A STUDY OF THE COMPOUNDS FORMED BY THE INTERACTION OF SUGARS WITH THE HYDROXIDES OF THE ALKALINE EARTH METALS.

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Thesis for the Degree of Ph.D.

CONTENTS.

A STUDY OF THE COMPOUNDS FORMED BY THE INTERACTION OF SUGARS WITH THE HYDROXIDES OF THE ALKALINE EARTH METALS.

The use of lime in the manufacture of sugar dates back at least to the 17th Century, and probably to a much earlier period. When the juice is heated with lime the albuminoid substances present as impurities are coagulated, and, together with the lime salts of any accompanying acids, form a scum on the surface which can be removed. On completion of the purification the excess of lime is precipitated by carbon dioxide, and the juice concentrated till crystallisation of cane sugar occurs. Notwithstanding this practical application, little was known of the chemical nature of the compounds formed by sugar with the alkaline earths until less than a hundred years ago, when, in 1838, Péligot published a paper "Recherches sur la nature et les propriétés chimiques des sucres"[1] in which he gave an account of his investigations on the compounds obtained by the union of various sugars with metallic oxides.

By the addition of alcohol to a solution of baryta in sugar solution a compound of Composition

C_{24} /

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[1] Compt. rend., 1838, 6, 232-236.

$C_{24}H_{22}O_{11}BaO$ was precipitated, and by the same treatment of a solution of lime in syrup of sugar the corresponding calcium oxide derivative $C_{24}H_{22}O_{11}Ca\,O$ $2\,H_2O$ was isolated.

Lead oxide compounds such as $C_{24}H_{22}O_{11}2\,Pb\,O$ and $C_{24}H_{18}O_9\ 2\,Pb\,O$ were also obtained.

At this period the atomic weight of carbon was assumed to be one half of that now adopted, so that C_{24} then becomes C_{12} now.

Reducing sugars such as glucose and fructose yielded acidic products following on the loss of water when acted on by alkalis.

The chemical literature of the subject may be summarised under the headings of the compounds as described, though in some cases the present author has been unable to confirm the existence of these compounds.

(1) SUCROSE.

(a) Lime-Sucrose Compounds.

(1) Monolime-monosucrose	$C_{12}\overset{H}{C}_{22}O_{11}\ CaO$
(2) Trilime-disucrose	$(C_{12}H_{22}O_{11})_2\ 3\ CaO$
(3) Dilime-monosucrose	$C_{12}H_{22}O_{11}\ 2\ CaO$
(4) Trilime-monosucrose	$C_{12}H_{22}O11\ 3\ CaO$
(5) Tetralime-monosucrose	$C_{12}H_{22}O_{11}\ 4\ CaO$
(6) Hexalime-monosucrose	$C_{12}H_{22}O_{11}\ 6\ CaO$
(7) Octalime-monosucrose	$C_{12}H_{22}O_{11}\ 8\ CaO$.

(b) Strontia-Sucrose Compounds.

(1) Monostrontia-monosucrose	$C_{12}H_{22}O_{11}\ SrO$
(2) Distrontia-trisucrose	$(C_{12}H_{22}O_{11})_3\ 2\ SrO$
(3) Distrontia-monosucrose	$C_{12}H_{22}O_{11}\ 2\ SrO$
(4) Tristrontia-monosucrose	$C_{12}H_{22}O_{11}\ 3\ SrO$

(c) Baryta-Sucrose Compounds.

(1) Monobaryta-monosucrose	$C_{12}H_{22}O_{11}\ BaO$
(2) Monobaryta-disucrose	$(C_{12}H_{22}O_{11})_2\ BaO$
(3) Dibaryta-monosucrose	$C_{12}H_{22}O_{11}\ 2\ BaO$

(2) GLUCOSE.

Lime-Glucose Compounds.

(1) Monolime-monoglucose	$C_6H_{12}O_6\ CaO$
(2) Trilime-diglucose	$(C_6H_{12}O_6)_2 3CaO$
(3) Trilime-tetraglucose	$(C_6H_{12}O_6)_4\ 3\ CaO$

(3) FRUCTOSE.

Lime-fructose compounds.

(1) Monolime-monofructose	$C_6H_{12}O_6\ CaO$
(2) Dilime-monofructose	$C_6H_{12}O_6\ 2\ CaO$
(3) Trilime-monofructose	$C_6H_{12}O_6\ 3\ CaO$

(4) MALTOSE.

Lime-Maltose Compounds.

(1) Monolime-monomaltose	$C_{12}H_{22}O_{11}\ CaO.$

(5) LACTOSE.

Lime-lactose Compound.

(1) Monolime-monolactose $C_{12}H_{20}O_{11}Ca$.

The state of hydration is not indicated in the above summary.

MONOLIME-MONOSUCROSE.

By precipitating with alcohol a solution containing for every molecular proportion of sucrose not quite one molecular proportion of lime, Peligot[1] isolated monolime-monosucrose $C_{12}H_{22}O_{11}.\ CaO\ 2H_2O$, which became on drying $C_{12}H_{22}O_{11}\ CaO$.

Benedikt[2] found that, when the lime in a sucrose solution containing excess of lime was precipitated with magnesium chloride so as to leave one molecular proportion of lime to one of sucrose, and the insoluble magnesium hydroxide filtered off, a compound of composition $C_{12}H_{20}O_{11}\ Ca\ H_2O$ was obtained when the solution was precipitated with alcohol. On drying at 100°C the compound lost one molecule of water and became $C_{12}H_{20}O_{11}\ Ca$.

Stromeyer[3], however, showed these formulae to be inaccurate, the correct form being $C_{12}H_{22}O_{11}\ CaO$.

[1] Compt. rend., 1864, 59, 980.
[2] Ber., 1873, 6, 413.
[3] Arch. Pharm., 1887, III, 25, 229.

TRILIME-DISUCROSE.

Trilime-monosucrose was prepared by Brendeke[1], who obtained it by precipitating with alcohol a lime sugar solution containing one part of sugar and one part of lime in water; by Soubeyran[2], who isolated it by evaporating a water solution containing thirteen parts sucrose and two parts lime; and by Peligot[3], who found that on precipating a concentrated sucrose solution saturated with lime with alcohol a compound of this composition was formed.

Stromeyer[4] and also Dubrunfaut[5] likewise claimed to have prepared it.

DILIME-MONOSUCROSE.

In 1864 Pelouze[6] in a report on a memoir by Boivin and Loiseau drew attention to the existence of yet another lime sucrose compound. When aqueous solutions of lime in sucrose solution were incompletely precipitated with alcohol, and the precipitate washed well with 60% alcohol and dried at 115°C., the percentage of lime present was more than was necessary for monolime-monosucrose, and further washings with aqueous alcohol soon raised the lime content to two for/

[1] Arch. Pharm., 1842, II, 29, 73.
[2] Annalen., 1842, 43, 229.
[3] Ann. Chim., 1858, III, 54, 384.
[4] Arch. Pharm., 1887, III, 25, 229.
[5] Jahresb. Fort. Chem., 1851, 550.
[6] Compt. rend., 1864, 59, 1073.

for one of sugar. Lime sugar solutions mixed with 60% alcohol at 50°-60°C. gave dilime-monosucrose very quickly.

Peligot[1], however, pointed out that in solution the proportions two of lime to one of sugar were never reached, and that though the quantity of lime dissolved was proportional to the density of the sugar solution, it did not attain to that required for dilime-monosucrose.

TRILIME-MONOSUCROSE.

By the action of three molecular proportions of lime on an alcoholic solution containing one molecular proportion of sucrose, Seyffart[2] prepared trilime-monosucrose, of formula $C_{12}H_{22}O_{11}3CaO.\ 4\ H_2O$.

It was more easily obtained by heating a lime sugar solution when Ramsay[3], Soubeyran[4], Wachtel[5] and Lippmann[6] all obtained $C_{12}H_{22}O_{11}3\ CaO\ 3\ H_2O$

Trilime-monosucrose was obtained only from solutions of sugar saturated with lime; from unsaturated solutions so-called compounds rising from $C_{12}H_{22}O_{11}\ 3\ CaO$ to $C_{12}H_{22}O_{11}\ 9\ CaO$ were precipitated, and finally, from very slightly alkaline solutions, almost pure lime.

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1. Compt. rend., 1864, 59, 930.
2. N.Z. Rubenzuckerind., 3, 178.
3. Bull. Pharm., 1, 510.
4. J. Pharm., 1842, 1, 469.
5. O.Z. Zuckerind., 7, 704; 8, 860.
6. O.Z. Zuckerind., 9, 95.

Lippmann[1] suggested that the reaction took place as follows:-

$$3\ C_{12}H_{22}O_{11}CaO = C_{12}H_{22}O_{11}3CaO + 2\ C_{12}H_{22}O_{11}$$

the trilime monosucrose being insoluble in hot sucrose solution. On cooling recombination was assumed to occur.

A brief description of the conditions under which the trilime-monosucrose can be precipitated on heating was given by Horsin Déon[2], who found that very concentrated and very dilute solutions act abnormally, little precipitation occurring.

TETRALIME-MONOSUCROSE.

This compound was prepared by Stulzer and Sostmann[3], and by Wolters[4], who gave some of its properties. Degener[5] was unable to isolate it, and its existence is improbable.

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1. Jahresb. Fort. Chem., 1883, 736.
2. J.C.S., 1872, 25, 810.
3. Z. Ver. deut. Zuckerind., 34, 85.
4. N.Z. Rubenzuckerind., 10, 287-298.
5. Z. Ver. deut. Zuckerind., 34, 283.

HEXALIME-MONOSUCROSE.

Hexalime-monosucrose was prepared by Soubeyran[1], but Peligot[2] was unable to confirm his work, though later Horsin Déon[3] claimed to have isolated it.

OCTALIME-MONOSUCROSE.

Wolters[4] claimed to have prepared this compound, but gave only a brief description of his method. Its existence is improbable.

There are few physical data to support the existence of most of these Compounds.

Petit[5] investigated the heats of formation of the lime sugar compounds by the action of sodium hydroxide on a mixed solution of sucrose and calcium chloride, and obtained:-

$$C_{12}H_{22}O_{11}\ (\text{diss.}) + Ca(OH)_2(\text{Sol}) = C_{12}H_{22}O_{11}CaO\ (\text{diss.}) + 7.2\ \text{Cal.}$$

$$C_{12}H_{22}O_{11}\ (\text{diss.}) + 2Ca(OH)_2(\text{Sol}) = C_{12}H_{22}O_{11}2CaO(\text{diss.}) + 11.7\ \text{Cal.}$$

The formation of more calcium hydroxide was unaccompanied/

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1. J. Pharm., 1842, III, 1, 469.
2. Compt. rend., 1851, 32, 333.
3. Bull. Soc. Chim., 1872, 17, 155.
4. N.Z. Rubenzuckerind., 10, 287-298.
5. Compt. rend., 1893, 116, 823.

unaccompanied by further heat production, and no trilime compound was formed.

The action of monolime-monosucrose on freshly precipitated calcium hydroxide led to the same value + 4.5 cal. for the formation of dilime-monosucrose.

A study of the solubility of lime in sucrose solution revealed that at infinite concentration two molecular proportions of calcium oxide to one of sugar would dissolve.

Claassen[1] pointed out that the solubility of lime in sucrose solutions, although independent of the kind of lime used, depended on its state of division, rate of addition, and many other factors.

Aten, Van Ginneken and Engelhard[2] determined the activities of hydroxyl ions in solutions containing sucrose and the hydroxides of potassium, lithium, barium or calcium respectively by means of the hydrogen electrode.

