CXXVII.—*Compounds of Hydroxides of the Alkaline Earths with Sugars.*

By JOHN EDWIN MACKENZIE and JAMES PATTERSON QUIN.

IN 1807, William Ramsay (*Nicholson's Journal*, **18**, 9) described experiments from which he concluded that sucrose, in aqueous solution at 50° F., dissolved half its weight of lime and an equal weight of strontia. From the latter solution, grey crystals separated, but no analytical data are given by Ramsay for what was in all probability monostrontia-monosucrose.

Peligot (*Compt. rend.*, 1838, **6**, 232) prepared and analysed a number of compounds of sucrose and "earths." The results recorded in numerous subsequent papers are so discordant that it seemed desirable to obtain exact data concerning these compounds and to distinguish between true compounds and intimate mechanical mixtures. In pursuance of this object, one of us (J. E. M.) incidentally repeated the isolation of calcium carbonate hexahydrate (J., 1923, **123**, 2409) from a lime–sugar solution. Preliminary experiments by Messrs. John Hume and H. B. Walker gave valuable results and a full description of the subsequent work appears in the thesis submitted by J. P. Quin to the University of Edinburgh.

Some of the names applied to these compounds are unsuitable, *e.g.*, "saccharate" (Peligot, *loc. cit.*), "sucrate" and "lactate" (Horsin-Déon, *Bull. Soc. chim.*, 1871, **16**, 26). Until more knowledge of the structure has been gained, the nomenclature of Soubeiran

(*J. Pharm. Chim.*, 1842, **1**, 469), in which the name of the alkaline earth and of the sugar are combined, will be used.

As many as seven lime-sucrose compounds have been described, but, as will be shown, the existence of more than three is very improbable.

Monolime-monosucrose (Peligot, *Compt. rend.*, 1864, **59**, 930; Benedikt, *Ber.*, 1873, **6**, 413; Stromeyer, *Arch. Pharm.*, 1887, **25**, 229) exists as an unstable hexahydrate, $C_{12}H_{22}O_{11},CaO,6H_2O$. We found it difficult to isolate this hydrate and, on triturating it with dilute alcohol, the lime content rose until it reached that required for dilime-monosucrose.

Brendeke (*Arch. Pharm.*, 1842, **29**, 73), Soubeiran (*loc. cit.*), and Stromeyer (*loc. cit.*) claim to have prepared trilime-disucrose. The product obtained by us on following the directions of these authors is probably a mixture of the unstable monolime-monosucrose with the more stable dilime-monosucrose, since on trituration with dilute alcohol it, like monolime-monosucrose, yields dilime-sucrose.

Dilime-monosucrose was first described by Pelouze (*Compt. rend.*, 1864, **59**, 1073). It is the final product obtained by washing with dilute alcohol the precipitate formed by adding alcohol to a sugar–lime solution. Peligot (*Compt. rend.*, 1864, **59**, 930) pointed out that the proportion of two molecules of lime to one of sugar is never attained in solution and that the precipitation by alcohol leaves a mother-liquor richer in sugar. Dilime-monosucrose is a comparatively stable substance.

Trilime-monosucrose ($C_{12}H_{22}O_{11},3CaO,4H_2O$) was obtained by Seyffart (*N.Z. Rübenzuckerind.*, **3**, 178) by the action of three molecular proportions of lime on an alcoholic solution containing one molecular proportion of sucrose. Soubeiran (*loc. cit.*), Wachtel (*O.Z. Zuckerind.*, **7**, 704; **8**, 860) and Lippmann (*ibid.*, **9**, 95) all claim to have obtained $C_{12}H_{22}O_{11},3CaO,3H_2O$ by heating a sugar–lime solution. As mentioned below (p. 957), our product appears to be a hexahydrate. Horsin-Déon (*loc. cit.*) observed that precipitation of trilime-sucrose does not take place on heating to 100° a lime–sugar solution containing excess of sugar, but, if the density of the solution be lowered by the addition of water, precipitation does take place. In other words, trilime-sucrose is more soluble in an aqueous solution of sugar at low than at high temperatures and also more soluble in a highly concentrated than in a less concentrated sugar solution.

Stulzer and Sostmann (*Z. Ver. deut. Zuckerind.*, 1884, **34**, 85) and Wolters (*N.Z. Rübenzuckerind.*, **10**, 287) claim to have prepared tetralime-monosucrose; Degener (*Z. Ver. deut. Zuckerind.*, 1884, **34**, 283) disclaims its existence. Soubeiran (*loc. cit.*) and

Horsin-Déon (*Bull. Soc. chim.*, 1872, **17**, 155) described the preparation of hexalime-monosucrose, but gave no analyses; Peligot (*Compt. rend.*, 1851, **32**, 333) denied its existence. Wolters (*loc. cit.*) affirmed the existence of octalime-monosucrose.

