386. *Mechanism of Saccharinic Acid Formation. Part III.* The α-Keto-aldehyde Intermediate in Formation of* D-*Glucometasaccharinic Acid.*

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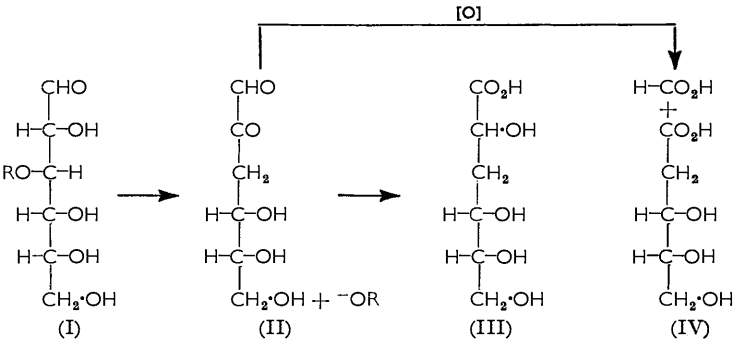
An α-keto-aldehyde intermediate has been isolated after treatment of 3-*O*-benzyl-D-glucose with sodium hydroxide, and shown by the preparation of derivatives and oxidative degradation to be 3-deoxy-D-glucosone. It rearranges in alkali to give an almost quantitative yield of D-glucometasaccharinic acids; rearrangement is faster in lime-water than in sodium hydroxide.

In the foregoing paper was described the isolation, in very small yield, of the precursor of D-glucoisosaccharinic acid formed from maltose by sodium hydroxide. Isolation of the corresponding postulated precursor (II) of D-glucometasaccharinic acid (III) would be expected to be more difficult, since the formation of D-glucometasaccharinic acid from 3-*O*-substituted glucose derivatives (I) is known to be faster than that of the iso-acid from 4-*O*-substituted glucose derivatives. It would therefore be of advantage to enhance the rate of the elimination step (I ⟶ II) relative to that of the subsequent rearrangement (II ⟶ III). The rate of the elimination is governed, *inter alia*, by the nature of the substituent group, R, being highest when R is benzyl;[1] 3-*O*-benzyl-D-glucose (I; R = CH_2Ph) was thus chosen as the starting material for this work. The formation of acid



from a solution of 3-*O*-benzyl-D-glucose in lime-water was faster than in sodium hydroxide solution of comparable normality (Table 1), indicating the same type of catalysis by calcium as was observed with 3-*O*-methyl-D-glucose.[1] Sodium hydroxide was therefore

* Part II, preceding paper.

[1] Kenner and Richards, *J.*, 1957, 3019.

used in attempts to isolate the D-glucometasaccharinic acid precursor. In conditions similar to those used for isolation of the D-glucoisosaccharinic acid precursor, 3-deoxy-D-glucosone (II) was obtained in 3·7% yield, while 72% of the 3-*O*-benzyl-D-glucose was recovered unchanged and some D-glucometasaccharinic acid was also obtained. The

TABLE 1. *Rate of acid formation in action of alkali on* 3-O-*benzyl*-D-*glucose at* 25°.

Time	Acid formed (equiv./mole)		Time	Acid formed (equiv./mole)	
(hr.)	0·04N-Lime-water	0·05N-NaOH	(hr.)	0·04N-Lime-water	0·05N-NaOH
0·5	0·070	0·034	4	0·510	0·264
1	0·150	0·066	5	0·578	0·330
2	0·290	0·150	7·5	0·715	0·450
3	0·418	0·196	24	0·910	0·736

product (II) gave a satisfactory elemental analysis; it was amorphous and presumably contained derived cyclic forms believed to be present in glucosone.[2]

The product (II) rapidly formed a bis-2,4-dinitrophenylhydrazone at room temperature and acetylation of the bishydrazone gave a triacetate. More complete proof of the structure resulted from oxidation with hydrogen peroxide. In absence of pH control a complex mixture of products was obtained, but when pH 8 was maintained during the oxidation, under the conditions previously found to be most suitable for oxidation of pyruvaldehyde,[3] formic and 2-deoxy-D-ribonic acid were obtained. The phenylhydrazide of the latter acid was identical with the phenylhydrazide of authentic 2-deoxy-D-ribonic acid prepared by oxidation of 2-deoxy-D-ribose with bromine.

