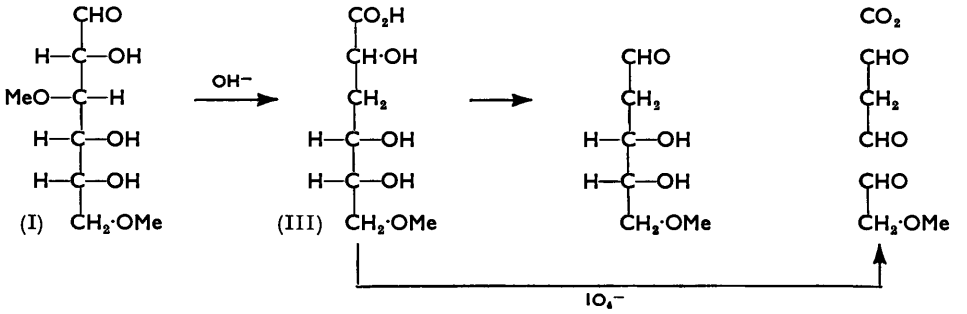
567. *The Degradation of Carbohydrates by Alkali. Part XII.** 6-O-*Methyl- and* 3 : 6- *and* 4 : 6-*Di*-O-*methyl*-D-*glucose.*

By J. KENNER and G. N. RICHARDS.

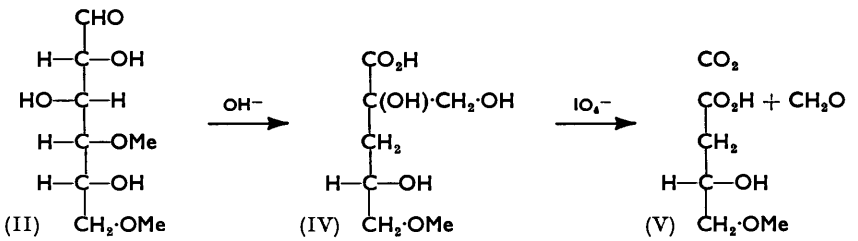
Conversion of 3 : 6- and of 4 : 6-di-*O*-methyl-D-glucose into 6-*O*-methyl-*meta*- and -*iso*-saccharinic acid respectively identifies the saccharinic acids prepared directly from 6-*O*-methyl-D-glucose as of predominantly the *meta*-type.

WHEREAS formation of saccharinic acids of predominantly the *meta*- and, to a smaller extent, the *iso*-type from glucose requires the action of strong alkali,[1] such acids are produced from melibiose (6-*O*-galactosyl-D-glucose) by the action of lime-water.[2] It was thus desirable to study the behaviour of 6-*O*-methyl-D-glucose from this point of view.

The substituted *meta*- (III) and *iso*-saccharinic acid (IV) were prepared, in line with the generalisation already enunciated,[3] by the action of lime-water on 3 : 6- (I) and 4 : 6-di-*O*-methyl-D-glucose (II) respectively, the presumed structures being confirmed by the



behaviour of the acids towards sodium metaperiodate : the mixed 6-*O*-methyl-D-gluco*meta*-saccharinic acids (III) gave malondialdehyde and methoxyacetaldehyde, and, as further confirmation, degradation by hydrogen peroxide yielded 2-deoxy-5-*O*-methyl-D-ribose; 5-*O*-methyl-D-gluco*iso*saccharinic acid (IV) similarly yielded formaldehyde and 2-deoxy-4-*O*-methyl-D-erythronic acid (V).



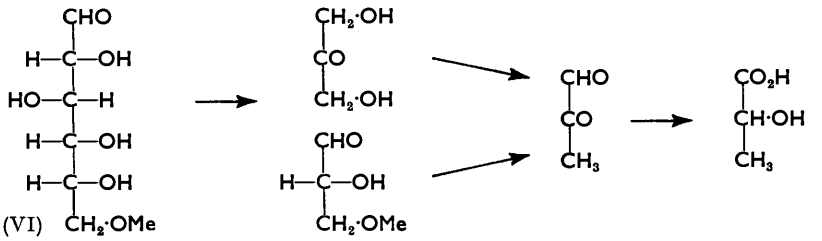
It was then shown that, when lime-water degraded 6-*O*-methyl-D-glucose (VI), lactic acid was obtained in 78% yield, the remainder being mainly 6-*O*-methyl-D-gluco*meta*saccharinic acids (III). Although no conclusive evidence of the formation of the corresponding *iso*saccharinic acid (IV) was found these results are in general accord with those obtained with melibiose.[2]

It thus appears that if the 6-hydroxyl group is inactivated by substitution the alkalinity of lime-water so stabilises the dienolate ion (VII) as to lead to formation of saccharinic acids of the *meta*-type (III). Otherwise, and in amendment of the earlier scheme,[2] as a result of

* Part XI, *J.*, 1955, 1810.