On heating sugar–lime solutions, unsaturated as regards lime, precipitates containing approximately the theoretical proportions of lime required for higher lime-monosucroses were obtained by us. These precipitates showed no trace of crystalline structure and on grinding with 90% alcohol, the lime content rose to 80% (see p. 958). It would appear that these so-called compounds are either sucrose, dilime- or trilime-sucrose adsorbed by lime.

Few physical data concerning sugar–lime compounds are available. Petit (*Compt. rend.*, 1893, **116**, 823) made a thermochemical investigation not only of the direct action of lime upon sucrose, but also of the interaction of sodium hydroxide with sucrose and calcium chloride in aqueous solution. His results may be summarised as follows :—

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11}} + \underset{\text{(solid)}}{Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},CaO} + 7{\cdot}2\ \text{Cal.}$$

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11}} + \underset{\text{(solid)}}{2Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},2CaO} + 11{\cdot}7\ \text{Cal.}$$

$$\underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},CaO} + \underset{\text{(solid)}}{Ca(OH)_2} = \underset{\text{(dissolved)}}{C_{12}H_{22}O_{11},2CaO} + 4{\cdot}5\ \text{Cal.}$$

The addition of more calcium hydroxide was unaccompanied by further heat production and no trilime compound was formed in solution.

An accurate study of the solubility of lime in aqueous sugar solutions was made by Claassen (*Z. Ver. deut. Zuckerind.*, 1911, 489). Cameron and Patten (*J. Physical Chem.*, 1911, **15**, 67) found that on addition of lime to sucrose solution, not only was a soluble lime-sucrose compound formed, but some of the sucrose was removed from solution by the undissolved lime and passed into the solid phase. Dedek (*Z. Zuckerind. Czechoslov.*, 1925, **26**, 349) concluded from his potentiometric measurements that trilime-sucrose was not present in solution, and suggested that a colloidal adsorption compound was obtained by adding powdered calcium oxide to a sucrose solution or by heating lime-sucrose solution, which was saturated in the cold. Waterman and van Aken (*J. Soc. Chem. Ind.*, 1927, **46**, 411T) agree with Dedek's view of the nature of trilime-sucrose. Aten, van Ginneken, and Engelhard (*Rec. trav. chim.*, 1926, **45**, 753) found that in dilute alkaline solution (up to $0{\cdot}1N$) sucrose behaves as a monobasic acid with dissociation constant $14{\cdot}6 \times 10^{-14}$ at 18°. They also observed that little change in the metal-ion concentration was produced by the addition of sucrose to alkaline solutions of less than normal concentration. Hence they concluded that the alkali-sucrose compounds in such solutions are largely ionised. Experiments made in this laboratory support this conclusion. In more concentrated solutions the low conductivities measured indicate the presence of undissociated molecules.

Diffusion experiments described below (pp. 958, 959, 960) proved that, in aqueous solution, the lime-sucrose, strontia-sucrose, and baryta-sucrose behave as crystalloids—diffusing readily.

Monostrontia-monosucrose was obtained in crystalline form by Ramsay (*loc. cit.*) and as pentahydrate by Scheibler (*N.Z. Rübenzuckerind.*, 9, 83; **10**, 143). Our experiments show the compound to be a hexahydrate (p. 959).

Scheibler (*loc. cit.* and **6**, 49) claims to have prepared distrontia-trisucrose and distrontia-monosucrose and also tristrontia-monosucrose. Wolfmann (*Z. Ver. deut. Zuckerind.*, **52**, 587) showed that the last-named product is a mixture of distrontia-monosucrose and strontium hydroxide, a result confirmed by our experiments. Our attempts to prepare distrontia-trisucrose were unsuccessful (p. 959).

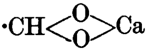
Monobaryta-monosucrose, $C_{12}H_{22}O_{11},BaO$, was first prepared by Peligot (*Annalen*, 1839, **30**, 69) and its composition has been confirmed by numerous investigators. Soubeiran (*Compt. rend.*, 1843, **14**, 648) claims also to have isolated dibaryta-monosucrose, but in our attempts to separate this compound the monobaryta compound has always been produced (p. 960).

Monolime-monoglucose was first described by Peligot (*Annalen*, 1839, **30**, 75) and the dihydrate by Soubeiran (*J. Pharm.*, 1842, **1**, 649). Though the instability of alkaline solutions of glucose is well known and has been the subject of very extensive investigations by Nef (*Annalen*, 1907, **357**, 294; 1910, **376**, 1) and others, anhydrous monolime-monoglucose is comparatively stable (p. 960). We have been unable to isolate any other compound than monolime-monoglucose.

