agreement with those required for the latter compounds. Most of our product was, however, the true *hexa-acetyl maltal* (I), m. p. 131—133°, the properties of which are now described for the first time. When boiled with water, hexa-acetyl maltal gave *penta-acetyl ψ-maltal*, m. p. 129°, which now had a free reducing group, and, like ψ-glucal, did not readily combine with bromine (compare Bergmann, *Annalen*, 1923, **434**, 79; 1925, **443**, 223).

(I.)  (II.) 

Maltal was obtained by de-acetylation of the hexa-acetate and on treatment with perbenzoic acid (compare Bergmann and Schotte, *Ber.*, 1921, **54**, 1564) it gave in good yield 4-α-*glucosido*-β-*mannose* (II), m. p. 216°, $[\alpha]_D$ + 97° ⟶ 115° in water. This sugar is epimeric with maltose and in view of the interest attached to the difference between the molecular rotations of pairs of epimeric substances (Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 1680. Contrast Haworth and Hirst, J., 1930, 2615) the α-octa-acetate of the sugar ($[\alpha]_D$ + 117° in chloroform) was also prepared.

The " epimeric difference " (7300) obtained by subtracting the molecular rotation of 4-α-glucosido-β-mannose (33,000) from that of β-maltose (40,300) is in good agreement with the figure usually obtained when β-glucose derivatives are compared with derivatives of β-mannose (*ca.* 6000). The " epimeric difference " derived by a comparison of α-glucose and α-mannose is markedly different (*ca.* 16,000). The α-octa-acetates of maltose and the new disaccharide show an abnormally small epimeric difference (4000), which nevertheless is very similar to that given by the corresponding acetates of cellobiose and 4-β-glucosido-mannose. Further confirmation is thus obtained of the unreliability of epimeric differences as a means of assigning ring structures to carbohydrate derivatives.

Experimental.

Hexa-acetyl Maltal.—β-Octa-acetyl maltose (110 g.), prepared by Zemplén's method (*Ber.*, 1927, **60**, 1560), was dissolved in glacial acetic acid (380 c.c.) and allowed to react with hydrogen bromide in acetic acid in accordance with Braun's method (*J. Amer. Chem. Soc.*, 1929, **51**, 1828). After 3 hours, chloroform (160 c.c.) was added, and the solution poured into a large volume of ice-water. The chloroform layer was washed until acid-free, dried over magnesium sulphate, and evaporated to a syrup (110 g.) under diminished pressure. The syrup was dissolved immediately in glacial acetic acid (600 c.c.), water (600 c.c.) added, and the solution cooled to 0°. Zinc dust (240 g.) was then added, the temperature lowered to — 5°, and the mixture vigorously stirred for 30 minutes. After filtration the solution was diluted with water until a faint permanent turbidity appeared. On addition of a crystal of hexa-acetyl maltal, rapid crystallisation ensued and was complete in about 6 hours.

The material as obtained was usually pure (yield, 80%). If necessary, purification could be effected by recrystallisation from methyl alcohol. This gave *hexa-acetyl maltal* as colourless short rods, m. p. 131—133°; $[\alpha]_D^{20°}$ + 68° in chloroform (*c*, 0·8), + 60° in tetrachloroethane (*c*, 0·8). It was soluble in chloroform, moderately soluble in alcohol, and insoluble in light petroleum and in cold water. In hot water it dissolved slowly with formation of penta-acetyl ψ-maltal (see below). Hexa-acetyl maltal did not reduce boiling Fehling's solution. It was

unsaturated, decolorising instantly a solution of bromine in chloroform. Titration showed that one double bond was present (0·1395 g. required 6·6 c.c. of a solution which contained 0·6178 g. of bromine in 100 c.c. of chloroform. Calc., 6·5 c.c.) (Found : C, 51·6; H, 5·9; CH_3·CO, 46·7; *M*, in chloroform by Barger's method, 580. $C_{24}H_{32}O_{15}$ requires C, 51·4; H, 5·7; CH_3·CO, 46·1%; *M*, 560).

The first crystalline specimen, used subsequently for inoculation as described above, was obtained by extracting with chloroform the solution of hexa-acetyl maltal in aqueous acetic acid. Evaporation of the chloroform left a syrup which, after being triturated with glacial acetic acid, was set aside to crystallise. The first crop, after recrystallisation from methyl alcohol, had m. p. 173°, $[\alpha]_D^{16°}$ 84° ⟶ 110° in chloroform (*c*, 1·9), reduced Fehling's solution, and did not decolorise a solution of bromine in chloroform. It was a mixture of the α- and the β-form of hepta-acetyl maltose (Hudson and Sayre, *J. Amer. Chem. Soc.*, 1916, **38**, 1867), from which the β-form was isolated after many crystallisations. After removal of this material hexa-acetyl maltal crystallised slowly.