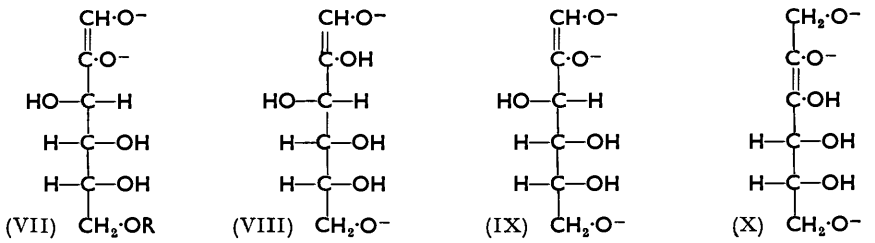
[1] Nef, *Annalen*, 1910, **376**, 89.
[2] Corbett and Kenner, *J.*, 1954, 3281.
[3] Kenner and Richards, (*a*) *J.*, 1954, 278; (*b*) 1955, 1810.

reactivity of the 6-primary alcoholic group there is produced a system (VIII) which rearranges to ordinary saccharinic acid.[4] In these circumstances more strongly alkaline conditions, *e.g.*, 8N-sodium hydroxide as employed by Nef,[1] are required to produce the



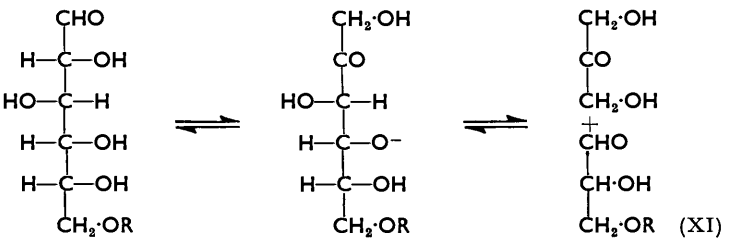
(VI)

ion (IX), thus restraining rearrangement. The restraint is, however, not quite complete since the small proportions of acids of the *iso*-type obtained under these conditions, and also noted among the products from melibiose, must arise from some rearrangement, *e.g.*, to the ion (X).



(VII) (VIII) (IX) (X)

Clearly, also, substitution of the 6-hydroxyl group is likely to result in more pronounced attack by alkali on the 4-hydroxyl group, and so to increase the formation of lactic acid. Further, it will be noted that, in such a case, a 3-*O*-alkylglyceraldehyde (XI) would be a primary product of the degradation and very readily subject to further attack. Thus the yields of the acid from melibiose and from 6-*O*-methylglucose are about 80%, as against 67% under comparable conditions from glucose.[4]



(XI)

The effect of substitution in the 6-*O*-position is also seen in the more rapid attack by lime-water on 3 : 6- and 4 : 6-di-*O*-methylglucose than on 3- and 4-*O*-methylglucose respectively. The apparent first-order rate constants ($\log_{10} k$; hr.$^{-1}$), calculated from acid formation, at 25° were: 3-*O*-methyl-,[4] $5{\cdot}3 \times 10^{-2}$; 3 : 6-di-*O*-methyl-, $6{\cdot}1 \times 10^{-2}$; 4-*O*-methyl-,[3b] $3{\cdot}9 \times 10^{-3}$; 4 : 6-di-*O*-methyl-, $5{\cdot}9 \times 10^{-3}$. The relatively low values of the last two constants reflect the fact that in these instances isomerisation to the corresponding fructose derivatives must precede formation of a saccharinic acid.