Monolime-monofructose dihydrate was prepared by Peligot (*Compt. rend.*, 1880, **90**, 153) and the hexahydrate by Winter (*Annalen*, 1888, **244**, 295). Peligot (*J. Fabr. Sucre*, **21**, 6) claims to have prepared dilime-monofructose, but the resulting product in our experiments has always been monolime-monofructose.

Monolime-monomaltose was prepared by Herzfeld (*Annalen*, 1883, **220**, 214) and monolime-monolactose by Dubrunfaut (Lippmann, "Chemie der Zuckerarten," 1904). No other lime derivatives of either of these sugars appear to have been made.

From our experiments we conclude that the following definite compounds can be prepared: monolime-monosucrose, dilime-monosucrose, trilime-monosucrose; monostrontia-monosucrose, distrontia-monosucrose; monobaryta-monosucrose; and monolime-monoglucose; monolime-monofructose; monolime-monomaltose; monolime-monolactose. It is further shown that the methylglucosides, -fructosides, -maltosides, and -lactosides are uninfluenced by calcium hydroxide. Our attempts to prepare compounds of reducing sugars with alkaline earths, other than those built up of one molecule of sugar and one molecule of earth, have not been successful.

The evidence at present on hand inclines us to suggest that in the compounds of the reducing sugars with lime the calcium is united to the "reducing" carbon group—possibly in the form  $\cdot CH\langle{}^{O}_{O}\rangle Ca$ or $:CH\cdot O\cdot Ca\cdot OH$; whereas in the non-reducing sugar, sucrose, the sucrose molecule attracts one, two or three molecules of lime, forming compounds comparable with those of sucrose with metallic salts, *e.g.*, $C_{12}H_{22}O_{11},KCl$ (Violette, *Compt. rend.*, 1873, **76**, 485).

In a future communication we hope to give an account of further experiments which will lead to a full discussion of the constitution of these substances.

Is it a coincidence that one molecule of sucrose can form a compound with three molecules of lime, with two molecules of strontia and with only one molecule of baryta? The molecular weights of these earths are: $3CaO = 168$; $2SrO = 207$; $BaO = 153{\cdot}4$. The mean of the three is 176, which is approximately half of the molecular weight of sucrose—$342/2 = 171$.

EXPERIMENTAL.

The glass used in the following experiments had had lengthened contact successively with alkali, acid, conductivity water, sugar, and lime–sugar solutions. The apparatus for making lime–sugar solutions consisted of a bottle of 2 l. capacity, provided with a three-holed rubber stopper through which passed (*a*) a small funnel with ground glass stopper, (*b*) a soda–lime tube, (*c*) a glass tube in which rotated a stirrer reaching nearly to the bottom of the bottle. (*b*) allowed easy access of air free from carbon dioxide; whereas very little air entered through (*a*) while lime was being added and none entered through (*c*)—the space between the glass tube collar and the stirrer being filled with vaselin.

Lime was prepared from either Buxton limestone or precipitated calcium carbonate (Kahlbaum) by heating it for 6 hours in a muffle, grinding the product to a very fine powder, and reheating it for 4 hours. The lime produced did not effervesce when mixed with dilute acid. In the sucrose experiments, so-called " Austrian crystals " were used, 100 g. being dissolved in conductivity water and the solution made up to 2000 c.c. Lime was added in small quantities at a time to the sucrose solution, which was vigorously stirred, each portion being allowed to dissolve before addition of the next. The rate of solution depended on the state of division of the lime and the temperature of the solution—the finer the powder and the lower the temperature the more rapid the solution. After 4 days no more lime would dissolve. A slight excess of lime was then added, the mixture stirred for 6 hours and allowed to settle overnight, and the solution siphoned off through a purified cotton-wool filter. In absence of carbon dioxide the solution may be kept for months without change.

By titration with 0·049*N*-hydrochloric acid and phenolphthalein, the amounts of calcium oxide in two solutions thus prepared were found to be 11·7 and 12·3 g. per litre. Calculated from the sucrose content, $[\alpha]_D^{18\cdot5^\circ} = +53\cdot3^\circ$ and $+53\cdot0^\circ$. Muntz (*Z. Ver. deut. Zuckerind.*, **26**, 737) found for a 10% sucrose solution (1 mol. CaO : 1 mol. $C_{12}H_{22}O_{11}$) $[\alpha]_D = +56\cdot9^\circ$ and (2 mols. CaO : 1 mol. $C_{12}H_{22}O_{11}$) $[\alpha]_D = +51\cdot8^\circ$. By extrapolation, our figure for the latter value is $+51\cdot12^\circ$.