In dilute alkaline solution (up to .1 N) sucrose behaved as a monobasic acid with dissociation constant 14.6×10^{-14} at 18°C. In solutions of higher concentration the constant could not be calculated. The activity of the metal ions in solutions of potassium,/

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[1] Z. Ver. deut. Zuckerind., 1911, 489-509.
[2] Rec. trav. Chim., 1926, 45, 753-771.

potassium, lithium, or barium hydroxides of concentrations up to normal was but slightly altered by the addition of sucrose; so that the alkali sucrose compounds are largely ionised in solution.

Conductivity measurements made on solutions containing sucrose and any one of the four given hydroxides were consistent with complete ionisation of the alkali sucrose compounds in dilute solution. In more concentrated solutions, especially with calcium hydroxide, low values of conductivity were obtained, which may be due to the presence of undissociated molecules of mono- di, or tri lime sucrose.

Waterman and Van Aken[1] from a consideration of the phenomena which appeared on treating lime with sucrose solution, suggested that trilime-monosucrose was an adsorption compound, and existed as a colloid. Their results were in agreement with those of Dedek[2], who made potentiometrical measurements of the hydroxyl ion concentration in aqueous solutions of calcium and sodium hydroxides with and without sucrose, and came to the conclusion that his tests gave no indication of the formation of a trilime compound. He suggested that a colloidal adsorptive compound was obtained by adding pulverised and solid calcium oxide/

[1] J.C.S.I., 1927, 46, 411T.
[2] Z. Zuckerind. Czechoslov., 1925, 26, 349.

oxide to the sucrose solution, or at the precipitation which occurred by heating a lime sugar solution saturated in the cold.

That the preparation of the lime sugar solution itself may give varying results is seen from the work of Cameron and Patten[1] who found that when excess of lime was added to a sucrose solution not only was a soluble compound of lime and sucrose formed, but also some of the sucrose was removed from solution by the undissolved lime, and passed into the solid phase.

The barium and strontium compounds described are not so numerous as those of calcium, but appear to be better defined.

MONOSTRONTIA-MONOSUCROSE.

By dissolving in a sucrose solution of about 20-25% concentration at about 70°C one molecular proportion of strontia and cooling with shaking, Scheibler[2] prepared crystals of monostrontia-monosucrose $C_{12}H_{22}O_{11}$ SrO $5H_2O$.

DISTRONTIA-TRISUCROSE.

Distrontia-trisucrose was prepared by Scheibler[3] by slowly cooling moist distrontia-monosucrose.

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[1] Cameron and Patten: J. Physical Chem., 1911, 15, 67-68.

[2] N.Z. Rubenzuckerind., 9, 83; 10, 143.

[3] N.Z. Rubenzuckerind., 9, 83.

DISTRONTIA-MONOSUCROSE.

Scheibler[1] obtained distrontia-monosucrose by dissolving in a boiling 15% sucrose solution three molecular proportions of strontia and continuing to boil for ten minutes, when crystals of the compound were precipitated in an anhydrous state as a sandy mass.

TRISTRONTIA-MONOSUCROSE.

Scheibler[2] claimed to have isolated this compound, but Wolfmann[3] showed that it was a mixture of strontium hydroxide and distrontia-monosucrose.

MONOBARYTA-MONOSUCROSE.

When a solution of one part sucrose in two parts of water was boiled with an equal volume of a barium hydroxide solution containing one part baryta in three of water, both Soubeyran[4] and Peligot[5] obtained a white precipitate of monobaryta-monosucrose of formula $C_{12}H_{22}O_{11}$ BaO.

Stein[6] rejected this formula for $C_{12}H_{20}O_{11}Ba$, but/

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1. N.Z. Rubenzuckerind., 6, 49.
2. N.Z. Rubenzuckerind., 6, 49.
3. Z. Ver. deut. Zuckerind., 52, 587.
4. J. Pharm; 1842, III, 1, 469.
5. Ann. Chim., II, 67, 125.
6. Annalen., 30, 82.

but Soubeyran[1], Dubrunfaut and Leplay[2], and Stromeyer[3] all supported it as correct.

The compound may also be prepared by the action of barium sulphide on sucrose, as Dubrunfaut and Leplay[4] showed. The action took place as follows:-

$$C_{12}H_{22}O_{11} - 2\ BaS - H_2O = C_{12}H_{22}O_{11}BaO - Ba(SH)_2$$

MONOBARYTA-DISUCROSE.

Brendeke[5] has described a compound which he claimed to be Monobaryta-disucrose.

DIBARYTA-MONOSUCROSE.

Soubeyran[6] claimed to have isolated this compound.

GLUCOSE.

Owing to their lack of industrial importance the compounds of the alkaline earths with other sugars have not been studied so fully as those of sucrose. Only the lime compounds are considered in this research.

1. J. pr. Chem., 1842, I, 26, 498.
2. Compt. rend., 1851, 32, 498.
3. Arch. Pharm., 1887, III, 25, 229.
4. Bull. Ass., 2, 243.
5. Arch. Pharm., 1842, II, 29, 73.
6. Compt. rend., 1843, 14, 648.

MONOLIME-MONOGLUCOSE.

Soubeyran[1] prepared a monolime-monoglucose of formula $C_6H_{12}O_6CaO$ by precipitating an aqueous solution of lime in glucose solution with alcohol.

In the same way Peligot[2] obtained from invert sugar a compound $C_6H_{12}O_6CaO\ 2H_2O$, as did Maumené[3] by the same process as Soubeyran.

TRILIME-DIGLUCOSE.

Maumené [4] also claimed to have isolated trilime-diglucose $(C_6H_{12}O_6)_2\ 3CaO.\ H_2O$, while Peligot[5] and Dubrunfaut[6] obtained $(C_6H_{12}O_6)_2\ \ 3CaO.\ 2H_2O$.

TRILIME-TETRAGLUCOSE.

Brendecke[7] described a compound which he termed trilime-tetraglucose.

FRUCTOSE.

MONOLIME-MONOFRUCTOSE.

By shaking 12-15 gms. of lime with 500 c.c. invert sugar solution at 25°C. for two minutes, and filtering into a cold flask surrounded by ice, Peligot/

[1] J. Pharm., 1842, III, 1, 649.
[2] Jahresb. Fort. Chem., 1880, 1018.
[3] Lippmann. Chem. der Zuckerarten, 1904, 1, 551.
[4] Annalen, 30, 73.
[5] Annalen, 30, 73.
[6] Ann. Chim., 1847, III, 21, 169.
[7] Arch. Pharm., 1842, II, 29, 84.

Peligot[1] obtained crystals of monolime-monofructose of formula $C_6H_{12}O_6CaO\ 2H_2O$.

By a similar process Winter[2] obtained the hexahydrate $C_6H_{12}O_6\ CaO\ 6H_2O$, which when dried gave $C_6H_{12}O_6\ CaO\ 1\frac{1}{2}\ H_2O$. Winter found no trace of any other lime fructose compounds.

DILIME-MONOFRUCTOSE.

Peligot[3] claimed to have prepared this compound. Its existence is very improbable.

TRILIME-MONOFRUCTOSE.

Dubrunfaut[4] obtained from invert sugar crystals of a compound of formula $C_6H_{12}O_6\ 3CaO$, soluble in about 300 parts water.

Subsequent workers have been unable to repeat this preparation, and have always obtained monolime-monofructose.

MALTOSE.

MONOLIME-MONOMALTOSE.

Herzfeld[5] obtained this compound by precipitating a lime maltose solution with 60% alcohol.

[1] Bull. Soc. Chim., 1881, 36, 224.
[2] Annalen, 1888, 244, 317.
[3] Jour. Fahr. d. Sucre., 21. 6.
[4] Ann. Chim., 1847, 21, 169.
[5] Annalen, 1883, 220, 214.

LACTOSE.

MONOLIME-MONOLACTOSE.

According to Lippmann[1] Dubrunfaut obtained monolime-monolactose by precipitating a lime lactose solution with alcohol.

It must be noted that the evidence adduced for the existence of many of the preceeding compounds is vague, and seems without sufficient foundation. The precipitates formed when alcohol is added to aqueous solutions of sugar and alkaline earths vary in composition with the concentrations of the components in solution, as does the composition of the precipitates obtained by heating such solutions, and no difficulty was experienced in the present investigation in producing white amorphous earths of vastly different composition even from the same solution.

The present investigation was designed to distinguish between true compounds formed by the union of various sugars with alkaline earth oxides, and intimate mechanical mixtures of such compounds with either sugar or oxide on proportions which simulate the composition of another compound; and to give exact data regarding the definite compounds. Before going further, it is necessary to say a word on/

[1] Chem. der Zuckerarten, (1904), 2, 1574.

on the nomenclature of these compounds. The matter appears to offer some difficulty, and various names are used indiscriminately. The terms are now considered in turn.

(1) **Saccharate.** This, of course, rightly applies to salts of saccharic acid, and not to combinations of alkali and sugar, such as are considered here.

(2) **Saccharose.** If saccharose be adopted, then the generic name must be saccharoses, which is the name of the sugars themselves.

This confusion may be avoided by the use of the somewhat similar term "saccharosate"; thus the compound formed by the union of lime and gluocse would be lime glucosate. As an attempt will be made later to name the lime hexoses from considerations of structure, the latter term is unsuitable.

(3) **Sucrate.** Sucrate would be excellent if only sucrose was considered, but a lactate is a salt of lactic acid.

The/

The nomenclature finally adopted was a simple combination of the name of the sugar and the alkaline earth, viz., lime glucose; and the composition was indicated as follows: trilime-monosucrose, monobaryta-monoglucose.

* * *

EXPERIMENTAL.

In the following experiments the work was carried out in glass vessels which had been used to contain both sugar and lime sugar solutions, and which were thoroughly washed with successive portions of alkali, acid, and finally with conductivity water.

Owing to the rapid decomposition of the compounds by carbon dioxide, great difficulty was experienced in obtaining them free from carbonate, but by ensuring that all solutions used in the work were prepared from conductivity water, and handling any precipitates in an atmosphere of purified air, the effects of this gas were largely avoided.

Rapidity of work, however, proved essential at the critical stages, and later precautions were little compensation for undue exposure during filtration.

The dried compounds were found to resist the action of carbon dioxide much more strongly than when wet, and crystals were comparatively stable.

The lime used during the work was prepared by heating either Buxton limestone or precipitated Calcium Carbonate (Kahlbaum) for six hours in a muffle furnace, powdering and grinding the resulting quicklime as finely as possible, and then reigniting for four hours. The calcium oxide, which must not give any/

any effervescence with acid, was preserved in the absence of carbon dioxide.

PREPARATION OF A SATURATED SOLUTION OF LIME IN SUCROSE SOLUTION.

A five per cent sucrose solution was prepared by making up 100 grm. pure sucrose (Austrian crystals) to 2000 c.c. with conductivity water. Powdered lime was added in small quantities to the sucrose solution, which was vigorously stirred, each portion being allowed to dissolve completely before any further addition was made. The amount of lime dissolved is irregular, and depends on many factors, such as (1) Concentration of sugar solution, (2) State of division of the calcium oxide, (3) Temperature of solution, more being dissolved in the cold, (4) Rate of addition of lime, more lime being dissolved when the addition is slow.

The rate at which the lime dissolved was observed to fluctuate considerably. After four days it was found that no more lime would dissolve.
A very slight excess was then added, making in all 26 grm., and after stirring six hours more, the solution allowed to stand overnight. In the morning the solution was syphoned off through cotton wool which had been well washed with distilled water, and the/

the clear product bottled and set aside. It is quite stable in the absence of carbon dioxide. Unless it is stated to the contrary, this solution was used in the following experiments.