Experimental

The following solvents and sprays were used for paper chromatography: solvents *a*, butanol–light petroleum (b. p. 100—120°)–acetic acid–water (2 : 1 : 1 : 2); *b*, butyl acetate–acetic acid–water (10 : 3 : 1); *c*, butanol–pyridine–water (6 : 4 : 3); *d*, butanol–ethanol–acetic acid–water (45 : 5 : 1 : 49); *e*, butanol–pyridine–benzene–water (5 : 3 : 1 : 3). Sprays were:

[4] Kenner and Richards, *J.*, 1954, 1784.

a, silver nitrate–sodium hydroxide;[5] *b*, naphtharesorcinol;[6] *c*, hydroxylamine–ferric chloride;[7] *d*, sodium metaperiodate–potassium permanganate.[8]

Degradation of 3 : 6-*Di*-O-*methyl*-D-*glucose*.—The ether, prepared by Bell's method,[9] was chromatographically homogeneous.

(a) *Qualitative*. A solution of 3 : 6-di-*O*-methyl-D-glucose (2·30 g.) in oxygen-free 0·04N-lime-water (650 ml.), after 5 days at 25°, was saturated with carbon dioxide, boiled for a few minutes, and filtered. The filtrate was evaporated to dryness and the yellowish solid residue (2·50 g., 99%) washed with ethanol [Found: C, 39·4; H, 6·2; Ca, 7·9. Calc. for $(C_7H_{13}O_6)_2Ca$: C, 39·4; H, 6·15; Ca, 7·3%]. To separate the mixed calcium 6-*O*-methyl-α- and -β-D-gluco*meta*-saccharinates, a column of Dowex-1 resin in the acetate form (200—400-mesh; 1 × 35 cm.) was prepared by washing the corresponding chloride form with N-hydrochloric acid (100 ml.), followed by 0·2M-sodium acetate until the effluent showed only a faint test for chloride. An aqueous solution (5 ml.) of the mixed calcium salts (0·30 g.) was then transferred to the column and eluted with 0·1M-acetic acid, 20 ml. fractions being collected at 0·25 ml./min. The β-form was removed first (200—250 ml.) and shown to be homogeneous by paper chromatography [R_F 0·31 (lactone) in solvent *b*, sprays *c* and *d*]. The free acid form reacted rapidly with the latter spray, but the lactone comparatively slowly (20 min.). Evaporation of the relevant fractions yielded the β-form as a colourless syrup (0·044 g.), from which was prepared, in the usual way, *brucine* 6-O-*methyl*-β-D-*gluco*meta*saccharinate* showing, after crystallisation from ethanol, m. p. 136—137°, $[\alpha]_D^{20}$ −35° (*c* 1 in H_2O) (Found: C, 61·2; H, 7·0; N, 4·6. $C_{30}H_{40}O_{10}N_2$ requires C, 61·2; H, 6·85; N, 4·8%).

Further elution of the column with the same solvent yielded first mixtures and then the pure α-form, showing R_F 0·51 (acid), 0·64 (lactone) in solvent *a*, and R_F 0·39 (lactone) in solvent *b*. The reactions with sprays *c* and *d* were as noted for the β-form. Evaporation of the relevant fractions yielded the α-form as a colourless syrup (0·104 g.) from which was prepared *brucine* 6-O-*methyl*-α-D-*gluco*meta*saccharinate* showing, after crystallisation from ethanol–ether, m. p. 125—135° (sintering at 105°), $[\alpha]_D^{21}$ −24° (*c* 2 in H_2O) (Found: C, 60·9; H, 7·2; N, 4·5%). Total recovery of material from the column with the above eluant was *ca.* 35%.

(b) The course of reaction in a solution of 3 : 6-di-*O*-methyl-D-glucose (0·356 g.) in oxygen-free 0·0400N-lime-water (100 ml.) at 25° was followed by treating samples (5 ml.) with 0·05N-sulphuric acid (5 ml.) and titration (phenolphthalein) with 0·025N-potassium hydroxide. The neutralised solutions were diluted to 25 ml. for polarimetry in a 4-dm. tube (see Table).