With lime-water or with 0·05N-sodium hydroxide at 25°, 3-deoxy-D-glucosone very rapidly yielded D-glucometasaccharinic acids in almost theoretical yield (Table 2), together with very small amounts of formic acid. Thus the present work provides the first direct verification of the postulated mechanism [1] for formation of D-glucometasaccharinic acids from alkaline degradation of 3-*O*-alkyl-D-glucoses. By analogy, this evidence also provides convincing support of Isbell's mechanism of formation of metasaccharinic acids from the unsubstituted hexoses.[4] The more rapid formation of acid from 3-deoxy-D-glucosone in lime-water than in 0·05N-sodium hydroxide (Table 3) indicates catalysis of

TABLE 2. *Acids* (% *of total acid equiv.*) *formed in alkali treatment of* 3-O-*benzyl*-D-*glucose and* 3-*deoxy*-D-*glucosone at* 25°.

		D-Glucometa-saccharinic		
Alkali	Substrate	α	β	Formic
0·04N-Lime-water	3-*O*-Benzyl-D-glucose	36	60	2
,,	3-Deoxy-D-glucosone	37	50	4
0·05N-NaOH	3-*O*-Benzyl-D-glucose	19	73	4

TABLE 3. *Rate of acid formation in action of alkali on* 3-*deoxy*-D-*glucosone at* 25°.

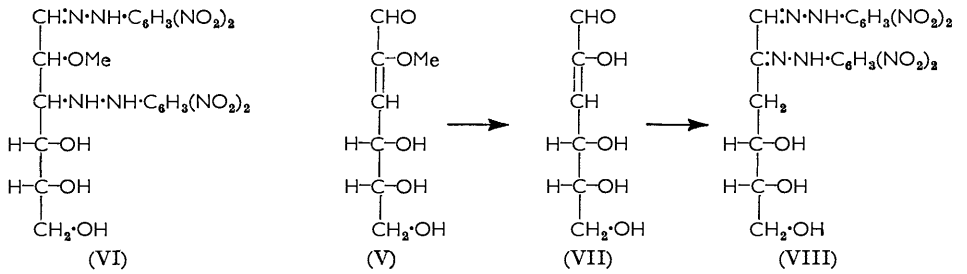
Time	Acid formed (equiv./mole)		Time	Acid formed (equiv./mole)	
(hr.)	0·04N-Lime-water	0·05N-NaOH	(hr.)	0·04N-Lime-water	0·05N-NaOH
0·5	0·56	0·31	4	0·73	0·65
1	0·63	0·43	7	0·77	0·72
2	0·68	0·53	24	0·90	0·85

the benzilic acid rearrangement (II ⟶ III) by calcium, similar to that observed with glyoxal.[5] Further, the fact that alkaline degradation of 3-deoxy-D-glucosone to D-glucometasaccharinic acid (Table 3) is much faster than the corresponding degradation of 3-*O*-benzyl-D-glucose (Table 1) is consistent with the earlier suggestion [1] that the elimination

[2] Bayne and Fewster, *Adv. Carbohydrate Chem.*, 1956, **11**, 43.
[3] Friedemann, *J. Biol. Chem.*, 1927, **73**, 331.
[4] Isbell, *J. Res. Nat. Bur. Stand.*, 1944, **32**, 45.
[5] O'Meara and Richards, Part IV, this series.

(I ⟶ II) is rate-controlling. Consequently the suggestion [1] of catalysis of the elimination by calcium remains an additional possibility to the now established calcium-catalysis of the subsequent rearrangement (II ⟶ III).