The % lime dissolved appeared to vary. Thus Sample I contained 11.7 grm. calcium oxide per litre, and its rotation in a 2 dcm. tube using sodium light at 18.5°C. was + 5.33°.

$$[\alpha]_D^{18.5} = +53.3^\circ$$

Sample II contained 12.3 grm. calcium oxide per litre, and its rotation in a 2 dcm. tube using sodium light at 15°C. was + 5.30°

$$[\alpha]_D^{15} = +53.0^\circ$$

According to Muntz[1] in a 10% sucrose solution one molecular proportion of lime gave

$$[\alpha]_D = +56.9^\circ$$

While 2 molecular proportions gave.

$$[\alpha]_D = +51.8^\circ$$

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[1] Z. Ver. deut. Zuckerind., 26, 737.

MONOLIME-MONOSUCROSE.

Peligot[1] claimed to have isolated this compound by precipitating a solution containing nearly equimolecular quantities of sucrose and lime with alcohol.

A 5% sucrose solution was therefore prepared, and sufficient lime added to give .9 of a molecular proportion of lime. On precipitation with 60% alcohol by adding about 500 c.c. to 200 c.c. of the solution a white amorphous earth was obtained which corresponded closely in composition to $C_{12}H_{22}O_{11}CaO\ 2H_2O$. Yield 60% theory.

Wt. of Crucible	=	15.1382 grm.
Wt. of Crucible + substance	=	15.5892 "
Wt. of Crucible + lime	=	15.1962 "

% lime = 12.86

On drying at 100°C. for three days, .2139 grm. of the compound lost .0169 grm. water.

% water = 7.90

$C_{12}H_{22}O_{11}CaO\ 2H_2O$ requires $CaO = 12.84\%$

$H_2O = 8.293\%$

There is reason to suppose these figures are entirely fallacious. Thus a small change in the proportions of lime and sucrose in the original solution was accompanied by a change in the composition of the precipitate. Again the compound obtained above showed the following behaviour when ground with 60% alcohol.

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[1] Compt. rend., 1864, 59, 980.

Number of times ground.	% CaO.
0	12.90
1	14.00
2	19.37
3	21.21
4	23.05
5	23.10
6	23.90
7	24.28
8	24.50
After 9 " Constant	24.50

The lime content therefore rises to very nearly that required for dilime-monosucrose.

$C_{12}H_{22}O_{11}$ 2 CaO H_2O requires 23.74% CaO.

$C_{12}H_{22}O_{11}$ 2 CaO requires 24.67% CaO.

150 c.c. of the solution used above were evaporated at 0°C. over phosphorus pentoxide in a vacuum, the pentoxide being changed when necessary and the vacuum renewed daily. At the end of three months the solution, which had turned a faint yellow, deposited a hard syrupy mass which, when examined under the microscope, appeared to contain ill-defined microscopic crystals. After pouring off the mother liquid the mass was well washed with ice cold conductivity water, ice cold 50% alcohol, and then ice cold conductivity water again. The substance was then dried/

dried between filter paper at 0°C. Four grm. of a slightly sticky solid were obtained.

Wt. of Crucible	=	14.5132 grm.	14.5133 grm.
Wt. of Crucible + lime sugar	=	14.6890 grm.	14.6546 grm.
Wt. of Crucible + lime	=	14.5342 grm.	14.5296 grm.
% lime	=	11.53	11.53

Two separately prepared samples had the same lime content as shown above.

When .1502 grm. of the substance was dried at 100°C. for four days .1201 grm. lime sugar remained.

% Water = 19.97.

$C_{12}H_{22}O_{11}$ CaO $6H_2O$ requires CaO = 11.48% H_2O = 18.44%

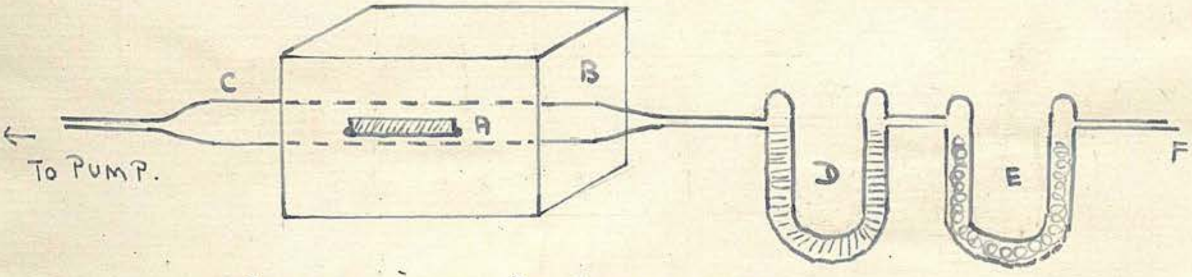
$C_{12}H_{22}O_{11}$ CaO $5H_2O$ requires CaO = 11.07% H_2O = 21.46%

On grinding those crystals, which may be monolime-monosucrose hexahydrate, the lime content rose till it reached that required for dilime-monosucrose. It must therefore be considered a matter of doubt whether monolime-monosucrose actually exists.

DILIME-MONOSUCROSE.

500 c.c. of 60% alcohol cooled at 0°C, were added to 250 c.c. lime sugar solution at the same temperature, and the white gelatinous precipitate formed filtered at the pump. When the process was carried out at room temperature filtration proved to be difficult. The precipitate was then well washed and ground with 60% alcohol several times, and a specimen dried as far as possible by blowing air free from carbon dioxide over it, and then between filter paper. Yield 6 grm.

This dry sample was then dehydrated at 100°C. in a vacuum of about 1 mm.



EXPLANATION OF LETTERING

A	BOAT.
B	STEAM BATH
C	WIDE GLASS TUBE
D	PHOSPHORUS PENTOXIDE TUBE
E	SODA LIME TUBE.
F	LEAK.

It was necessary to have the mass of compound evenly distributed over the bottom of a copper boat, which was heated to 100°C or thereby, and purified air was passed over it slowly by having a leak which communicated with the pump through a tube containing soda lime and several containing phosphorus pentoxide. During the process the compound turned slightly yellow, probably owing to traces of lower sugars. It should not char or turn deep brown, and if it showed any tendency to do so the temperature was lowered slightly and a fresh sample introduced into the boat. The time of drying was lengthy.

Time.	Wt. of lime sugar.	Time.	Wt. of lime sugar.
0	5.4400 grm.	0	1.9060 grm.
35 days	4.4210 grm.	32 days	1.5667 grm.

At the end of this period constant weight was reached.

H_2O = 18.42% H_2O = 17.80%

$C_{12}H_{22}O_{11}$ 2CaO $6H_2O$ requires H_2O = 19.22%

$C_{12}H_{22}O_{11}$ 2CaO $5H_2O$ requires H_2O = 16.54%

Several attempts were made to obtain crystals of dilime-monosucrose from ice cooled solutions of lime sucrose (Lippmann[1]). No crystals could be isolated, but on standing crystals of calcium carbonate appeared whereupon the process was abandoned.

[1] Z. Ver. deut. Zuckerind., 33, 883.

The solubility of the amorphous precipitated compound was found by shaking a sample at 15°C. for twelve hours in conductivity water.

10 c.c. of the saturated solution required 22.2 cc. .121 N. hydrochloric acid using phenolphthalein as indicator.

Solubility = 30.50 grm. per litre.
Compare Lippmann[1] who gave 1 part in 33 of water.

This method of drying was very tedious. The following method gave good results in a much shorter time.

A sample of dilime-monosucrose was prepared in the usual way, and dried at room temperature in a vacuum. The white powder was then ground several times with 60% alcohol, a little pyridine, and then with absolute alcohol several times, and dried in a vacuum again. From 250 c.c. lime sucrose solution 7 grm. final product was obtained.

It was observed that on drying in this way some samples of the compound took on a crystalline appearance, although when examined under the microscope the crystals could not be distinguished positively from a glass. For a crystallographic examination I am indebted to Dr R. Campbell who found the crystals to be all isotropic, showing conchoidal fracture, but with/

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[1] Ö Z. Zuckerind., 9. 35.

with no definite cleavage. These facts point either to cubic crystals or glass. The appearance of faults in the unformed material points to the former.

Refractive Index 1.5245 1.5294

Refractive Index Sucrose α 1.5397, β 1.5667, γ 1.5716

Several attempts were made to recrystallise this compound without success. A saturated solution of the crystals obtained above was made at 0°C, and the temperature then allowed to rise to 15°C. very slowly in a constant temperature vessel. A syrupy paste was obtained. Eventually crystals of calcium carbonate appeared, and the process was stopped.

The solubility of the crystalline compound was found to be 4.523 grm. per 100 c.c. at 15°C. This is greater than the value given by Lippmann[1], which is 1 in 33 parts water.

A 2.5% solution gave a rotation of + 1.6° in a 2 dcm. tube at 17°C. using sodium light.

$$[\alpha]_D^{17} = +32.1^\circ.$$

The dried product gave the following analytical data.

Wt. of Crucible = 14.5133 grm.

Wt. of Crucible + lime sugar = 14.6382 grm.

Wt. of Crucible + lime = 14.5435 grm.

% CaO = 24.75

The/

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[1] Ö Z. Zuckerind., 9, 35.

The determination of carbon and hydrogen in the lime sugar compounds in general is not easy as calcium carbonate is formed in the process. After various attempts at combustions with lead chromate, the method finally adopted was to heat very strongly using a copper oxide tube. The compound was introduced in a platinum boat.

.1210 grm. dilime-monosucrose gave .0540 grm water and .1460 grm. carbon dioxide.

C = 31.68% H = 5.00%

$C_{12}H_{22}O_{11}$ 2 CaO requires CaO = 24.67%
H = 4.85%
C = 31.72%

TRILIME-MONOSUCROSE.

300 c.c. of lime sucrose solution were heated in a conical flask on the water bath. At about 58°C. a white precipitate began to form, and, on raising the temperature to 80°C., collected in a thick mass at the bottom of the flask. The precipitate was then filtered as rapidly as possible through a hot funnel, and well washed with hot conductivity water. The white earth was now thoroughly dried between filter paper for about half an hour in a carbon dioxide free atmosphere and/

and then dried in the same apparatus as was used for the dilime compound.

Samples that show any marked colour must be rejected, but it is impossible to prevent the appearance of a golden tint.

Time of drying.	Wt. of lime sugar.	Time of drying.	Wt. of lime sugar.
0	1.7640 grm.	0	4.2180 grm.
66 days	1.4597 grm.	56 days	3.5143 grm.

At the end of these periods constant weight was reached.

$$H_2O \quad = \quad 17.23\% \qquad 16.68\%$$

$$C_{12}H_{22}O_{11} \ 3\,CaO\ 6H_2O \quad \text{requires} \quad H_2O = 17.28\%.$$

It was found that trilime monosucrose could be largely dried by treatment with absolute alcohol as in the case of dilime-monosucrose.

Trilime-monosucrose is a white amorphous earth which turns a light yellow on drying at 100°C. It is readily attacked by carbon dioxide, and dried samples are very hygroscopic. Thus it is difficult to obtain pure. The results, however, point to the existence of either a pentahydrate or a hexahydrate.

No trace of crystalline structure could be detected under the microscope, and all attempts to obtain crystals by slow precipitation were failures.

In this Laboratory an attempt was made to obtain this/

this compound in a crystalline state. Some lime sugar solution was enclosed in a sealed tube, which was suspended in a thermostat, and the temperature slowly raised from 10°C to 58°C during a period of eight days, when the solution became turbid. From the 8th day to the 12th the temperature was kept between 62° and 72°C. No evidence of crystalline structure was obtained (private communication by Dr J.E. Mackenzie).

The solubility is slight in water, and almost negligible in organic solvents.