Monolime-monosucrose.—Following Peligot's method (*loc. cit.*), 0·9 mol. of calcium oxide was added to 1·0 mol. of sucrose in 5% aqueous solution. On the addition of 500 c.c. of 60% alcohol to 200 c.c. of this solution, an amorphous white precipitate was produced, which, after drying between filter-papers, amounted to 60% of the theoretical yield of $C_{12}H_{22}O_{11},CaO,2H_2O$ (Found : CaO, 12·9; H_2O, 7·9. Calc. for $C_{12}H_{22}O_{11},CaO,2H_2O$: CaO, 12·9; H_2O, 8·3%). These figures, however, appear to be fortuitous, since small changes in the proportion of calcium oxide and sucrose are accompanied by changes in the composition of the precipitate. Moreover, if the precipitate be triturated repeatedly under 60% alcohol, the percentage of calcium oxide gradually rises and after nine triturations becomes constant (Found : CaO, 24·5. Calc. for $C_{12}H_{22}O_{11},2CaO$: CaO, 24·7%).

By the evaporation of 150 c.c. of the above aqueous solution at 0° in a vacuum over phosphoric oxide during a period of 3 months, a syrupy mass containing microscopic crystals was obtained. After it had been washed successively with conductivity water at 0°, with 50% alcohol, and again with water, and then dried between filter-papers, there remained about 4 g. of slightly sticky solid (Found : CaO, 11·6, 11·9; H_2O, 20·05. Calc. for $C_{12}H_{22}O_{11},CaO,5H_2O$: CaO, 11·5; H_2O, 18·45. Calc. for $C_{12}H_{22}O_{11},CaO,6H_2O$: CaO, 11·2; H_2O, 21·3%). On being ground with 60% alcohol, this product behaved in a similar manner to the dihydrate, dilime-monosucrose being formed. Monolime-monosucrose is an unstable substance at room temperature.

Dilime-monosucrose.—The white precipitate formed by mixing 500 c.c. of 60% alcohol with 250 c.c. of the lime-saturated sugar solution (p. 956) at 0° was rapidly collected, washed and triturated with 60% alcohol, and dried between filter-papers. A thin layer of the product contained in a copper boat was heated at 100° under 1 mm. pressure in a slow current of air purified by passage through soda–lime and phosphoric oxide. This operation proved very lengthy, constant weight being attained only after 35 days in one experiment, and 32 days in another. The time may be shortened very much if, after the grinding with 60% alcohol, the precipitate is ground with small quantities of pyridine and finally with absolute alcohol several times before being heated under reduced pressure. During these operations some of the product appeared to become crystalline. We are indebted to Dr. R. Campbell for an examination of the substance, which he found to be isotropic, showing conchoidal fracture but no definite cleavage, and a refractive index between 1·5245 and 1·5294. The refractive indices for sucrose crystals are α 1·5397, β 1·5667, and γ 1·5716, so there can be no question of its identity with sucrose. The solubility of the crystalline part of the product was 45·23 g. per litre, and that of the amorphous precipitate was 37·7 (calc. as $C_{12}H_{22}O_{11},2CaO,6H_2O$). (Lippmann, *O.Z. Zuckerind.*, **9**, 35, gave the solubility as 1 in 33 of water.) $[\alpha]_D^{17^\circ} = +32{\cdot}1^\circ$ in 2·5% aqueous solution (Found: H_2O, 18·7, 17·8. Calc. for $C_{12}H_{22}O_{11},2CaO,6H_2O$: H_2O, 19·2%. Found: CaO, 24·2; C, 31·65; H, 4·8. Calc. for $C_{12}H_{22}O_{11},2CaO$: CaO, 24·6; C, 31·7; H, 4·85%).

Trilime-monosucrose.—This substance began to separate as a white precipitate from the lime-saturated sucrose solution (p. 956) when this was heated to 58°; on further heating to 80°, the precipitate settled and was easily collected on a hot funnel. It was thoroughly washed with hot conductivity water and then dried between filter-papers. Dehydration and analyses were carried out as described above [Found: H_2O, (1) constant after 66 days, 17·25, (2) constant after 56 days, 16·45; CaO, 33·0; C, 28·2; H, 4·45. Calc. for $C_{12}H_{22}O_{11},3CaO,6H_2O$: H_2O, 17·5%. Calc. for $C_{12}H_{22}O_{11},3CaO$: CaO, 33·0; C, 28·2; H, 4·3%]. An attempt to obtain this substance in crystalline form was made by sealing up some lime–sucrose solution in a tube, which was then immersed in a large volume of water. During a period of 8 days the temperature of the water was gradually raised from 17° to 58° and then more slowly to 72°. The precipitate was examined in the tube with the aid of a lens at intervals during the heating, and thereafter on a slide under a microscope, but no crystalline structure was observed.