A significant difference was observed (Table 2) in the relative amounts of α- and β-D-glucometasaccharinic acid obtained in the alkaline degradation of 3-*O*-benzyl-D-glucose by lime-water and by sodium hydroxide, while the same ratio of isomers was obtained from 3-*O*-benzyl-D-glucose as from 3-deoxy-D-glucosone in lime-water. The stereospecificity of the benzilic acid rearrangement (II ⟶ III) thus appears to be influenced by cationic catalysis. There is considerably less fragmentation in alkaline degradation of both 3-*O*-benzyl-D-glucose and 3-deoxy-D-glucosone than of 4-*O*-substituted glucose derivatives and 4-deoxy-3-oxo-D-fructose (Part II). This is no doubt due at least in part to the



relatively faster overall reaction in the former cases, and may be compared to the alkaline degradation of glyoxal [5] where only the rearrangement type of reaction was detected.

In an earlier paper [6] the product (V) of alkaline degradation of 2,3-di-*O*-methyl-D-glucose was treated with 2,4-dinitrophenylhydrazine, and the resulting derivative tentatively identified as (VI). This derivative has now been found to be identical with the 3-deoxy-D-glucosone bis-2,4-dinitrophenylhydrazone described above. It is concluded therefore, that under the prevailing conditions, the aldehyde (V) probably suffered acidic hydrolysis of the vinyl ether grouping (cf. ref. 7) to yield the enol (VII) of 3-deoxy-D-glucosone, which would readily yield the bishydrazone (VIII).

The bishydrazone (VIII) has been reported [8] to be produced by prolonged treatment of 3-deoxy-D-mannose with 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid at 100°. The product of this reaction (A; m. p. 206°), however, was evidently not the same as the 3-deoxy-D-glucosone bis-2,4-dinitrophenylhydrazone (VIII) (m. p. 273°) obtained in the present work. Repetition of the experiment of Foster *et al.*[8] yielded a product of similar melting point (212°) and nitrogen content to those reported for (A), but the analysis of this product for carbon and hydrogen and its molecular weight did not correspond to the value required for (VIII). Similar treatment of 3-*O*-methyl-D-glucose with acidic 2,4-dinitrophenylhydrazine at 100° yielded a product very similar to (A). The products of these reactions have not been identified, but it is possible that they are mixtures and that their formation involves acidic degradation of the original carbohydrate moiety.

Experimental

Paper chromatography was carried out with Whatman No. 1 paper at 25° and the following solvents and sprays. Solvents: A, butan-1-ol–pyridine–water (6 : 4 : 3); B, ethyl methyl ketone–water azeotrope; C,[9] ethyl acetate–acetic acid–water (10 : 1·3 : 1). Sprays: *a*,[10] silver

[6] Kenner and Richards, *J.*, 1956, 2921.
[7] Zahorka and Weimann, *Monatsh.*, 1938, **71**, 229.
[8] Foster, Overend, Stacey, and Vaughan, *J.*, 1953, 3308.
[9] Richtzenhain and Moilanen, *Acta Chem. Scand.*, 1954, **8**, 704.
[10] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.

nitrate–sodium hydroxide; *b*, a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid; *c*,[11] B.D.H. 4·5 indicator; *d* [12] hydroxylamine–ferric chloride.

Preparation of 3-O-*Benzyl*-D-*glucose*.—A modification of the method of Adams *et al.*[13] was employed. A mixture of 1,2:5,6-di-*O*-isopropylidene-D-glucose (80 g.), powdered potassium hydroxide (100 g.), and toluene (200 ml.) was heated (reflux), and benzyl chloride (200 ml.) added during 3 hr. with stirring. After cooling and storage overnight, the 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-D-glucose was isolated in the usual manner, and purified by distillation (b. p. 126°/<0·01 mm.) (Found: C, 65·5; H, 7·3. Calc. for $C_{19}H_{26}O_6$: C, 65·2; H, 7·4%). Acidic hydrolysis of this compound afforded a product which crystallised readily from ethyl methyl ketone–light petroleum, to give 3-*O*-benzyl-D-glucose (50 g., 61%), m. p. 127—129°, $[\alpha]_D^{20}$ +41·9° (24 hr. equil.; *c* 1·5 in H_2O) (Found: C, 57·9; H, 6·4. Calc. for $C_{13}H_{18}O_6$: C, 57·8; H, 6·65%).