Time (hr.)	$[\alpha]_D^{25}$	Acids formed (equiv./mole)	Paper chromatography * G	F	S	Time (hr.)	$[\alpha]_D^{25}$	Acids formed (equiv./mole)	Paper chromatography * G	F	S
0·25	+52°	0·02	4	—	—	7·0	+13°	0·61	1	0·5	2
0·5	+46	0·05	4	—	—	24	− 3	0·94	0·5	—	3
1·0	+41	0·11	3	1	0·5	31·5	− 3	0·95	0·5	—	3
2·0	+34	0·22	2	1	1	48	− 3	0·97	—	—	3
3·0	+31	0·33	2	0·5	1	72	− 3	0·98	—	—	3
4·5	+25	0·45	2	0·5	2	144	− 3	0·99	—	—	3

* Solvent *c*, sprays *a*, *b*. Numbers denote relative intensity. G = 3 : 6-di-*O*-methyl-D-glucose (R_F 0·63); *F* = supposed 3 : 6-di-*O*-methyl-D-fructose (R_F 0·67); S = 6-*O*-methyl*meta*saccharinic acids (R_F <0·10).

Periodate Oxidation of 6-O-*Methyl*-D-*gluco*meta*saccharinic Acids*.—A solution of the mixed calcium salts described above (0·0566 g.) was shaken with Amberlite resin IR-120 (H) (1 g.) for 5 min., then filtered, and the resin washed with water. 0·4M-Sodium metaperiodate (5 ml.) was added to the combined filtrate and washings, and the solution diluted to 50 ml. and kept at 25°. The rate of consumption of periodate, measured by reaction with potassium iodide and subsequent titration with sodium arsenite, was as follows, the " over-oxidation " presumably being due to the slow destruction of malondialdehyde.[10]

Time (hr.)	1·0	4·0	24	198
$NaIO_4$ consumed (moles/mole)	1·50	1·57	1·98	2·85

In a separate experiment the same mixture of calcium salts (0·206 g.) was freed from calcium ions as described above, 0·4M-periodic acid (5 ml.) was added to the resulting solution (20 ml.),

[5] Trevelyan, Procter, and Harrison, *Nature*, 1950, **166**, 444.
[6] Hough, Jones, and Wadman, *J.*, 1950, 1702.
[7] Abdel-Akher and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 5859.
[8] Lemieux and Bauer, *Analyt. Chem.*, 1954, **26**, 920.
[9] Bell, *J.*, 1936, 1553.
[10] Fleury, *Bull. Soc chim. France*, 1955, 1126, and references therein.

and the mixture evaporated to dryness under reduced pressure at 35—40°. The distillate, treated with a saturated solution (50 ml.) of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid at 100° for 10 min. and then left overnight at room temperature, gave a precipitate which was extracted with boiling ethanol and recrystallised from nitrobenzene. The malondialdehyde bis-2 : 4-dinitrophenylhydrazone thus prepared showed m. p. 300° (decomp.) (cf. ref. 11) (Found : C, 41·25; H, 2·8; N, 26·4. Calc. for $C_{15}H_{12}O_8N_8$: C, 41·65; H, 2·8; N, 25·9%). The ethanol extract, when fractionally precipitated with water, yielded methoxyacetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 122—124°.

2-Deoxy-5-O-methyl-D-ribose.—Barium acetate (0·2 g.) and ferric sulphate (0·1 g.) were added to a solution of mixed calcium 6-*O*-methyl-α- and -β-D-gluco*meta*saccharinate (1·13 g.) in water (10 ml.). After boiling, the mixture was filtered, cooled to 40°, and treated with 30% hydrogen peroxide (1 ml.). After being warmed to 70° to initiate reaction, the solution was allowed to cool to 40°, then more hydrogen peroxide (1 ml.) was added and the solution heated as before. Finally the solution was de-ionised by stirring it with mixed Amberlite resins IR-120 (H) (5 g.) and IR-4B (OH) (10 g.) and evaporated to a colourless syrup (0·288 g., 37%). Paper chromatography (solvent *c*, spray *a*) indicated that the crude 2-deoxy-5-*O*-methyl-D-ribose (R_F 0·81) so obtained was contaminated with traces of reducing impurities (R_F 0·26, 0·61). Part of the syrupy product (0·15 g.) was converted in the usual way into N-*2-deoxy-5-O-methyl-D-ribosylaniline*, m. p. 139—140° (Found : N, 5·9; OMe, 14·1. $C_{12}H_{17}O_3N$ requires N, 6·3; OMe, 13·9%).