Although trilime-monosucrose probably does not dissolve as such in water, the amount of lime in a saturated solution obtained by mixing anhydrous trilime-monosucrose with conductivity water at 15° was found to correspond to 15·33 g. of anhydrous trilime-monosucrose per litre (Lippmann, *loc. cit.*, records 10 g. per litre). $[\alpha]_D^{15^\circ} = +36{\cdot}52^\circ$ for this solution.

After it had been proved by qualitative experiments that both lime and sucrose in an aqueous solution of trilime-sucrose diffuse through collodion membrane, two experiments, in which 50 c.c. of trilime-sucrose solution were placed in a collodion membrane suspended in 100 c.c. of conductivity water, were carried out with the following results :

	Sucrose.	Lime.	Sucrose : lime.
(1) Initial conc. per 100 c.c.	0·6706	0·3294	2·03
Conc. after 12 hours	0·4201	0·1187	3·56
(2) Initial conc. per 100 c.c.	0·6706	0·3294	2·03
Conc. after 24 hours	0·5129	0·1534	3·34

In the hope that methyl sulphate might react with trilime-monosucrose and produce a trimethylsucrose, methylation experiments were performed, but the products were always mixtures of more highly methylated sucroses. Some oxidation experiments, with calcium permanganate as oxidising agent, led to no definite conclusions.

Higher Lime-sucrose Compounds.—Amorphous, white precipitates were obtained on heating sucrose solutions in which less lime than that required for saturation had been dissolved. For instance, a 5% sucrose solution containing 8 g. of lime per litre gave a precipitate on heating, which, after being triturated three times with 60% alcohol and dried, appeared to have the composition $C_{12}H_{22}O_{11},4CaO,H_2O$ (Found : CaO, 38·4. Calc. : 38·4%). In another experiment starting with the same solution, the precipitate was shaken with 90% alcohol for 2 hours and then dried (Found : CaO, 38·35%). In a third experiment with 5% sucrose solution containing 5 g. of lime per litre, the precipitate after three triturations with 60% alcohol and drying gave CaO, 58·5 (Calc. for $C_{12}H_{22}O_{11},9CaO,H_2O$: CaO, 58·3%). After repeated triturations of this same precipitate with alcohol, the lime content rose (Found : CaO, 79·6%). Similar results were obtained with the other precipitates, the lime content rising to 80—90%.

Sucrose-potassium Chloride.—This colourless crystalline compound was prepared by mixing solutions of sucrose (1 mol.) and of potassium chloride (1 mol.) in the minimum quantities of boiling water. The mixture, on cooling over sulphuric acid in a vacuum desiccator, deposited crystals (Found: KCl, 16·5; Cl, 7·8. Calc. for $C_{12}H_{22}O_{11},KCl,2H_2O$: KCl, 16·5; Cl, 7·8%). Violette (*Compt. rend.*, 1873, **76**, 485) gives the formula $C_{12}H_{22}KClO_{11}$, but without any analytical data, and describes the crystals as being isomorphous with those of sucrose itself—a very curious coincidence!

Monostrontia-monosucrose.—200 C.c. of 20% sucrose solution, in which strontia (1 mol.) had been dissolved at 75°, were shaken vigorously while being cooled: the hexahydrate was obtained in bunches of short, needle-like crystals. If the solution was allowed to cool undisturbed, or if seeded with a crystal of strontium hydroxide, crystals of the latter separated. After drying between filter-papers, the product appeared to be the hexahydrate. The solubility was 43·95 g. per litre at 16°, calculated as $C_{12}H_{22}O_{11},SrO$, and the solution showed $[\alpha]_D^{16°} = +42{\cdot}09°$. Scheibler (*N.Z. Rübenzuckerind.*, **10**, 229) gives for the solubility the interpolated figure 43·9 (Found: H_2O, 17·8; SrO, 18·7; C, 32·3; H, 4·9. Calc. for $C_{12}H_{22}O_{11},SrO,6H_2O$: H_2O, 19·5; SrO, 18·7%. Calc. for $C_{12}H_{22}O_{11},SrO$: C, 32·3; H, 4·9%). In a diffusion experiment (compare p. 958) 20 c.c. of solution were placed in a collodion membrane suspended in 50 c.c. of conductivity water. The initial concentration per 100 c.c. was sucrose 3·28, strontia 0·993 (ratio, 3·3) and the concentration after 24 hours was sucrose 1·50, strontia 0·163 (ratio, 9·21).