Paper chromatography of the crystalline product with solvent A and spray *a* established its purity further.

Degradation of 3-O-*Benzyl*-D-*glucose in* 0·05N-*Sodium Hydroxide at* 25°.—(a) *Reaction rate*. 3-*O*-Benzyl-D-glucose (0·27 g.) was dissolved in an equivalent amount (20 ml.) of 0·05N-sodium hydroxide in the absence of oxygen at 25°. Aliquot portions (1 ml.) of the solution were withdrawn at intervals, added to an excess of 0·01N-hydrochloric acid (5 ml.), and titrated immediately with 0·01N-sodium hydroxide. Results are given in Table 1.

Further aliquot portions (1 ml.) withdrawn at similar intervals were deionised by treatment with a mixture of the Amberlite resins IR-120(H) (0·5 ml.) and IRA-400(carbonate) (1 ml.). Paper chromatography of the deionised solutions in solvent A with spray *a* revealed unchanged 3-*O*-benzyl-D-glucose, R_F 0·78, and a component, R_F 0·50, which reacted rapidly with spray *b*. The concentration of the latter component appeared to reach a maximum after 3 hours' reaction.

(b) *Isolation of products*. 3-*O*-Benzyl-D-glucose (27 g.) was treated with 0·05N-sodium hydroxide (2 l.) as described under (a). After 3 hr., the pH of the solution was quickly reduced to 8 by the step-wise addition of Amberlite IR-120(H) resin (*ca.* 50 ml.) with stirring, the resin filtered off, and the filtrate evaporated under reduced pressure to 100 ml. The concentrate was then deionised by adding with stirring a mixture of the Amberlite resins IR-120(H) (30 ml.) and IRA-400(carbonate) (70 ml.), the pH of the solution being kept above 4·5 by adjusting the rate of addition. When the conductivity of the solution had fallen to 10 μmho, the mixed resins, on which were adsorbed the acidic products of the reaction, were filtered off and further treated as under (ii). The filtrate containing the neutral products was examined as under (i).

(i) Neutral products. The solution was evaporated under reduced pressure, and paper chromatography of the resulting syrup in solvent B with spray *a* revealed a component, R_F *ca.* 0·13, which reacted rapidly with spray *b*, and unchanged 3-*O*-benzyl-D-glucose, R_F 0·70. The whole of the syrup was transferred to a cellulose column (75 × 4·5 cm.) and eluted with ethyl methyl ketone–water azeotrope. Evaporation of the initial 2 l. of eluate afforded pure 3-*O*-benzyl-D-glucose (19·5 g.), which crystallised readily. Further elution gave the desired carbonyl compound; on drying over phosphoric oxide at 50°/0·01 mm., the initial syrup frothed to give, in a light, extremely hygroscopic form, 3-*deoxy*-D-*glucosone* (0·63 g.), $[\alpha]_D^{20}$ 0° ± 1° (*c* 2 in H_2O) (Found: C, 44·8; H, 6·3. $C_6H_{10}O_5$ requires C, 44·4; H, 6·2%). The absorption spectrum of this material in water showed no peak in the range 2200—3400 Å.

(ii) Acidic products. The mixed resins used in the deionisation above were eluted with N-ammonium carbonate (2·5 l.) during 24 hr., and the eluate was evaporated to dryness at 70°/15 mm. to decompose the excess of eluant. An aqueous solution of the residue was then passed through a column of Amberlite IR-120(H) resin (100 ml.) and the acids (18·5 milliequiv.) in the effluent were separated into volatile (0·92 milliequiv.) and non-volatile (17·58 milliequiv.) fractions by distillation. Formic acid (0·74 milliequiv.) in the former was then determined.[14] Paper chromatography of the non-volatile fraction in solvent C with sprays *c* and *d* revealed components corresponding to the D-glucometasaccharinic acids, R_L *ca.* 0·15, and the related α- and β-lactones, R_L 0·55 and 0·62 respectively (subscript L refers to lactic acid).