4 : 6-Di-*O*-methyl-D-glucose was prepared by stirring a solution of methyl 2 : 3-di-*O*-benzyl-4 : 6-di-*O*-methyl-α-D-glucoside [12] (24·0 g.) in ethanol (200 ml.) with Raney nickel (*ca.* 40 g.) in the same solvent (100 ml.) while the temperature was raised from 60° to 85° during 6 hr. The solution, after a further 2 hours' refluxing, was filtered and evaporated almost to dryness. The filtered aqueous solution of the residue (100 ml.) was washed with chloroform (4 × 50 ml.) and evaporated. The yield of 4 : 6-di-*O*-methyl-α-D-glucoside, after distillation at 172—174°(bath temp.)/0·17 mm., n_D^{20} 1·4742, was 10 g. (76%). Bell and Lorber [12] give $n_D^{18\cdot5}$ 1·4715.

Hydrolysis by N-sulphuric acid for 20 hr. at 100° furnished 4 : 6-di-*O*-methyl-D-glucose, m. p. 163—163·5° (from ethanol), $[\alpha]_D^{20}$ +65° (equil.; *c* 2 in H_2O) (Found : C, 46·1; H, 8·1; OMe, 29·5. Calc. for $C_8H_{16}O_6$: C, 46·1; H, 7·75; OMe 29·8%). Bell and Lorber [12] give m. p. 156—157°, $[\alpha]_D$ +65·7° (equil.).

Degradation of 4 : 6-*Di*-O-*methyl*-D-*glucose.*—(a) *Qualitative.* A solution of 4 : 6-di-*O*-methyl-D-glucose (5·05 g.) in oxygen-free water (500 ml.) was treated with calcium hydroxide (5 g.) at 35° with occasional shaking for 8 days, filtered from excess of lime, and worked up as described for 3 : 6-di-*O*-methyl-D-glucose, to yield a colourless amorphous solid (4·94 g., 96%), which was fractionally precipitated with ether from moist methanol. The first fraction was *calcium* 5-O-*methyl*-α-D-iso*saccharinate*, $[\alpha]_D^{20}$ +5·6° (*c* 1 in H_2O) [Found : C, 39·5; H, 6·5; Ca, 9·7. $(C_7H_{13}O_6)_2Ca$ requires C, 39·4; H, 6·15; Ca, 9·4%]. This was shown to be homogeneous by shaking its aqueous solution with Amberlite resin IR-120 (H) and subsequent paper chromatography in solvent *d* (spray *c*), a single spot only being observed (R_F 0·62). The *brucine salt*, prepared from the calcium salt in the usual way, after crystallisation from ethanol–ether, had m. p. 152—154°, $[\alpha]_D^{19}$ −24° (*c* 1 in H_2O) (Found : N, 4·7; OMe, 15·5. $C_{30}H_{40}O_{10}N_2$ requires N, 4·8; OMe, 15·8%).

(b) *Quantitative.* A solution of 4 : 6-di-*O*-methyl-D-glucose (0·365 g.) in oxygen-free 0·0400N-lime-water (100 ml.) was kept at 25° and examined as described for 3 : 6-di-*O*-methyl-D-glucose, except that paper chromatography was carried out in solvent *e* (see Table).

Time (hr.)	$[\alpha]_D^{25}$	Acids formed (equiv./mole)	Paper chromatography * G	F	S	Time (hr.)	$[\alpha]_D^{25}$	Acids formed (equiv./mole)	Paper chromatography * G	F	S
0	+64°	0	4	—	—	75	+24°	0·61	2	0·5	2
1·0	+61·5	0	4	0·25	—	100	+17	0·74	1	0·5	2
3·0	+60	0·01	4	0·5	—	193	+ 7	0·93	—	—	3
5·0	+58	0·02	3	1	—	244	+ 3	0·985	—	—	3
7·0	+56·5	0·04	3	1	—	341	+ 3	1·02	—	—	3
24	+44·5	0·22	3	1	—	414	+ 3	1·01	—	—	3
50	+31	0·47	2	1	1	505	+ 3	1·01	—	—	3

* G = 4 : 6-di-*O*-methyl-D-glucose (R_F 0·60); F = supposed 4 : 6-di-*O*-methyl-D-fructose (R_F 0·72); S = saccharinic acid (R_F 0·05).