Distrontia-monosucrose.—To a boiling, 15% sucrose solution, strontia (slightly more than 3 mols.) was added and ebullition continued for 2 minutes. (With prolonged boiling, the precipitate becomes more difficult to filter.) The clear solution was decanted from the precipitate, which was washed with hot 10% strontia solution until colourless and then with boiling water, and dried between filter-papers or in a vacuum desiccator (Found: SrO, 37·6; C, 26·75; H, 3·4. Calc. for $C_{12}H_{22}O_{11},2SrO$: SrO, 37·7; C, 26·2; H, 4·0%). The solubility was found to be 11·89 g. per litre at 100° (Sidersky, *Bull. Asoc.*, **3**, 240, gives 1 in 84 at the boiling point). $[\alpha]_D^{15°} = +37{\cdot}79°$ for this solution cooled to 15°. The dry preparation remains unchanged for a long period, but in presence of cold water the white sandy crystals break up, monostrontia-monosucrose and strontium hydroxide being produced.

In experiments designed to obtain higher strontia-sucroses, mixtures of either or both of the above compounds with strontium hydroxide were obtained.

Monobaryta-monosucrose.—This compound appears to be the only combination of baryta with sucrose and was obtained in the anhydrous state by several methods. (*a*) To a 5% sucrose solution saturated at room temperature with baryta, an equal volume of

60% alcohol was added. The white granular precipitate which separated was filtered off, washed with 60% alcohol, and dried between filter-papers. (*b*) On boiling the 5% sucrose–baryta solution (*a*), the same precipitate was formed. (*c*) By shaking a saturated solution of sucrose with excess of powdered baryta for 10 minutes and seeding the filtered liquid with a crystal from a previous preparation, a copious crop of monobaryta-monosucrose crystals was produced (Found : BaO, 31·1; C, 29·05; H, 4·4. Calc. for $C_{12}H_{22}O_{11}$,BaO : BaO, 30·95; C, 29·1; H, 4·4%). Solubility, 22·10 g. per litre of solution at 20° (Peligot, *Ann. Chim.*, 1858, **54**, 379, gave 21·0 at 15°). $[\alpha]_D^{20°} = +43·89°$ for this solution. Dr. R. Campbell kindly examined the small crystals and reported them to be prismatic in habit, showing straight extinction and very weak double refraction.

In a diffusion experiment (compare p. 958) in which 20 c.c. of solution were placed in a collodion membrane suspended in 50 c.c. of water, the initial concentration per 100 c.c. was sucrose 1·38, baryta 0·62 (ratio, 2·22) and the concentration after 24 hours was sucrose 0·67, baryta 0·325 (ratio, 2·08).

Monolime-monoglucose.—The rapid decomposition of glucose in presence of alkali and water renders the preparation of this compound difficult. Within 1 hour lime (1 mol.) was added to 500 c.c. of 5% glucose solution at 0°, the solution filtered, and the filtrate mixed with an equal volume of 60% alcohol. The white precipitate formed was repeatedly triturated with small volumes of 60% alcohol, dried between filter-papers, and ground with absolute alcohol several times and finally with ether. It is essential to carry out these processes rapidly. Even after drying over phosphoric oxide the compound appears to be the monohydrate (Found : CaO, 21·6. Calc. for $C_6H_{12}O_6$,CaO,H_2O : CaO, 22·05%). This white amorphous powder remains unchanged for months; but if wetted, it decomposes over-night.

Attempts to isolate other hydrates gave inconclusive results. For instance, after the precipitate first produced when the lime–glucose solution and 60% alcohol were mixed had been dried between filter-papers, the lime content was 12·0% (Calc. for $C_6H_{12}O_6$,CaO,$13H_2O$: CaO, 11·9%). As mentioned above, by treatment with alcohol and ether, this precipitate eventually gives a monohydrate when dried over phosphoric oxide. If instead of phosphoric oxide, calcium chloride is used, the dihydrate appears to be the product (Found : CaO, 20·6. Calc. for $C_6H_{12}O_6$,CaO,$2H_2O$: CaO, 20·6%). A 5% glucose solution was shaken with excess of lime for 15 minutes and rapidly filtered and its rotation and lime content were measured. $[\alpha]_D^{15°} = +40·5°$ and CaO, 0·435 g. per

100 c.c. of solution. After removal of the lime by precipitation as oxalate the solution showed $[\alpha]_D^{15^\circ} = 52{\cdot}3^\circ$, whereas the value for the original 5% glucose solution was $[\alpha]_D^{15^\circ} = 52{\cdot}5^\circ$. Owing to the rapid decomposition of the solution, no consistent results were obtained in solubility measurements.

Attempts to prepare Compounds of Lime, Strontia, and Baryta with α- and β-Methylglucosides.—α-Methylglucoside, m. p. 165°, $[\alpha]_D^{15^\circ} + 157^\circ$, prepared by Fischer's method as modified by Bourquelot (*Ann. Chim.*, 1915, **3**, 298), and β-methylglucoside, m. p. 108°, $[\alpha]_D^{15^\circ} - 33^\circ$, obtained by Maquenne's method (*Bull. Soc. chim.*, 1905, **33**, 469), were used in these experiments.