A portion (2·54 milliequiv.) of the solution of non-volatile acids was transferred to two Whatman No. 3 MM papers (56 × 61 cm.), and the chromatograms were developed in solvent

[11] Nair and Muthe, *Naturwiss.*, 1956, **43**, 106.
[12] Abdel-Akher and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5859.
[13] Adams, Reeves, and Goebel, *J. Biol. Chem.*, 1941, **140**, 653.
[14] Richards and Sephton, *J.*, 1957, 4492.

C.[15] Subsequent application of spray *d* showed that the two lactones were almost completely separated, and that there appeared to be a much larger amount of the β- than of the α-lactone. Consequently, only the former lactone was isolated, and freed from paper extractives by repeated extraction of the lactone with ethyl acetate. Crystallisation of the product from ethyl acetate then gave β-D-glucometasaccharinolactone, m. p. and mixed m. p. 90—92°.

A further portion (1·27 milliequiv.) of the non-volatile acid fraction was transferred to a Whatman No. 3 MM paper and the chromatogram developed as above. The fractions corresponding to the D-glucometasaccharinic acids and the related α- and β-lactones were then separately eluted, and the respective amounts determined by titration. After application of the approximate correction for loss on the paper,[14] the following results were obtained: D-glucometasaccharinic acids, 0·20; α-lactone, 0·21; β-lactone, 0·82; total 1·23 milliequiv.

From these results the proportions of all the acids produced, on an equivalent basis, were as follows: formic, 4%; other volatile acids, 1%; α-D-glucometasaccharinic, 19%; β-D-glucometasaccharinic, 73%.

Derivatives of 3-*Deoxy*-D-*glucosone*.—3-Deoxy-D-glucosone (0·049 g.) was added to a saturated solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid (200 ml.) at 20°. A flocculent orange-red precipitate was formed at once, and after 15 min. this was collected; the filtrate gave virtually no further precipitate during the ensuing 24 hr. The solid was washed with hot ethanol to remove any monohydrazone, and the dried residue (0·126 g., 80%) crystallised from anisole, yielding red needles of 3-*deoxy*-D-*glucosone bis*-2,4-*dinitrophenylhydrazone*, m. p. 273—274° (Found: C, 41·2; H, 3·7; N, 21·5. $C_{18}H_{18}O_{11}N_8$ requires C, 41·4; H, 3·45; N, 21·5%). When this compound was mixed with the bis-2,4-dinitrophenylhydrazone from the product of alkaline degradation of 2,3-di-*O*-methyl-D-glucose [6] the mixture had m. p. 267—269° (decomp.), and the two bishydrazones gave very similar *X*-ray powder photographs.

The bishydrazone (0·037 g.) was treated in pyridine with an excess of acetic anhydride for 24 hr. at 20°. After isolation in the usual way and crystallisation from ethyl acetate–ethanol, the *triacetate* had m. p. 183° (Found: C, 44·4; H, 3·8. $C_{24}H_{24}O_{14}N_8$ requires C, 44·4; H, 3·7%).

Oxidation of 3-*Deoxy*-D-*glucosone with Hydrogen Peroxide*.—(a) *At* 100°. 3-Deoxy-D-glucosone (0·025 g.) was treated with 30% hydrogen peroxide (0·5 ml.) in water (0·5 ml.) for 1 hr. at 100°. After cooling, the solution was diluted with water (25 ml.) and the unused peroxide destroyed by catalase. The acidic products (0·29 milliequiv.) were separated into volatile (0·13 milliequiv.) and non-volatile (0·16 milliequiv.) fractions, and formic acid (0·10 milliequiv.) in the former was determined.

Paper chromatography of the non-volatile acids in solvent C with sprays *c* and *d* revealed two unknown acids, R_L 0·59 and 0·79 severally, and a component corresponding to 2-deoxy-D-ribonolactone, R_L 0·83 (see below).