In order to determine the solubility of the dried trilime-monosucrose a sample was stirred six hours with conductivity water at 0°C.
The temperature was then allowed to rise to about 15°C. and any precipitated trilime sucrose filtered off through cotton wool.

10 c.c. of the resulting solution required 14.91 c.c. .121 N. hydrochloric acid for neutralisation using phenolphthalein as indicator.

Solubility = 15.39 grm. per litre at 15°C.
This is considerably higher than the value obtained by Lippmann[1], which was 1 part in 100 cold water.
This saturated solution gave a rotation of + 1.12° in a 2 dcm. tube using sodium light at 15°C.

$$[\alpha]^{15}_{D} = +36.52^\circ.$$

Analytical data.

.0941 grm. compound gave .0974 grm. carbon dioxide and .0377 grm. water.

[1] Ö. Z. Zuckerind., 9, 35.

C = 28.23%　　H = 4.49%

Wt. of Crucible = 15.4500 grm.

Wt. of Crucible + lime sugar = 15.5541 grm.

Wt. of Crucible + lime = 15.4843 grm.

% CaO = 32.96

$C_{12}H_{22}O_{11}\ 3CaO$ requires C = 28.23%

H = 4.31%

CaO = 32.94%

HIGHER LIME SUCROSE COMPOUNDS.

When unsaturated solutions of lime in sucrose solution were heated precipitates of lime content approximating to tetralime-monosucrose, hexalime-monosucrose, and octalime-monosucrose were obtained. The precipitates showed no trace of crystalline structure, and by using original solutions of slightly different concentrations, could be obtained in a series where the lime content of each member very gradually increased. On grinding with 90% alcohol, the lime content invariably rose to about 90-100%. It is therefore highly probable that these so-called compounds consist of sucrose adsorped by lime, or a mixture of a lime sucrose compound with lime itself.

MONOSTRONTIA-MONOSUCROSE.

200 c.c. of a 20% sucrose solution was saturated at 75°C. with one molecular proportion of strontia, and the clear solution formed cooled with vigorous shaking, when crystals of monostrontia-monosucrose crystallised out. If the solution was allowed to cool undisturbed, or if it was seeded with a crystal of strontia, crystals of strontium hydroxide were obtained.

Monostrontia-monosucrose is a white solid which showed small needle like crystals clustered together in masses when examined under the microscope. It was difficult to obtain the compound dry, but by constant pressing between filter paper for ¾ of an hour the adherent water was eliminated. Scheibler found the crystals to correspond to $C_{12}H_{22}O_{11}SrO\ 5\ H_2O$, but the present results point to the hexahydrate instead.

The solubility of monostrontia-monosucrose was 43.95 grm. per litre at 16°C. Scheibler[1] by interpolation gave 43.90 grm. per litre at 16°C. (It should be noted that the monostrontia-monosucrose was calculated as $C_{12}H_{22}O_{11}SrO$).

The rotation of this saturated solution was + 3.70° in a 2 dcm. tube at 16°C. using sodium light.

$$[\alpha]_D^{16} = +42.09^\circ$$

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[1] N.Z. Rubenzuckerind., 10, 229.

Boderbender[1] by extrapolation gave $[\alpha]_D = + 41.07^\circ$ for the rotation given when one molecular proportion of sucrose and one molecular proportion of strontia were dissolved in water. Neglect of concentration, as Pellet[2] has pointed out, render his results useless.

On analysis of the monostrontia-monosucrose it was found that the % strontia was approximately that required for the hexahydrate, but that the water content itself was always a trifle low.

Wt. of Crucible = 17.5195 grm.
Wt. of Crucible + Stronita Sugar = 18.2185 grm.
Wt. of Crucible + Strontia = 17.6501 grm.
% Strontia = 18.69

.2513 grm. Compound lost .0448 grm. on heating to 100°C. for six hours.

$$H_2O = 17.80\%$$

$C_{12}H_{22}O_{11}$ SrO $6H_2O$ requires Sro = 18.71% H_2O = 19.16%
$C_{12}H_{22}O_{11}$ SrO $5H_2O$ requires Sro = 19.33% H_2O = 16.80%

It may be that the last traces of water are difficult to remove, and thus the water content does not reach that required for the hexahydrate.

It was possible to obtain a dry sample of the compound/

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1. Z. Ver. deut. Zuckerind., 15, 167.
2. Bull. Soc. Chim., 1877, 28, 250.

compound by treatment with absolute alcohol in the usual way. A combustion was performed on this anhydrous sample with the following results.

.2101 grm. monostrontia-monosucrose gave .2486 grm. carbon dioxide, and .0933 grm. water.

C = 32.28%
H = 4.94%

$C_{12}H_{22}O_{11}$ SrO requires C = 32.36%
H = 4.95%

DISTRONTIA-MONOSUCROSE.

A little more than three molecular proportions of crystalline strontium hydroxide were added to a boiling 15% sucrose solution, and boiling continued for a few minutes, when complete precipitation of sucrose as distrontia-monosucrose took place. Filtration should prove easy if the instructions have been carried out properly, but excessive boiling rendered it difficult. The compound was well washed with hot 10% strontia solution, and, when quite white, with boiling water. It may be dried either between filter paper, which was difficult, or in a vacuum.

Distrontia-monosucrose/

Distrontia-monosucrose is a white and sandy crystalline compound, which decomposes in the presence of cold water into monostrontia-monosucrose and stronium hydroxide.

The same decomposition was observed when a partially dry sample was kept for a few days, granular crystals of strontium hydroxide appearing in the mass. Completely dry samples may be kept without decomposition for much longer periods.

An attempt was made to find the solubility in boiling water by filtering a saturated and boiling solution through cotton wool, and rapidly cooling to 15°C. 10 c.c. of the resulting solution required 6.83 c.c. .1296 N. hydrochloric acid for neutralisation, thus

Solubility in boiling water = 1.189 gms. in 100 grm. water at 102°C.

This was in agreement with the result of Sidersky[1] - 1 in 84 parts water, - but it cannot be regarded as other than an approximation.

The rotation of this solution at 15°C. in a 2 dcm. tube using sodium light was + .90°

$$[\alpha]_D^{15} = +37.79^\circ.$$

The following analytical data were obtained.

Strontia/

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[1] Bull. Ass., 3, 240.

Strontia Content.

Wt. of Crucible = 14.3210 grm.

Wt. of Crucible + Strontia Sucrose = 15.3278 grm.

Wt. of Crucible + Strontia = 14.7001 grm.

% Strontia = 37.64

$C_{12}H_{22}O_{11}$ 2SrO requires = 37.73% strontia.

.1575 grm. of the compound gave .1544 grm carbon dioxide and .0483 grm. water; thus it was found

C = 26.12%

H = 3.40%

$C_{12}H_{22}O_{11}$ 2 SrO requires C = 26.22%

H = 3.18%

DISTRONTIA-TRISUCROSE.

No other strontia sucroses could be isolated, and their existence is improbable. In particular, distrontia-trisucrose could not be prepared, a mixture of monostrontia-monosucrose and strontia crystals being obtained instead.

MONOBARYTA-MONOSUCROSE.

A 5% solution of sucrose was saturated with baryta, and then precipitated by the addition of an equal/

equal volume of 60% alcohol. The white granular earth so formed quickly subsided to the bottom of the vessel used, and could be filtered without difficulty.

After washing well with 60% alcohol, the precipitate was dried between filter paper at room temperature. The composition was in agreement with that of anhydrous monobaryta-monosucrose, and no hydrate could be isolated.

Monobaryta-monosucrose is a finely crystalline powder which is not completely decomposed by carbon dioxide. It is insoluble in alcohol and other organic solvents, and also in baryta solution, but readily soluble in sugar solution. In water the solubility was found to be 22.10 grm. per litre at 20°C. (Compare Peligot[1], who gave the result 21.0 grm. per litre at 15°C.). This saturated solution gave a rotation of $+ 1.94^\circ$ in a 2 dcm. tube at 20°C. using sodium light.

$$[\alpha]_D^{20.} = + 43.89^\circ$$

All attempts to obtain other baryta sucrose compounds resulted in the preparation of monobaryta-monosucrose. Thus a saturated solution of baryta in sucrose solution gave a precipitate of the mono-compound on boiling. A similar result may be obtained by shaking a/

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[1] Ann. Chim. 1858 (3), 54, 379.

a saturated solution of sucrose with excess of powdered baryta for ten minutes, filtering at the pump, and seeding the filtrate with a crystal of the already prepared compound. A copious formation of monobaryta-monosucrose occurred in a few hours, but the crystals were always small. They are prismatic in habit, show straight extinction to polarised light, and exhibit very weak double refraction. (I am indebted to Dr R. Campbell for these crystallographic data).

The baryta content approached very closely that required for monobaryta-monosucrose.

Wt. of Crucible = 17.3815 grm.
Wt. of Crucible + Compound = 17.5775 grm.
Wt. of Crucible + Barium Carbonate = 17.4600 grm.
% baryta = 31.05.

.2010 grm. compound gave .2141 grm. carbon dioxide and .0796 grm. water.

C = 29.05%
H = 4.45%

$C_{12}H_{22}O_{11}BaO$ requires C = 29.01%
H = 4.43%

STRUCTURE OF ALKALINE EARTH SUCROSES.

As these compounds are readily decomposed by carbon dioxide the investigation of their structure is a matter of very great difficulty.

A/

A number of trials were made, however, to find if, when dimethyl sulphate was added to the solution of an alkaline earth sucrose compound the alkali of the compound would interact with the methylating agent, and evacuate its position in the sucrose molecule in favour of a methyl group. Thus if the alkaline earth is attached to a definite hydroxyl group in the sucrose, that group and no other should be methylated. Unfortunately alkylation did not appear to be quantitative and a great deal of pure sucrose was obtained, as well as a syrup of low methoxy content. All efforts to obtain definite products of methylation were failures, and the process had to be abandoned.

LIME GLUCOSE.

A lime glucose solution was prepared in the following way.

500 c.c. 5% glucose solution was cooled to $0^\circ C.$ in ice, and one molecular equivalent of lime added with vigorous stirring over about an hour.

At the end of this time any excess of lime was filtered off, and the solution, which was faintly yellow, used to prepare lime glucose.

MONOLIME-MONO GLUCOSE.

To 250 c.c. of the above solution an equal volume of 60% alcohol was added, and after stirring for several minutes, the white earthy precipitate filtered at the pump. It was then well washed and ground at least six times with 60% alcohol, and dried as far as possible between filter paper. The precipitate was then ground several times with absolute alcohol, and finally with ether, and the drying completed in a vacuum over phosphorus pentoxide.
It was absolutely essential that the process should be carried out rapidly, and that drying should be complete, as it was found that traces of water brought about decomposition of the compound in a few hours.
In the anhydrous state no such change took place, and a sample may be kept for months without apparent decomposition.

In/

In order to obtain the pure compound it was often necessary to repeat the grindings two or three times, taking care to dry carefully after each treatment. Yield 10 grm. An analysis of the compound gave the following results.

Wt. of Crucible = 17.3828 grm.
Wt. of Crucible + Compound = 17.5179 grm.
Wt. of Crucible + lime = 17.4120 grm.
% CaO = 21.62.
$C_6H_{12}O_6CaO$ requires CaO = 23.73%
$C_6H_{12}O_6CaO\ H_2O$ requires CaO = 22.00%

The monolime-monoglucose when dry is a white amorphous powder which can be preserved for months; when wet it is a pasty earth which decomposes overnight.
No hexahydrate could be isolated, but when the freshly prepared compound was dried between filter paper, and then the drying completed by standing in a desiccator at 0°C for 5 hrs. over calcium chloride the dihydrate was obtained.