Deacetylation of hexa-acetyl maltal by methyl-alcoholic ammonia gave maltal as a pale yellow syrup which decolorised a solution of bromine in water and had no action on boiling Fehling's solution.

Penta-acetyl ψ-Maltal.—Hexa-acetyl maltal (4 g.) was suspended in water (200 c.c.), glacial acetic acid (1 c.c.) added, and the mixture heated at 100° until all the solid had dissolved. The solution was concentrated to 30 c.c. and cooled. A syrup was precipitated which slowly crystallised. Recrystallisation from ether–methyl alcohol gave *penta-acetyl ψ-maltal* in feathery rosettes, m. p. 129°, $[\alpha]_D^{20°}$ + 162° in chloroform (*c*, 0·9). This substance reduced Fehling's solution on boiling and did not decolorise a solution of bromine in chloroform. It was soluble in chloroform and alcohol and moderately soluble in hot water (Found : C, 51·1; H, 5·8; CH_3·CO, 40·9. $C_{22}H_{30}O_{14}$ requires C, 51·0; H, 5·8; CH_3·CO, 41·5%).

4-α-*Glucosido*-β-*mannose.*—Hexa-acetyl maltal (20 g.) was de-acetylated by methyl-alcoholic ammonia and the mixture of maltal and acetamide obtained was dissolved in water (100 c.c.). The aqueous solution was shaken at 10—15° with perbenzoic acid (12 g.) in ether (60 c.c.). After 2 hours, the emulsion which had formed was allowed to separate and the aqueous layer, after several extractions with ether, was evaporated to a syrup under diminished pressure. The syrup was boiled with ether, dissolved in the minimum quantity of water, and alcohol was added to the aqueous solution until a slight permanent turbidity appeared. Rapid crystallisation of 4-α-*glucosido*-β-*mannose* followed in short thick rods with pointed ends (yield, 60%). After treatment with charcoal in aqueous solution, followed by several recrystallisations from aqueous alcohol, the pure sugar had m. p. 215—216° (decomp.). $[\alpha]_D^{17°}$ + 97° (initial value in water; *c*, 1·0); 99° (2 mins.); 103° (5 mins.); 106° (10 mins.); 109° (15 mins.); 114° (30 mins.); 115° (60 mins., constant value). The velocity of mutarotation was therefore similar to that of β-mannose (Found : C, 42·0; H, 6·8. $C_{12}H_{22}O_{11}$ requires C, 42·1; H, 6·5%).

4-α-Glucosidomannose was unaffected by *N*-hydrochloric acid at 15° (tested for 16 hours). At 95° hydrolysis was complete in 90 minutes. At this stage the rotation, $[\alpha]_D^{19°}$ + 33·5° calculated on the concentration after hydrolysis, corresponds to that required by an equimolecular mixture of glucose and mannose (+ 33°). Addition of phenylhydrazine in acetic acid to the concentrated neutralised solution resulted in the immediate formation of mannose phenylhydrazone (yield, 80%), m. p. 195—197°. A mixed m. p. showed no depression. Treatment of 4-α-glucosidomannose with phenylhydrazine in acetic acid at 100° gave maltosazone. An estimation of the reducing power of 4-α-glucosidomannose towards Fehling's solution showed that 170 parts of the disaccharide were equivalent to 100 parts of glucose.

When 4-α-glucosidomannose was boiled for 2 minutes with acetic anhydride containing a little fused sodium acetate, the *octa-acetate* was formed. This was isolated in the usual manner and after recrystallisation from alcohol was obtained in short rods (yield, 80%), m. p. 157°; $[\alpha]_D^{17°}$ + 117° in chloroform (*c*, 1·2). The m. p. of β-octa-acetyl maltose (which has, however, $[\alpha]_D$ + 63°) is 158°. A mixed m. p. of the latter with the new acetate showed a depression of 20° (Found : C, 49·4; H, 5·9; CH_3·CO, 52·5. $C_{28}H_{38}O_{19}$ requires C, 49·5; H, 5·7; CH_3·CO, 50·7%).

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