(b) *At* 20° *in presence of alkali*. 3-Deoxy-D-glucosone (0·253 g.) was dissolved in a mixture of 30% hydrogen peroxide (5 ml.) and water (10 ml.). To this was added 0·1N-sodium hydroxide, the rate of addition being controlled to maintain the pH of the reaction mixture at 8. After 26·8 ml. of alkali had been added in 45 min., the pH of the solution began to increase, and the reaction was judged to be complete. The solution was treated with catalase, then with Amberlite IR-120(H) resin (5 ml.), and the resulting mixture of acids separated into volatile (0·78 milliequiv.) and non-volatile (1·35 milliequiv.) fractions. The former appeared to contain formic acid only, identified as 4-bromophenacyl formate, m. p. and mixed m. p. 138—139°.

Paper chromatography of the non-volatile fraction as above indicated that the main component corresponded to 2-deoxy-D-ribonolactone, R_L 0·83. There were also traces of unknown lactones, R_L 0·51 and 0·63, and a trace of an unidentified acid, R_L 0·43. The whole of the non-volatile fraction was transferred to a Whatman No. 3 MM paper, and the component, R_L 0·83, isolated in the pure state by chromatography and subsequent elution. Attempts to crystallise this lactone were unsuccessful, and the whole of the product was treated with phenylhydrazine (0·3 ml.) for 30 min. at 100°. After removal of unchanged base in ice-cold ether, the residue was crystallised from ethanol–ethyl acetate, affording 2-deoxy-D-ribonic phenylhydrazide, m. p. and mixed m. p. 147—149° (see below for authentic compound) (Found: C, 54·9; H, 6·8; N, 11·3. Calc. for $C_{11}H_{16}O_4N_2$: C, 55·0; H, 6·7; N, 11·65%). (Overend *et al.*[16] give m. p.

[15] Cf. Machell and Richards, *J.*, 1957, 4500.
[16] Deriaz, Overend, Stacey, Teece, and Wiggins, *J.*, 1949, 1879.

145—146° for the corresponding compound of the L-series, whereas Gakhokidze [17] reports m. p. 176—178° for the D-compound.)

Action of Lime-water on 3-Deoxy-D-glucosone.—(a) *Rate of acid formation.* 3-Deoxy-D-glucosone (0·0652 g.) was added to 0·043N-lime-water (20 ml.) in the absence of oxygen at 25°. A deep yellow solution resulted but the colour disappeared as reaction proceeded. At intervals, aliquot portions (3 ml.) of the solution were added to 0·05N-hydrochloric acid (3 ml.), and the excess of mineral acid was immediately titrated with 0·01N-sodium hydroxide. Results are shown in Table 3.

(b) *Isolation of products.* 3-Deoxy-D-glucosone (0·34 g.) was treated with 0·043N-lime-water (200 ml.) for 48 hr. as in (a). The solution was then neutralised with carbon dioxide, evaporated under reduced pressure to *ca.* 25 ml., and passed through a column of Amberlite IR-120(H) resin (10 ml.) on to a stirred suspension of De-acidite FF resin (200—400 mesh; low cross-linked) (carbonate) (10 g.).[18] After 2 hours' stirring the resin was filtered off and washed with water, and the acids were eluted with N-ammonium carbonate (200 ml.) during 3 hr. The acids (1·71 milliequiv.) were isolated from the eluate as described earlier, and separated into volatile (0·16 milliequiv.) and non-volatile (1·55 milliequiv.) fractions; the former contained formic acid (0·07 milliequiv.).

Paper chromatography of the non-volatile acids as above indicated the presence of the D-glucometasaccharinic acids and their lactones only. As there appeared to be comparable amounts of the α- and β-lactones, the isolation of both by preparative paper chromatography was undertaken. The β-lactone obtained was crystallised from ethyl acetate (m. p. and mixed m. p. 91—92°), while the α-lactone crystallised readily from ethyl acetate–light petroleum (m. p. and mixed m. p. 104—106°).

A further portion of the non-volatile acids was separated on Whatman No. 3 MM paper, and the proportions of the acids and lactones were determined as above. All the results under this heading are now summarised as follows: formic, 4%; other volatile acids, 5%; α-D-glucometasaccharinic, 37%; β-D-glucometasaccharinic acid 50%.