Wt. of Crucible - = 12.4286 grm.
Wt. of Crucible + lime glucose = 12.7875 grm.
Wt. of lime = 12.5025 grm.
% lime = 20.6
$C_6H_{12}O_6\ CaO\ 2H_2O$ requires CaO = 20.59%.

It was found that lime lowered the rotation of a glucose solution considerably. A 5% glucose solution of rotation +5.25° in a 2 dcm. tube at/

at 150°C. using sodium light, fell to $+4.40^\circ$ when shaken with excess of lime for 15 minutes.

i.e. $[\alpha]^{15}_{D} = + 52.5^\circ$ fell to $[\alpha]^{15}_{D} = + 44.^\circ$.

On precipitation of the lime with oxalic acid the rotation rose again to $+ 52.30^\circ$. 10 c.c. of this solution required 12.85 c.c. .121 N. hydrochloric acid for neutralisation using phenolphthalein as indicator, and it therefore contained .4854 grm. lime per 100 c.c.

When this solution was precipitated with alcohol in the usual way a white earth was obtained, which after drying well between filter paper gave the following analytical results.

Wt. of Crucible = 12.4285 grm.
Wt. of Crucible + lime glucose = 12.8296 grm.
Wt. of lime = 12.4766

% CaO = 11.99

$C_6H_{12}O_6\ \frac{1}{2}CaO\ 2H_2O$ requires CaO = 11.52%.

On grinding with 60% alcohol and drying, however, the lime content rose to that required for monolime-monoglucose.

No consistent results were obtained for the solubility, which Peligot[1] gave as .73 parts in 100 parts water. The rotation presented similar difficulties, /

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1. Jahresb. Fort. Chem., 1880, 1018.

difficulties, as the solution, unless quite fresh, was too discoloured for polarimetric work.

A solution containing .7366 grm. monolime-monoglucose per 100 c.c. gave a rotation of $+ 1.48^\circ$ at 16°C. in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{16} = + 10.07^\circ$$

HIGHER LIME GLUCOSE COMPOUNDS.

An attempt has been made to show that the so-called compounds of lime and glucose containing more than one molecular proportion of glucose to one of lime are really impure monolime-monoglucose.
No higher combinations of lime and glucose were encountered, and their existence is doubtful.

α AND β METHYL GLUCOSIDES.

α METHYL GLUCOSIDE.

A sample of α methyl glucoside was prepared by the method of Fischer (Bourquelot's modification[1]), using acetone free methyl alcohol.

$$\text{M.P.} = 165^{\circ}\text{C.} \qquad [\alpha]_D^{15} = +157^{\circ}$$

Fischer[2] found M.P. = 165°C and $[\alpha]_D^{15} = +157^{\circ}$.

β METHYL GLUCOSIDE.

As it is not possible to obtain a good yield of β methyl glucoside from the above preparation, that compound was prepared by the methylation of glucose. This partial methylation is important from the point of view of the structure of the alkali sugars, and therefore must be considered carefully. Maquenne's[3] process was used, with slight modifications.

20 grm. glucose was dissolved in the minimum amount of water, and 24 grm. dimethyl sulphate added. The mixture was vigorously stirred at 30°C, and the equivalent amount of potassium hydroxide (10.34 grm.) dropped in slowly in the form of a saturated solution over a period of three hours. After standing overnight, the neutral solution was found to be without action/

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[1] Ann. Chim., 1915, (9), 3, 298.
[2] Ber., 1895, 28, 1151.
[3] Bull. Soc. Chim., 1905, (3), 33, 469-471.

action on Fehlings solution. After evaporating to small bulk under reduced pressure, five volumes of alcohol were added, the mixture boiled, and, after cooling most of the potassium methyl sulphate filtered off as a precipitate. The filtrate was concentrated to a syrup, and placed in the refrigerator at - 6°C. for one day. A large crop of crystals was then filtered from the mother liquor, and recrystallised from methyl alcohol after the removal of any potassium by the addition of a very slight excess of perchloric acid. The temperature must be kept low.

Yield 6 grm.

M.P. = 108°C. $[\alpha]_D^{15}$ = - 33°

Fischer found M.P. = 108°C. $[\alpha]_D^{15}$ = - 33°.

ATTEMPTED ISOLATION OF LIME METHYL GLUCOSIDE COMPOUNDS.

1.94 grm. methyl glucoside was dissolved in water and the solution made up to 100 c.c. .56 grm. finely powdered freshly burnt lime was then added, and the mixture shaken vigorously for six hours, at the end of which time very little lime appeared to have gone into solution.

To 5 c.c. of the filtered solution 4 c.c. absolute alcohol were added slowly, when a thick gelatinous precipitate was formed. It may be filtered at the pump with ease, provided the operation is carried/

carried out quickly, and the resulting jelly-like mass appeared quite dry.

The filtrate was a clear liquid containing methyl glucoside but only a trace of lime. Large quantities of water appeared to be present in the jelly in spite of its apparent dryness, for on drying in a vacuum for several days the substance shrank to small bulk, giving a white mass consisting essentially of lime, and containing very little organic matter.

It was obvious no combination of lime and glucoside had occurred; lest the action should be a slow one a similar experiment was carried out, maintaining the solution at 0^oC. for one month, and shaking frequently. The results did not differ from those given by the freshly prepared solution.
A ten times more concentrated solution of glucoside showed the same behaviour.

It is possible the lime methyl glucoside compound is soluble in alcohol, though this is most improbable. Similar results, however, were obtained using acetone.

When strontium and barium hydroxides respectively were substituted for lime in the above experiments, white precipitates were obtained on the addition of alcohol or acetone which consisted essentially of inorganic hydroxide.

When a solution of the glucoside was boiled after saturating with lime, strontia, or baryta, no visible change/

change could be observed save in the case of the first mentioned hydroxide, when precipitation occurred due to the lower solubility of lime at higher temperatures. Cooling a solution of alkaline earth in glucoside solution produced no effect, even over several weeks.

Methyl glucoside showed similar behaviour. The rotation of α and β Methyl glucosides were not influenced by the addition of these hydroxides to their aqueous solutions.

It was therefore concluded that neither α nor β Methyl glucosides formed compounds with the alkaline earths.

LIME FRUCTOSE.

A fructose solution was prepared by the method of Soxhlet[1].

100 grm. sucrose was dissolved in 300 c.c. alcohol containing 12 c.c. concentrated hydrochloric acid at 45°C, and, after standing several days, the deposited crystals of glucose filtered off. Yield = 45 grm. glucose. The filtrate was neutralised with silver carbonate, and, after filtration, concentrated to a syrup in a vacuum. Sufficient water was then added to give a 10% solution. As most of the previous investigators of the interaction of lime and fructose have used such a solution, it is to be preferred to one of pure fructose when attempting to repeat their work.

MONOLIME-MONOFRUCTOSE.

This compound was first prepared by Peligot[2], who found it to be the dehydrate, and later by Winter[3], who isolated the hexahydrate. The method of preparation is in both cases the same.

500 c.c. of fructose solution were shaken with excess of slaked lime for two minutes at 20-25°C, and then filtered rapidly into a wide-necked conical flask. On/

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[1] J. pr. Chem., 1880, (2), 21, 245.
[2] Bull. Soc. Chim., 1881, 36, 224.
[3] Annalen, 1888, 244, 317.

On standing at 0°C. for twelve hours small crystals began to form on the bottom of the vessel. To obtain the maximum yield, however, it was essential to let the flask stand several days. The yield was poor, but it may be slightly increased by filtering off the crystals and repeating the process.

The filtered crystals were well washed with ice water. The method of drying was important. Various dryings were attempted in a vacuum, but the best results were obtained by spreading about 5 grm. crystals on filter paper at room temperature in carbon dioxide free air, and constantly pressing them till a white crystalline mass free from adherent water was obtained. It is not advisable to prolong the drying more than half an hour. The dry product may be preserved several days at 0°C. without change. The composition agreed very closely with that required for Winter's monolime-monofructose hexahydrate.

Wt. of Crucible = 18.5178 grm.
Wt. of Crucible + Compound = 19.2610 grm.
Wt. of Crucible + lime = 18.6382 grm.
% lime = 16.20

$C_6H_{12}O_6\ CaO\ 6H_2O$ requires CaO = 16.28%.

I am indebted to Dr R. Campbell for a crystallographic examination of the compound. The crystals showed weak double refraction, and gave oblique extinction to polarised light; they are very small and needle shaped, and/

and are either triclinic or monoclinic. As lime appeared to attack fructose even at low temperature, attempts to obtain larger crystals by letting the solution stand at 0°C. for some weeks merely resulted in the decomposition of those already formed.

When Winter's compound was placed over concentrated sulphuric acid at 0°C. for several days in a low vacuum, the lime content gradually rose till it approached that of Peligot's compound, which is described as being of a golden colour. It was suspected that the coloration was due to decomposition, but even when the dehydration took place at low temperature the same colour change was observed. The loss of water corresponded to that required for the convertion of monolime-monofructose hexahydrate to monolime-monofructose dehydrate.

Wt. of Crucible = 17.3840 grm.
Wt. of Crucible + Compound = 17.8012 grm.
Wt. of Crucible + dried Compound = 17.7140 grm.
% H_2O = 20.90

$C_6H_{12}O_6CaO\ 6\ H_2O$ requires loss of 20.93% water to give $C_6H_{12}O_6CaO\ 2\ H_2O$.

The lime content of the compound corresponded with that required for the dehydrate.

Wt. of Crucible = 17.5195 grm.
Wt. of Crucible + Compound = 18.0296 grm.
Wt. of Crucible + lime = 17.6246 grm.
% CaO = 20.60

$C_6H_{12}O_6\ CaO\ 2H_2O$ requires $CaO = 20.59\%$. Further drying did not completely remove the water, and a compound $C_6H_{12}O_6CaO\ \frac{1}{2}\ H_2O$ or $C_6H_{12}O_6CaO\ H_2O$ was obtained.

According to Peligot, the solubility is 1 part compound in 137 parts "cold" water, while Winter gives it as 1 part in 118 parts water at 17°C. Excess of the compound was therefore shaken in a Jena glass vessel at 15°C. for eight hours in the presence of conductivity water. The resulting solution, which must be quite colorless, was filtered in a carbon dioxide free atmosphere, and the alkalinity estimated by titration, using standard hydrochloric acid and phenolphthalein as indicator. 10 c.c. of the saturated solution required for neutralisation 5.51 c.c. .121 N. hydrochloric acid.

∴ Solubility of compound calculated as $C_6H_{12}O_6\ CaO\ H_2O$.

$$= .8451 \text{ grm. per } 100 \text{ c.c. at } 15^\circ C.$$

This is in agreement with the result of Winter. The saturated solution gave a rotation of $-.66^\circ$ in a 2 dcm. tube at 15°C. using sodium light.

$$[\alpha]_D^{15} = -39.05^\circ$$

PREPARATION OF FRUCTOSE FROM MONOLIME-MONOFRUCTOSE.

In order to test the purity of the compound a sample of fructose was prepared from it by precipitating the lime with the calculated amount of oxalic acid,/

acid, filtering, and seeding the concentrated filtrate with fructose, whereon the syrup completely crystallised. The crystals of fructose obtained were then recrystallised from aqueous alcohol.

M.P. 94-95°C $[\alpha]_D^{19}$ = - 91.8 after 1 hour.

HIGHER LIME FRUCTOSE COMPOUNDS.

An attempt was made to prepare other lime-fructose compounds by the method of Dubrunfaut[1].