[11] Rothstein, *J.*, 1940, 1557.
[12] Bell and Lorber, *J.*, 1940, 453.

Periodate Oxidation of 5-O-*Methyl*-α-D-iso*saccharinic Acid.*—(*a*) A solution of calcium 5-*O*-methyl-α-D-*iso*saccharinate (0·102 g.) in water (5 ml.) was shaken for 10 min. with freshly washed Amberlite resin IR-120 (H) (*ca.* 1 g.) and filtered. The filtrate and washings from the resin, together with 0·4M-sodium metaperiodate (5 ml.), were diluted to 50 ml. and kept at 25°. At intervals aliquot portions were treated in the usual way with potassium iodide and titrated with sodium arsenite, and after 20 hr. 0·1N-sodium hydroxide (1 ml.) was added to the remaining solution (20 ml.) to facilitate completion of the oxidation (cf. ref. 13). Results were :

Time (hr.)	0·25	0·5	1·0	1·5	2·5	20	22	92	188
$NaIO_4$ consumed (moles/mole)	0·83	0·95	1·07	1·13	1·20	1·38	1·58	1·97	2·07

(*b*) The sodium salt of the saccharinic acid (prepared from 0·70 g. of the calcium salt) was treated with sodium metaperiodate (3·5 g.) and sodium hydrogen carbonate (1·5 g.) in aqueous solution (50 ml.) for 2 hr. at room temperature. The solution was then steam-distilled for 30 min. and subsequently evaporated to dryness, the distillate being cooled to −40°. The dimedone derivative of formaldehyde, prepared from the distillate in the usual way,[14] had m. p. and mixed m. p. 189—190° (0·72 g., 75·5%).

The aqueous solution of the residue was shaken with excess of Amberlite resin IR-120 (H), filtered, and extracted with ether to yield a pale yellow syrup (0·43 g.) which was converted into the sodium salt and with 4-phenylphenacyl bromide yielded 4-phenylphenacyl 2-deoxy-4-*O*-methyl-D-erythronate, which after repeated crystallisation from ether–light petroleum had m. p. 102—103°, $[\alpha]_D^{18}$ +4° (*c* 1 in MeOH), but was apparently still not quite pure (Found : C, 70·9; H, 6·4. Calc. for $C_{19}H_{20}O_5$: C, 69·45; H, 6·1%). Owen and Sultanbawa reported[15] m. p. 96° for the optically inactive ester.

Action of Lime-water on 6-O-*Methyl*-D-*glucose.*—6-*O*-Methyl-D-glucose was prepared by the method of Levene and Raymond[16] and shown to be homogeneous by paper chromatography (R_F 0·48; solvent *a*, spray *a*).

(a) *Qualitative.* An oxygen-free aqueous solution (1 l.) of 6-*O*-methyl-D-glucose (15·25 g.) was treated with calcium hydroxide (20 g.) at 25° for 14 days with occasional shaking. After removal of the excess of lime at 50°, the filtrate was saturated with carbon dioxide, boiled for a few minutes, again filtered, and concentrated. Calcium lactate (0·76 g., 3%) gradually separated at room temperature and was characterised by conversion into the corresponding 4-bromophenacyl ester, m. p. and mixed m. p. 111—113°. The mother-liquor was treated with excess of Amberlite resin IR-120 (H), neutralised with zinc carbonate, boiled for a few minutes to decompose bicarbonates, and filtered. Zinc lactate (4·24 g., 18%) gradually separated from the resulting solution at 0°, and yielded the corresponding 4-bromophenacyl ester identical with that obtained from the calcium salt. The liquor on evaporation to dryness yielded a white powder (13·2 g.), faintly reducing Fehling's solution. Part of this product (1·5 g.) was transferred in water (10 ml.) to a column of Dowex-1 resin in the acetate form (2 × 35 cm.; 200—400-mesh) and eluted with 0·1M-acetic acid (1 ml./min.), the following products being obtained by evaporation of fractions of the effluent in the order given.