A mixture of 1·94 g. of α-methylglucoside in 100 c.c. of aqueous solution and 0·56 g. of lime was shaken vigorously for 6 hours. Alcohol (4 c.c.) was added to 5 c.c. of the filtered liquid and the gelatinous precipitate was rapidly collected and dried over calcium chloride in a vacuum desiccator. A small quantity of lime was the ultimate product. From the alcoholic filtrate, α-methylglucoside was recovered unchanged.

The experiment was repeated at 0° and the period of shaking extended over a month. It was also performed with a ten times more concentrated solution. Acetone was also used in place of alcohol. In each case, the lime and the glucoside were recovered unchanged.

Solutions of the glucoside, saturated at room temperature with lime, strontia, and baryta, respectively, were heated to boiling point. No visible change was apparent except in the lime solution, which became turbid owing to the decreased solubility of lime in hot water.

Measurements of the rotations of the solutions before and after the addition of the alkaline earths showed no change.

Similar experiments with β-methylglucoside produced negative results.

Monolime-monofructose.—The hexahydrate was prepared according to Winter's method (*loc. cit.*) (Found: CaO, 16·2. Calc. for $C_6H_{12}O_6,CaO,6H_2O$: CaO, 16·3%). The colourless needle-shaped crystals were examined by Dr. R. Campbell and found to show oblique extinction and feeble double refraction and to be either mono- or tri-clinic. In a vacuum desiccator at 9° over concentrated sulphuric acid, the hexahydrate loses four molecules of water (Found: H_2O, 20·9; CaO, 20·6. $C_6H_{12}O_6,CaO,6H_2O - 4H_2O$ requires H_2O, 20·9. $C_6H_{12}O_6,CaO,2H_2O$ requires CaO, 20·6%). This hydrate is fairly stable and it was not found possible to remove all the water. Solubility at 15°, 0·847 g. (calculated as $C_6H_{12}O_6,CaO,H_2O$) per 100 c.c. $[\alpha]_D^{15^\circ} = - 39{\cdot}05^\circ$.

Efforts to prepare higher lime-fructoses showed the formation of precipitates of mixtures of lime and monolime-monofructose.

β-Methylfructoside and the Hydroxides of the Alkaline Earths.—β-Methylfructoside was prepared according to the method of Hudson and Brauns (*J. Amer. Chem. Soc.*, 1916, **38**, 1216). The first intermediate product—tetra-acetyl fructose—showed m. p. 130° and $[\alpha]_D^{15^\circ}$ $-$ 92·5°, whereas Hudson and Brauns's data are m. p. 120—130° and $[\alpha]_D^{15^\circ}$ $-$ 92·30°. The next product—tetra-acetyl methylfructoside—gave m. p. 75° and $[\alpha]_D^{15^\circ}$ $-$ 124°, the corresponding figures of Hudson and Brauns being 75—76° and $-$124·6°. The β-methylfructoside was obtained in faintly yellow crystals, readily soluble in water and in alcohol, and with difficulty in benzene; m. p. 119°, $[\alpha]_D^{15^\circ}$ $-$ 171°. Hudson and Brauns found m. p. 119—120° and $[\alpha]_D^{15^\circ}$ $-$ 172·1°.

Similar experiments to those done with α- and β-methylglucosides were performed (compare p. 961), but no evidence of the formation of compounds with the alkaline earths was forthcoming. The rotation of solutions of the fructoside was unaffected by the addition of the alkaline earths.

Monolime-monomaltose.—The preparation of this substance was carried out in the same manner as that of lime-glucose. The amorphous, white powder obtained probably is hydrated and even after drying over phosphoric oxide in a vacuum at 0°, still shows the presence of water (Found : CaO, 13·8. Calc. for $C_{12}H_{22}O_{11},CaO$: CaO, 14·1%. Calc. for $C_{12}H_{22}O_{11},CaO,H_2O$: CaO, 13·5%). The solubility of the monohydrate is 18·9 g. per litre, and the rotation of the saturated solution $[\alpha]_D^{15^\circ}$ + 120·4°. The rotation calculated for the maltose in the solution is $[\alpha]_D^{15^\circ}$ + 146·4°, whereas a pure maltose solution shows $[\alpha]_D^{15^\circ}$ + 137·9°.