200 c.c. fructose solution was shaken two minutes with 12 grm. freshly prepared slaked lime, at - 5°C. filtered through a funnel surrounded with ice, and kept at about 0°C. for 24 hours. Small crystals of a lime fructose then appeared. The composition was variable; some samples, however, gave a lime content approximating closely that required for trilime-monofructose. On grinding with alcohol, however, the lime content rose to about 95%; while miscoscopic examination revealed crystals strongly resembling those of monolime-monofructose embedded in a matrix of much less definite crystals. It is therefore very doubtful whether trilime-monofructose exists.

No other lime fructoses were met with, and their existence is improbable.

[1] Compt. rend., 1847, 25, 307; 1869, 69, 1366.

β METHYL FRUCTOSIDE.

The preparation was carried out according to the method of Hudson and Braums[1].

20 grm. finely powdered fructose was added to a solution of 1.8 grm. zinc chloride in 100 c.c. acetic anhydride at 0°C. over a period of half an hour. The solution was then maintained at 0°C. for two hrs., at 10°C. for half an hour, at 16°C. for one hour, and finally at 0°C for three hours again. After stirring with 100 c.c. water at 0°C. for two hours the excess of acid was neutralised with sodium carbonate, and the neutral solution extracted with chloroform. The extract was dried and reduced to small bulk under reduced pressure, ether was added to the syrup, and the mixture allowed to crystallise. The white crystals of tetracetyl fructose obtained were recrystallised from absolute alcohol containing a little ether.

Yield 16 grm. M.P. = 130°C.

A 5% chloroform solution gave a rotation of -9.25° at 15°C. in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{15} = -92.50^\circ$$

Hudson and Braums found M.P. = 120-130°C.

$$[\alpha]_D^{15} = -92.30^\circ$$

The tetracetyl fructose was then converted into tetracetyl/

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[1] J.A.C.S., 1916, 38, 1216.

tetracetyl methyl fructoside.

14 grm. tetracetyl fructose was dissolved in 85 c.c. methyl iodide and 93.75 grm. silver oxide added slowly with shaking. The reagents must be dry. After six hours boiling to complete the reaction, the excess of methyl iodide was distilled off, and the residue extracted with ether. On evaporating the dried ether extract in air at room temperature a yellow syrup was obtained which was recrystallised from hot petrol ether. As the solubility was only about 1 part in 400 parts solvent a very large quantity of petrol ether was necessary. Yield 7 grm. The crystals obtained had a slightly yellow tint.

$$M.P. = 75^\circ C.$$

A 1% chloroform solution gave a rotation of -2.48° at $15^\circ C.$ in a 2 dcm. tube using sodium light

$$[\alpha]_D^{15} = -124^\circ.$$

Hudson and Braums found $M.P. = 75\text{-}76^\circ C.$

$$[\alpha]_D^{20} = -124.6^\circ$$

METHYL FRUCTOSIDE.

70 grm. crystalline barium hydroxide was heated with one litre water on the steam bath till solution occurred, and then filtered into a stoppered bottle and/

and cooled to 5°C. The solution was supersaturated, but no precipitation occurred during the experiment. The tetracetyl methyl fructoside was then added slowly, and after shaking well, the whole maintained at 5°C for one hour, and then at 0°C. for twelve hours. Any excess of baryta was now removed by carbon dioxide, and, after evaporating down in a large flask to a much smaller volume the solution filtered and evaporated to dryness under reduced pressure. The residue was extracted with aqueous alcohol, which removed most of the fructoside from the insoluble barium acetate, and, after again taking to dryness, the methyl fructoside was crystallised several times from absolute alcohol. Yield 25% theory.

Methyl fructoside is a faintly yellow crystalline substance, readily soluble in water and alcohol, and very slightly soluble in benzene.

M.P. 119°C.

The rotation of a 1% solution at 15°C. in a 2 dcm. tube using a sodium light was -3.42°

$$[\alpha]_D^{15} = -171.0^\circ$$

Hudson and Braums found M.P. = 119-120°C; $[\alpha]_D = -172.1^\circ$. Several attempts were made to isolate a lime methyl fructoside compound by the same methods as were adopted in the case of the glucosides, but without success. The rotation was uninfluenced by barium, strontium or calcium oxides and no evidence of combination could be found.

LIME MALTOSE.

Monolime-monomaltose was prepared in a similar manner to monolime-monoglucose. The yield, however, was poorer, being about 25% theory. The calcium oxide content indicated the presence of about a molecule of water even after the most vigorous drying at 0°C.

Wt. of Crucible = 17.3843 grm.
Wt. of Crucible + Compound = 17.8845 grm.
Wt. of Crucible + lime = 17.4532 grm.
% lime = 13.77.

$C_{12}H_{22}O_{11}\,CaO$ requires $CaO = 14.07\%$
$C_{12}H_{22}O_{11}\,CaO\,H_2O$ requires $CaO = 13.46\%$

Lime maltose is an amorphous white earth which tends to decompose unless dehydrated. It probably contains water of crystallisation, but to what extent was not possible to determine. A saturated solution was prepared by shaking the dried compound with conductivity water at 15°C. for six hours. Longer shaking resulted in very marked decomposition. The alkalinity of the solution was then found by titration with standard hydrochloric acid using phenolphthalein as indicator.
10 c.c. solution required 7.50 c.c. .121 N. hydrochloric acid.

Solubility = 19.36 grm. per litre.
This solution gave a rotation of + 4.55° at 15°C in/

in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{15} = + 117.6^\circ$$

If the rotation is calculated for the % maltose in the solution then

$$[\alpha]_D^{15} = + 137.8^\circ.$$

thus it may be seen the rotation of maltose was unaffected by lime. This might be ascribed to non-formation of any compound, but it is very probable that it is due simply to coincidence.

β METHYL MALTOSIDE.

β Methyl maltoside was first prepared by Fischer and Armstrong[1], who prepared it from acetochloromaltose. Later Koenigs and Knorr[2] obtained it from acetonitromaltose. Irvine[3] introduced some modifications into the former method but the process became somewhat tedious, although a very pure product was obtained. An attempt was therefore made to prepare methyl maltoside using the method of Koenigs and Knorr. The work may be divided into four stages.

STAGE I./

1. Ber., 1901., 34, 2885.
2. Ber., 1901, 34, 4343.
3. J.C.S., 1926, 1, 873.

STAGE I. MALTOSE OCTACETATE.

A solution of 5 grm. anhydrous sodium acetate in 500 c.c. acetic anhydride was raised to boiling point, and after the removal of the flame, 50 grm. maltose added in quantities sufficient to maintain the temperature at boiling point. When the reaction was complete the solution was boiled 15 minutes and then poured into a large excess of water. After washing the syrupy mass several times by decantation it was allowed to stand six hours under water, when it became quite brittle, and could be filtered at the pump. It was then recrystallised several times from alcohol.

Yield 80% theory. M.P. = 157°C.

STAGE II. ACETONITROMALTOSE.

Slight modifications were introduced into the method in order to apply it to larger quantities than were used by the previous workers.

50 grm. dry maltose octacetate was dissolved in 500 c.c. dry chloroform and cooled to - 5°C. 500 c.c. red fuming nitric acid were prepared by the distillation of the green fuming acid with two volumes of sulphuric acid and a little starch, and the freshly distilled acid mixed with 750 c.c. chloroform and cooled to -5°C. The two solutions were now mixed and maintained at 0°C. for 2½ hours with gentle stirring./

stirring. The mixture was then poured on ice, and, after being well washed with ice water, the separated chloroform shaken with ice cold sodium bicarbonate solution, and then with water again. After drying over anhydrous sodium sulphate the chloroform was distilled off and the acetonitromaltose crystallised from ether.

Yield 27 grm. M.P. 94°C.

Koenigs and Knorr found M.P. = 93-95°C.

When the mother liquor was further concentrated a yellow paste was deposited which, after standing in the ice house for 48 hrs., became crystalline. The melting point of the white crystals obtained from it was 177°C, so that it was obvious a further yield of acetonitromaltose had not been obtained. An isomer was suspected, but the crystals contained no nitrogen. After one recrystallisation from chloroform + ether the melting point rose to 178°C. The rotation of a .6934% solution in chloroform at 15°C. in a 2 dcm. tube using sodium light was + 1.10°

$$[\alpha]_D^{15} = +79.34^\circ$$

On the addition of a drop of ammonia this rose in one day to + 1.53°.

$$[\alpha]_D^{15} = 110.4^\circ.$$

This is obviously maltose heptacetate, for which Hudson[1] gave the following figures.

M.P./

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1. J.A.C.S., 1916, 38, 1871.

M.P. = 181°C. after sixteen recrystallisations from chloroform + ether.

$[\alpha]_D^{20} = 678^\circ$ rising to $+ 111^\circ$.

(Initial rotation = 78·0°)

The acetyl content was found by boiling with $\frac{N}{4}$ sulphuric acid for four hours. Found = 47.15%, theoretial = 47.36%.

The formation of maltose heptacetate may be due to traces of water present in the chloroform, and probably could be eliminated by very careful drying, and also by the use of smaller quantities of reagents.

STAGE III. HEPTACETYL METHYL MALTOSIDE.

26 grm. dry acetonitromaltose was dissolved in 500 c.c. absolute acetone free methyl alcohol, and a drop of pure dried pyridine added.

When solution was complete 80 gm. barium carbonate which had been well dried at 200°C. for several days was introduced, and the whole boiled for 12 hrs. under the reflux on the water bath, after which time a filtered sample of the solution was almost without action on Fehlings solution. After filtering off any excess of barium salts, the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with ether, and after shaking successively with dilute hydrochloric acid, sodium bicarbonate and water, the etheral extract was dried over anhydrous sodium/

sodium sulphate. On standing crystals of heptacetyl methyl maltoside were found in good yield. The product was recrystallised twice in alcohol.

Yield 15 grm. M.P. 128°C.

A 2.5% chloroform solution gave a rotation of + 2.69° at 15°C. in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{15} = + 53.6^\circ$$

Koenigs and Knorr found M.P. = 129°C, while Hudson[1] gave the rotation as $[\alpha]_D$ = 53.8° in chloroform.

STAGE IV. METHYL MALTOSIDE.

15 grm. heptacetyl methyl maltoside was dissolved in 150 c.c. absolute methyl alcohol by heating, and dry ammonia passed in at 0°C. till the solution was saturated.[2] After standing twenty-four hours at room temperature, the alcohol and any acetamide that had been formed were removed under reduced pressure at 50°C.

The resulting mass was crystallised from absolute alcohol to which a little ether had been added, and 3.8 grm. of methyl maltoside hydrate were obtained.

M.P. 105°C.

A 1.3548% aqueous solution gave a rotation of + 2.05° in a 2 dcm. tube at 20°C. using sodium light.

$$[\alpha]_D^{20} = + 76.79.$$

On/

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[1] J.A.C.S., 1916, 38, 1870.

[2] Helferich and Becker, Annalen, 1924, 440, 17.

On saturating with baryta or strontia the rotation fell slightly, i.e. to + 2.03°.

$$[\alpha]_D^{20} = 74.91°.$$

Lime produced no change, and no compounds of the maltoside with the alkaline earths could be isolated. This fall in the rotation may be regarded as due to impurities. The maltoside was now recrystallised several times from alcohol and a little ethyl acetate. The loss is great however, and a final yield of .5 gm. was obtained. After drying two days in a vacuum at 100°C. it was found that a 1% solution gave a rotation of + 1.65° in a 2 dcm. tube at 15°C. using sodium light.

$$[\alpha]_D^{15} = +82.5°.$$

No trace of a lime methyl maltoside could be isolated with the purified substance. The calculated value for the rotation of β methyl maltoside is

$$[\alpha]_D = +85°.$$

LIME LACTOSE.