Action of Sodium Hydroxide on 3-Deoxy-D-glucosone at 25°.—The rate of acid formation from 3-deoxy-D-glucosone (0·080 g.) in 0·05N-sodium hydroxide (25 ml.) was followed as for the lime-water reaction, and gave the results recorded in Table 3. The solution (2 ml.) remaining from the sampling was treated with Amberlite IR-120(H) resin; paper chromatography of the resulting non-volatile acids as described showed the presence of the D-glucometasaccharinic acids and their lactones only.

Degradation of 3-O-Benzyl-D-glucose in Lime-water at 25°.—(a) *Rate of acid formation.* 3-*O*-Benzyl-D-glucose (0·54 g.) was dissolved in an equivalent amount of 0·04N-lime-water (50 ml.), and the rate of acid formation followed as described in earlier sections. Results are given in Table 1.

(b) *Isolation of products.* 3-*O*-Benzyl-D-glucose (1·35 g.) was treated with an excess of 0·04N-lime-water (250 ml.) for 72 hr., and the acidic products (4·65 milliequiv.) were isolated as detailed previously. The acids were then separated by distillation into volatile (0·80 milliequiv.) and non-volatile (4·57 milliequiv.) fractions; quantitative analysis of the latter gave the following results for the proportions of acids produced in the original reaction: volatile (mainly formic), 2%; α-D-glucometasaccharinic, 36%; β-D-glucometasaccharinic, 60%.

Preparation of 2-Deoxy-D-ribonic Acid.—A portion (7·2 g.) of 3-*O*-benzyl-D-glucose, recovered from the column-chromatographic procedure described above, was treated with oxygen-free 0·04N-lime-water (2 l.) for 42 hr. at 25°. The mixture of calcium α- and β-D-glucometasaccharinate formed was degraded by the Ruff procedure, and crude 2-deoxy-D-ribose (1·75 g.) isolated as a syrup.[19] Oxidation of the latter in water (10 ml.) with bromine (3·5 ml.) in the presence of an excess of barium carbonate afforded 2-deoxy-D-ribonic acid, which was converted into the lactone (1·63 g.) by drying over phosphoric oxide at 50°/0·01 mm. Paper chromatography of the lactone syrup with solvent C and sprays *c* and *d* gave a main lactone spot, R_L 0·83, with traces of unknown lactones, R_L 0·64 and 1·02, and a trace of an unidentified free acid, R_L 0·58.

A portion (0·25 g.) of the crude lactone was purified by chromatography on Whatman No. 3 MM paper, and then converted, as described above, into 2-deoxy-D-ribonic phenylhydrazide, m. p. 148—149° (Found: C, 55·1; H, 6·7; N, 11·4%).

[17] Gakhokidze, *Zhur. obshchei Khim.*, 1945, **15**, 539.
[18] Cf. Machell, *J.*, 1957, 3389.
[19] Richards, *J.*, 1954, 3638.

Interaction of 3-*Deoxy*-D-*mannose and* 3-O-*Methyl*-D-*glucose with* 2,4-*Dinitrophenylhydrazine.* —The experiment of Foster *et al.*[8] was repeated. 3-Deoxy-D-mannose was treated with 2,4-dinitrophenylhydrazine (3 mol. equiv.) in 2N-hydrochloric acid containing 1% of methanol for 6 hr. at 100°. The dark red product had m. p. 212° after recrystallisation from nitrobenzene (Foster *et al.* report m. p. 206°) [Found: C, 45·1; H, 3·1; N, 21·5%; *M*, 367 (Rast). Calc. for 3-deoxy-D-mannose 2,4-dinitrophenylosazone, $C_{18}H_{18}O_{11}N_8$: C, 41·4; H, 3·5; N, 21·5%: *M*, 522]. This compound gave an *X*-ray powder photograph different from that of 3-deoxy-D-glucosone bis-2,4-dinitrophenylhydrazone.

Similar treatment of 3-*O*-methyl-D-glucose with 2,4-dinitrophenylhydrazine in hydrochloric acid yielded a product, m. p. 218° (Found: C, 45·4; H, 3·3; N, 21·3%), identical in appearance and with a very similar *X*-ray powder photograph to that of the product obtained from 3-deoxy-D-mannose.

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