β-Methylmaltoside and the Alkaline Earths.—β-Methylmaltoside was prepared according to the method of Koenigs and Knorr (*Ber.*, 1901, **34**, 4343), ten times the quantities employed by these investigators being used. A mixture of 500 c.c. of red fuming nitric acid and 750 c.c. of chloroform was added to a solution of 50 g. of maltose octa-acetate (m. p. 157°), and the whole gently stirred for 2½ hours, the temperature throughout being kept below $-$5°. The product was then poured on ice, and the chloroform solution separated from the water solution and washed successively with water, sodium bicarbonate solution and water—all at 0°. After the solution had been dried by sodium sulphate, the chloroform was distilled off and the residue dissolved in ether. From the ethereal solution there separated 27 g. of colourless crystals of acetonitromaltose, m. p. 94° (Koenigs and Knorr, 93—94°).

On further concentration of the mother-liquor, a yellow oil, which became crystalline on standing for two days at 0°, was obtained. This product, after recrystallisation from chloroform–ether, showed m. p. 178° and $[\alpha]_D^{15°}$ initially + 79·3° in chloroform and, after addition of a trace of ammonia, finally + 110·4°. The crystals were free from nitrogen [Found: $CH_3{\cdot}CO$, 47·15. Calc. for $C_{12}H_{15}O_{11}(CO{\cdot}CH_3)_7$: $CH_3{\cdot}CO$, 47·3%]. Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1871) gives the melting point of maltose hepta-acetate as 181° and $[\alpha]_D^{20°}$ initial + 67·8°, final + 111°. The hepta-acetate appears to have been produced by the hydrolysis of some of the acetonitromaltose.

From 26 g. of acetonitromaltose, 15 g. of hepta-acetylmethylmaltoside were obtained in colourless crystals, m. p. 128°, $[\alpha]_D^{15°}$ + 53·6° in 2·5% chloroform solution (Koenigs and Knorr, m. p. 129°; Hudson, $[\alpha]_D$ + 53·8°).

The deacetylation of 15 g. of hepta-acetylmethylmaltoside by Helferich and Becher's method (*Annalen*, 1924, **440**, 17) gave 3·8 g. of crystals, m. p. 105°, $[\alpha]_D^{20°}$ + 75·7° in 1·355% aqueous solution (Helferich and Becher give m. p. 105° and $[\alpha]_D^{19°}$ + 76°).

On saturating the methylmaltoside solution with baryta, strontia, and lime respectively, a very slight fall in the rotation (0·02°) was observed in the first two cases and no change in the last. The recovered methylmaltoside was recrystallised from alcohol–ethyl acetate: the rotation rose to $[\alpha]_D^{15°}$ + 82·5°, the calculated value being + 85°.

Monolime-monolactose.—The preparation was carried out in the same manner as that of the maltose compound. No definite hydrate was obtained, and decomposition took place when moisture was present. The dry substance may, however, be kept for weeks without appreciable change (Found: CaO, 13·9. Calc. for $C_{12}H_{22}O_{11},CaO$: CaO, 14·1%). The solubility of the white amorphous powder was 18·6 g. per litre of solution, and this solution gave $[\alpha]_D^{15°}$ + 46·06°. These numbers are, however, only approximately correct, decomposition setting in immediately the substance has dissolved.

Efforts to obtain higher lime-lactoses were fruitless.

β-Methyl-lactoside and the Hydroxides of the Alkaline Earths.—Anhydrous lactose was converted into acetobromolactose by Dale's method (*J. Amer. Chem. Soc.*, 1916, **38**, 2187). Yield, 60% of the theoretical. M. p. 140°. $[\alpha]_D^{20°}$ in chloroform = + 106·5°. E. and H. Fischer (*Ber.*, 1910, **43**, 2521) give m. p. 143—144° and $[\alpha]_D^{20°}$ + 104·9°.

From the acetobromolactose, hepta-acetylmethyl-lactoside was obtained by the action of methyl alcohol and silver carbonate (Ditmar, *Monatsh.*, 1902, **23**, 865). The product was without action upon Fehling's solution, and had m. p. 79—80°, $[\alpha]_D^{15°}$ in chloroform $= -8°$. Ditmar found m. p. 76—77° and $[\alpha]_D^{15°} - 6°$. Ditmar obtained crystals, but our product was not distinctly crystalline.

The deacetylation was carried out as in the methylmaltoside preparation (p. 963). The methyl-lactoside was obtained as a brittle glass, m. p. 173°, $[\alpha]_D^{15°} + 12°$ (Found: C, 41·3; H, 6·9; OMe, 7·8. Calc. for $C_{12}H_{21}O_{11}Me,H_2O$: C, 41·7; H, 7·0; OMe, 8·3%). Fehling's solution was unaffected by the product. Ditmar found m. p. 171° and Hudson calculated $[\alpha]_D = +6°$. The rotation of the aqueous solution was unaffected by the addition of lime, strontia, or baryta, and no alkaline-earth methyl-lactoside was isolated.

Our thanks are due to the Moray Bequest for a grant in aid of the above research.

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