A sample of monolime-monolactose was prepared by the same method as was used for lime glucose. The yield was about 50% theory. The compound is probably hydrated, but to what extent was not possible to determinate.

Dehydration, however, gave a compound which corresponded in composition to monolime-monolactose $C_{12}H_{22}O_{11}$ CaO or $C_{12}H_{22}O_{11}$ CaO H_2O and not to $C_{12}H_{20}O_{11}CaO$, as has been claimed by Dubrunfaut.

Wt. of Crucible = 17.5156 grm.
Wt. of Crucible + Compound = 17.6620 grm.
Wt. of Crucible + lime = 17.5360 grm.
% lime = 13.93

$C_{12}H_{22}O_{11}$ CaO requires CaO = 14.07%

$C_{12}H_{22}O_{11}$ CaO H_2O requires CaO = 13.46%

Lime Lactose is a white amorphous earth, and readily decomposes on standing in the presence of moisture. If it is thoroughly dry, however, it may be preserved for weeks without appreciable change.

An attempt was made to find the solubility by shaking a dried sample of the compound with conductivity water at 15°C. for five hours, but as decomposition almost invariably set in the result cannot be regarded as other than an approximation.

10 c.c./

10 c.c. saturated solution required 7.2 c.c. .1296 N. hydrochloric acid for neutralisation, using phenolphthalein as indicator.

Solubility = 18.58 grm. per litre.
This solution gave a rotation of + 1.70° at 15°C. in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{15} = + 46.06^\circ$$

HIGHER LIME LACTOSES.

No higher lime lactoses were encountered.

β METHYL LACTOSIDE.

β Methyl lactoside was prepared by Ditmar[1] but he did not find its rotation, which Hutson[2] calculated as + 6° in water. The rotation of the intermediate products also by no means agreed with the calculated value. However, the same method was used in the present research.

STAGE I. ACETOBROMOLACTOSE.

A sample of acetobromolactose was prepared by the method of Dale[3].

25 grm. powdered anhydrous lactose was dissolved in/

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1. Monatsh., 1902, 23, 865.
2. J.A.C.S. 1916, 47, 277.
3. J.A.C.S., 1916, 38, 2187.

in 125 c.c. acetic anhydride saturated with hydrobromic acid at room temperature. Much shaking was necessary to maintain the reaction within bounds. All the lactose dissolved and the resulting straw coloured solution was cooled, mixed with 300 c.c. chloroform, washed with water, sodium bicarbonate, and water once more, and then dried over anhydrous sodium sulphate. The solution was then evaporated to a thick syrup at 50°C. under reduced pressure, precipitated with petrol ether, and crystallised by stirring in an ice bath. The crystals were then filtered off and recrystallised from dry ether.

Yield 60% theory. M.P. = 140°C.

A 1% solution in chloroform gave a rotation of $+ 2.13^{\circ}$ in a 2 dcm. tube at 20°C. using a sodium light.

$$[\alpha]_D^{20} = + 106.5.$$

E. and H. Fischer[1] found M.P. 143-144°C, and $[\alpha]_D^{20} = 104.9^{\circ}$.

The above compound, however, would not permit of further purification.

STAGE II. HEPTACETYL METHYL LACTOSIDE.

25 grm. dried acetobromolactose crystals were dissolved in 300 c.c. anhydrous methyl alcohol, and boiled with dry freshly precipitated silver carbonate for/

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[1] Ber., 1910, 43, 2521.

for 48 hrs., when it was found that no bromine was present in the solution. After filtering off the excess of silver salts, and evaporating to dryness under reduced pressure, the resulting product was dissolved in the minimum amount of benzene, and, after filtering to remove any traces of inorganic matter, precipitated with petrol ether. On cooling in the ice bath and stirring vigorously the syrupy mass became sufficiently solid to permit filtration. It was then dissolved in alcohol and reprecipitated by cold water, when it was found to be without power to reduce Fehling's solution. The substance simulated the crystalline state very closely when dry, but was not actually crystalline, and could not be obtained so, although Ditman claimed to have got crystals.

A 1% solution in chloroform at 15°C. in a 2 dcm. tube using sodium light gave a rotation of - .16°.

$$[\alpha]_D^{15} = -8^\circ.$$

According to Hudson[1] $[\alpha]_D = -15^\circ$. The result obtained by Ditman was - 6°. Several other samples prepared as above gave varying results some even having a positive rotation. It should be noted that the compound failed to crystallise.

M.P. 79°-80°C. sintered, melted at 113°C.
Ditman found 76°-77°C sintered, melted at 110°C.

[1]. J.A.C.S., 1925, 47, 277.

STAGE III. METHYL LACTOSIDE.

Heptacetyl methyl lactoside was deacetylated by the same method as was used for heptacetyl methyl maltoside.

From 10 gms. heptacetyl methyl maltoside 3 grm. methyl lactoside was obtained in the form of a thick syrup which when dried became a brittle glass. The lactoside did not reduce Fehlings solution. It could not be obtained crystalline, however, and the rotation was considerably greater than the calculated value of Hudson.

A 5% solution gave a rotation of $+ 1.20^\circ$ at 15°C. in a 2 dcm. tube using sodium light.

$$[\alpha]_D^{15} = + 12^\circ.$$

M.P. = 173°C.

Ditman found M.P. = 171°C. He did not give any value for the specific rotation.

The rotation was not influenced by baryta, strontia, or lime.

Another and presumably less pure sample gave a specific rotation of $+ 20^\circ$. It also was uninfluenced by the alkaline earths.

No alkaline earth methyl lactosides could be isolated. Thus the impurity of the lactoside was immaterial for the present research.

:1732/

.1732 grm. lactoside gave .2625 gm. Carbon dioxide and .1063 grm. water.

C = 41.33%

H = 6.87%

$C_{12}H_{21}O_{11}$ CH_3 H_2O requires

C = 41.70%

H = 7.00%

.2020 grm. lactoside gave .1203 grm. Silver Iodide.

OCH_3 = 7.8%

$C_{12}H_{21}O_{11}$ CH_3 H_2O requires OCH_3 = 8.29%.

DOUBLE SALTS.

Gunning[1] prepared samples of double salts of sucrose with organic acid salts by mixing solutions containing one molecular proportion of a potassium salt of an organic acid with solutions containing one molecular proportion of sucrose. He obtained thick uncrystallisable syrups which dialysed freely.

Potassium acetate sucrose and potassium citrate sucrose were accordingly prepared by mixing one molecular proportion of potassium acetate and one molecular proportion of potassium citrate with one molecular/

[1] N.Z. Rubenzuckerind., 21, 338.

molecular proportion of sucrose in aqueous solution. Both double salts yielded thick non-crystalline syrupy masses.

The preparation of definite crystalline double salts was more difficult. According to Lippmann[1] Maumené claimed to have prepared double salts of lactose, but subsequent workers have been unable to repeat his work.

An attempt was made to isolate potassium acetate lactose by adding one molecular proportion of potassium acetate to a concentrated solution of lactose in water. On evaporating either in the air or over concentrated sulphuric acid, crystals of lactose were obtained, and on further concentration, the potassium acetate began to crystallise also.

Similar results were obtained in the case of lactose and potassium chloride, and no trace of any double salt could be found.

One molecular proportion of sucrose was dissolved in the minimum amount of boiling water, and added to a saturated and boiling solution containing one molecular proportion of potassium chloride. On cooling in a vacuum over concentrated sulphuric acid, crystals of the double salt were obtained. (Violette[2])

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1. Lippmann. Chem. der. Zuckerarten, (1904), 2, 1575.
2. Compt. rend., 1873, 76, 485.

The following analytical data were obtained:-

Wt. of Crucible = 17.5105 grm.

Wt. of Crucible + Sucrose potassium chloride. = 18.0208 grm.

Wt. of Crucible + potassium chloride = 17.6181 grm.

% Kcl = 21.10.

$C_{12}H_{22}O_{11}$ Kcl $2H_2O$ requires Kcl = 21.14%.

The percentage chlorine was found using silver nitrate and potassium thiocyanate.

One grm. compound was equivalent to 22.12 c.c. .1003 N. Silver nitrate.

∴ One grm. contained 22.12 x .1003 x 35.5/1000 grm. chlorine.

∴ One grm. contained .7860 grm chlorine.

∴ % Chlorine = 78.60.

$C_{12}H_{22}O_{11}$ Kcl 2 H_2O requires Chlorine = 78.76%.

DIFFUSION.

In order to test the colloidal nature of trilime-monosucrose a solution of that compound on conductivity water was placed in a collodion membrane and suspended in water in the absence of carbon dioxide. Diffusion occurred readily. Similar behaviour was met with in the case of the sucrose compounds of strontia and baryta. Thus when 20 c.c. of a saturated solution of monostrontia-monosucrose containing 9.93 grm. strontia/

strontia and 32.8 grm. sucrose per litre at 15°C. was suspended in a collodion membrane in 50 c.c. conductivity water for twenty-four hours, it was found that 10 c.c. of the solution of monostrontia-monosucrose was neutralised. 2.6 c.c. .121 N. hydrochloric acid using phenolphthalein as indicator

∴ Concentration of Strontia = 1.746 grm. per litre.

When the excess of alkali was precipitated by oxalic acid this solution gave a rotation of + 2.20° in a 2 dcm. tube at 15°c. using sodium light.

∴ Concentration of Sucrose = 15.0 grm. per litre.

Thus in the original solution the ratio of sucrose to strontia was 32.8 ÷ 9.93 = 3.3, and after dialysis this has risen to 15.0 ÷ 1.746 = 8.6. It will therefore be seen that the basic portion dialyses considerably faster than the sucrose portion of the compound. This separation has already been observed for the double salts of sucrose.

A similar experiment was carried out using baryta sucrose.

20 c.c. of a saturated solution of monobaryta-monosucrose containing 13.80 grm. sucrose and 6.20 grm. baryta per litre at 15°C. was suspended in a collodion membrane in 50 c.c. water for twenty-four hours;it was found that 10 c.c. of the monobaryta-monosucrose solution required 3.50 c.c. .1210 N hydrochloric acid for/

for neutralisation, using phenolphthalein as indicator.

∴ Concentration of baryta = 2.53 grm. per litre.

The rotation of a precipitated solution in a 2 dcm. tube at 15°C. using sodium light was + .86°.

∴ Concentration of Sucrose = .630 grm. per litre.

Thus the proportion of sucrose to baryta which was originally 13.80 ÷ 6.2 = 2 has now risen to

6.30 ÷ 2.530 = 2.5.

The membranes used in the above experiments were tested with various colloidal solutions, such as silver and gold sols, and gelatine, and were found to be impermeable to them.

DISCUSSION.

It would appear that the compounds formed by the union of sugars with the alkaline earths are not so numerous as has been claimed by previous investigators.

In the case of sucrose only three lime sucrose compounds could be isolated and the existence of any others is improbable.

Monolime-monosucrose was prepared as a hexahydrate and also as a dihydrate, but the compound is certainly unstable and is probably decomposed by slight temperature rises if it actually exists at all, for its behaviour would point to its being really a mixture of sugar and dilime-monosucrose.

Dilime-monosucrose and trilime-monosucrose were found to be hexahydrates. In the past these compounds have been considered as containing three or at the most four molecules of water of crystallisation, and, as the water content seems to vary with the time of drying, the existence of the hexahydrates cannot be claimed with certainty. The amorphous nature of these compounds makes removal of the adherent water without affecting the water of crystallisation a matter of difficulty. The lengthy time of complete dehydration may also account for the low values obtained for their water content in previous investigations.

The/

The strontia sucroses, on the other hand, exist as microscopic crystals and are therefore more easily handled than the lime sucroses.