(i) Minute amounts of lactone, possibly 5-*O*-methylsaccharinolactone. Paper chromatography (sprays *c*, *d*) showed that, besides the main component (R_F 0·74, solvent *a*; R_F 0·54, solvent *b*), there was also a very small amount of another lactone (R_F 0·83 and 0·63), the two components presumably corresponding to the α- and the β-form respectively.

(ii) Mainly 6-*O*-methyl-β-*meta*saccharinolactone (0·045 g.), R_F 0·43 (acid), 0·54 (lactone) (solvent *a*, sprays *c*, *d*). The brucine salt was prepared and when fractionally recrystallised from ethanol–ether had m. p. 134—136°, not depressed by admixture with the corresponding compound obtained from 3 : 6-di-*O*-methyl-D-glucose. This fraction probably contained a small amount of 5-*O*-methyl-α-*iso*saccharinolactone showing R_F 0·66 (solvent *a*), but reacting rapidly with spray *d*, and so distinct from the *meta*saccharinolactone derivative of similar R_F value.

(iii) 6-*O*-methyl-α-*meta*saccharinolactone was obtained as a colourless syrup (0·040 g.), R_F 0·51 (acid), 0·64 (lactone) (solvent *a*, sprays *c*, *d*) and readily yielded a crystalline brucine salt, m. p. 125—135° (sintering at 105°) not depressed by admixture with the corresponding product obtained from 3 : 6-di-*O*-methyl-D-glucose; the salt had $[\alpha]_D^{20}$ −23° (*c* 1 in H_2O).

[13] Sprinson and Chargaff, *J. Biol. Chem.*, 1946, **164**, 433.
[14] Reeves, *J. Amer. Chem. Soc.*, 1941, **63**, 1476.
[15] Owen and Sultanbawa, *J.*, 1949, 3098.
[16] Levene and Raymond, *J. Biol. Chem.*, 1932, **97**, 751.

(iv) Lactic acid, shown to be homogeneous by paper chromatography (R_F 0·70, solvent *a*, spray *d*); it yielded the 4-bromophenacyl ester, m. p. and mixed m. p. 111—113°. Total recovery of material from the column was *ca.* 30%.

(b) *Quantitative.* A solution of 6-*O*-methyl-D-glucose (0·347 g.) in oxygen-free 0·0388N-lime-water was kept at 25° while the formation of acid was determined by back-titration after addition of excess of sulphuric acid. Duplicate determinations by the resin method (cf. ref. 17) yielded identical results. Lactonised acids were estimated as described earlier;[4] comparison of the results obtained with authentic calcium 5-*O*-methyl-α-*iso*saccharinate and 6-*O*-methyl-*meta*saccharinate indicated that lactonisation was approx. 78% complete in each case and accordingly the appropriate correction factor was applied. The results are expressed in the Table, an assumption being that the non-lactonised acid corresponds to lactic acid.

Acid yields from 6-O-*methyl*-D-*glucose in lime-water.*

Time (hr.)	$[\alpha]_D^{25}$	Total acid (equiv./mole)	Lactonised acid (equiv./mole)	Lactic acid (equiv./mole)	Paper chromatography * G	F	M	S
1·0	+56°	0	0	0	4	0·5	—	—
3·0	+52°	0·02	†	†	3	1	—	—
6·0	+47°	0·07	†	†	3	1	—	—
23	+38°	0·44	0·04	0·44	2	1	0·5	0·5
30	+36°	0·57	0·05	0·52	2	1	0·5	0·5
47	+25°	0·80	0·06	0·74	2	0·5	0·5	1
144	+12	1·54	0·18	1·36	1	0·5	0·5	2
216	+ 9	1·69	0·20	1·49	0·5	—	—	3
288	+ 2	1·78	0·21	1·57	—	—	—	3
528	+ 2	1·79	0·22	1·57	—	—	—	3

* Solvent *c*, sprays *a* and *b*. † Not determined.

G = 6-*O*-methyl-D-glucose (R_F 0·48), *F* = supposed 6-*O*-methyl-D-fructose (R_F 0·62), *M* = supposed 6-*O*-methyl-D-mannose (R_F 0·54), S = saccharinic acids (R_F <0·10).

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WYTHENSHAWE, MANCHESTER. [*Received, March 9th,* 1956.]

[17] Corbett and Kenner, *J.*, 1955, 1431.