Monostrontia-monosucrose was found to have a water content slightly above that required for the pentahydrate, while the strontia content was almost the theoretical value required for the hexahydrate. It is probable complete dehydration is difficult, while partial dehydration occurs readily.

Distrontia-monosucrose was completely anhydrous. No other strontia sucroses were encountered.

Only one baryta-sucrose was met with, and all the usual methods of preparation yielded only monobaryta-monosucrose, which is an anhydrous crystalline powder. Glucose, fructose, maltose and lactose were found to unite with lime to form a mono compound only.

Monolime-monoglucose was prepared as a dihydrate, but all attempts to isolate a hexahydrate were unsuccessful.

Monolime-monofructose, on the other hand, gave two crystalline hydrates, the hexahydrate and the dihydrate, which could be obtained with ease.

The water content of monolime-monolactose and monolime-monomaltose was doubtful; but all these four compounds retained at least ½ a molecule of water which could not be eliminated, although it did not seem to influence the stability of the compounds, which/

which could be kept over long periods, whereas in the presence of water they invariably decomposed overnight. It is probable that we really have a molecule of water in the oxonium position, as in glucose hydrate, where Armstrong[1] supposes the water molecule to form an oxonium compound.

It should be noted that the composition of lime lactose corresponded to $C_{12}H_{22}O_{11}$ CaO and not to $C_{12}H_{20}O_{11}Ca$, as was suggested by Dubrunfaut.

As has been already mentioned, combinations of lime with glucose and fructose which contain more than one molecule oxide to one of sugar are said to have been prepared at various times, though that they are true compounds is doubtful. Maltose and lactose, probably because they have not been the subject of so much research as the commoner sugars, are given as forming only one compound with lime.

Owing to its practical utility in the preparation of fructose, the union of lime with that sugar has been studied somewhat extensively, and with widely different results. The present research revealed only one definite compound, viz. monolime-monofructose, but a so-called trilime-monofructose was prepared by shaking lime with fructose solution at - 5°C., and allowing the temperature to remain at about 0°C. for 24 hours, when fine crystals were obtained.

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[1] Simple Carbohydrates and Glucosides, 1924, 42.

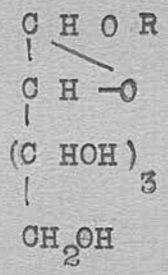
A great objection to this method is that, lime being more soluble in cold fructose solution than in hot, as the temperature rises from -5°C. to 0°C. lime itself may be precipitated as well as lime fructose. That this was actually the case was supported by microscopic examination, which revealed crystals strongly resembling those of monolime-monofructose, embedded in less definite crystals, and by the fact that on grinding with alcohol a residue of high lime content remained.

On an analogy with sucrose, fructose would be expected ~~by~~ to yield a trilime compound by heating a lime fructose solution to about 70°C. As alkalis attack reducing sugars even at moderate temperatures, such a procedure is clearly impossible. It was thought, however, that if the reducing group were protected, it might be possible, by boiling a solution of lime in such a non-reducing sugar solution, to precipitate a lime sugar compound without fear of decomposition. The glucosides of the reducing sugars are well known to resist decomposition in the presence of alkalis, and there seemed no reason why they should not react with lime without the troublesome enolisation which takes place for the sugars themselves. The glucosides are also the simplest disaccharides, and their behaviour with lime should throw light on the probable structure of lime sucrose. Before going further, the previous theories/

theories as to the structure of the lime hexoses must be considered.

The constitution of the compounds formed by the union of the alkaline earths and sugars is not understood. In the case of glucose the formation of the saccharins in alkaline solution suggested that the aldehydic group was at least influenced by the alkali.

From a consideration of the fact that alkali glucose compounds, such as the sodium derivative, and also glucosides, the formula of which was then not known, did not react with phenylhydrazin, Schunck and Marchlewski[1] suggested that both types of compounds could be represented by a formula such as



It must be noted[2] however, that the failure of the alkaline earth derivatives of glucose to unite with phenylhydrazin is of little significance, for the structure of metallic derivatives frequently differs from that of their parent compound, and also that small/

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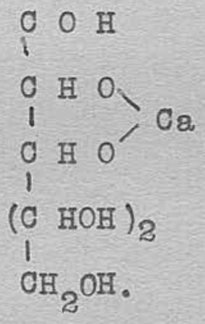
[1] Ber., 1893, 26, 2928.
[2] Lippmann Chem. der. Zuckerarten, (1904), 2, 1690.

small quantities of alkali greatly hindered the union of glucose and phenylhydrazin, although very little alkali glucose compound was formed.

There thus was no experimental evidence for the suggestion of Schunck and Marchlewski.

Maquenne[1], however, has put forward a similar constitution for monolime-monofructose; but these formulae failed to explain the constitution of the numerous other compounds of glucose and fructose with lime that were supposed to exist. Herzfeld[2], on the other hand regarded these compounds as loose compounds of the alcoholate type.

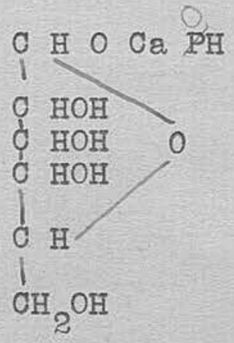


In the present research it was found that neither α nor β methyl glucosides formed compounds with the alkaline earths, and β methyl fructoside showed similar behaviour.

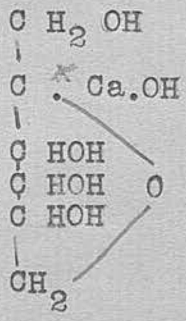
Thus it would seem that it is the reducing group of the hexose which possesses the property of uniting with metallic oxides, and that the hydroxyl groups are comparatively inactive. In order to permit this, a close/

[1] Lippmann Chem. der Zuckerarter, (1904), 1, 882.
[2] Z. Ver. deut. Zuckerind., 44, 293.

closedchain structure must be regarded as existing in the hexoses



Lime glucose.



Lime fructose.

As there is only one labile hydrogen atom it is to be expected that only one molecule of lime can react with it splitting off water to give a lime glucose compound. When this labile hydrogen is replaced with a non-labile group, as in the glucosides, no interaction can take place between the sugar and the metallic oxide.

It may seem strange that the remaining hydroxyl groups do not unite with lime to give other lime sugar compounds, but it must be remembered that the lower alcohols, such as ethyl and methyl alcohol, do not unite with lime in aqueous solution, and they would be expected to be more reactive than a hexose.

The decomposition by alkali of methylated hexoses which still contain a free reducing group such as tetramethyl glucose[1] is in harmony with this suggestion.

If alkalis unite only with the reactive group in a hexose, it would be expected that on methylation of glucose/

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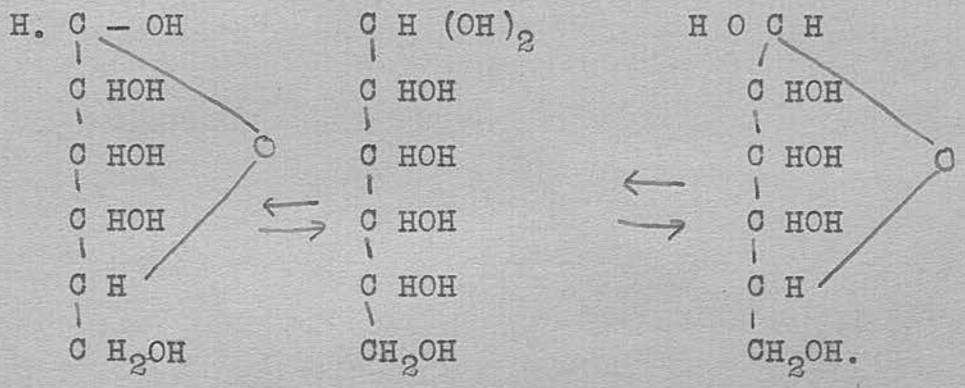
1. Wolfrom and Lewis, J.A.C.S., 1928, 50, 837.

glucose with sodium hydroxide and dimethyl sulphate, methyl glucoside would be the first produce of the reaction. When all the glucose had been transformed into glucoside, then either no further action would take place, or else momentary combination between the remaining hydroxyl groups and the alkali would enable complete methylation to occur.

Maquenne observed that when glucose was methylated the reactive group interacts first, and β methyl glucoside may be isolated; further methylation resulted in the formation of the pentamethyl compound.

Indeed, that the methylation of glucose occurs in this manner is essential for the interpretation of Lowry's[1] theory of mutrarotation in terms of fact.

According to Lowry's view the change is represented by the scheme of equilibrium:-



Lowry holds that an aqueous solution of glucose contains a considerable proportion of the open chain/

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[1] J.C.S., 1903, 83, 1314-1323.

chain form. If all the hydroxyl groups reacted with alkali with equal readiness it would be expected that on methylation the open chain form would yield heptamethyl glucose or at least hexamethyl glucose, whereas penta methyl glucose is actually obtained. This can be explained by the fact that the glucose and alkali first interact at the reducing group, and that when the alkali there is replaced with a methoxy group, the resulting methyl glucoside, which has a closed ring structure, is further methylated to give the pentamethyl derivative.

As the alkaline earth molecule is attached to the reducing group, these compounds must be in the nature of glucosides, and should therefore exist in α and β forms, though no trace of any such differentiation can be observed.

As methylation of glucose with potassium hydroxide and dimethyl sulphate gave the β Compound only, it might be assumed either that the lime glucosides are the β isomers, or that an equilibrium of α and β exists, but that the β reacts with the dimethyl sulphate first, any α then passing over instantaneously into the β to replace what has been removed, so that only β glucoside is produced. That the latter suggestion is the case is what would be expected from a consideration of the properties of methyl glucoside, glucose or hydrogen glucoside, and lime glucoside. Methyl glucoside/

glucoside does not show mutarotation, a solution of glucose, whether α or β, gradually changes to an equilibrium mixture of both forms, and with lime glucoside any change takes place so rapidly that it cannot be observed. Thus when the methyl group of methyl glucoside is replaced by hydrogen the tendency of the sugar to undergo isomeric change is greatly increased. In the same way when the hydrogen is replaced by a - Ca.OH. group the isomeric change becomes very rapid indeed. It is therefore probable that lime glucoside exists not as β lime glucoside but as a mixture of the α and β forms.

It was thought that in nonaqueous solution mutarotation might not be so rapid, and an attempt was made to prepare a solution of lime glucoside in a number of organic solvents; but it proved most insoluble except in water. The rapid mutarotation of glucose in the presence of organic bases such as pyridine[1], or when dissolved in formamide[2], would lead us to suspect that these bases also unite with the hexoses to form some sort of a labile glucoside, although the reaction is generally considered as due to the formation of oxonium compounds.

In order to complete the study of the lime glucosides, and also to obtain an idea of what might occur/

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1. Lowry and Faulkner J.C.S., 1925, 2883.
2. Mackenzie and Ghosh. Proc. Roy. Soc. Edin., 1914, 35, 22.

occur in the case of disaccharides, methyl maltoside and methyl lactoside were prepared. Only the β forms are known, and methyl lactoside could not be obtained pure. No compounds of either the maltoside or the lactoside with alkaline earths could be isolated, thus making it very probable that monolime-monomaltose and monolime-monolactose, or more properly lime maltoside and lime lactoside, are the only compounds these sugars form with lime. The work of Haworth[1] on the methylation of maltose and lactose revealed that, as in the case of glucose, the reducing group was methylated first.

It might be argued that α methyl maltoside and α methyl lactoside would interact with the alkaline earths, although their β isomers do not. However, Michaelis[2] found that the dissociation constant K of α methyl glucoside $= 1.97 + 10^{-14}$, and for β methyl glucoside $K = 2.64 \times 10^{-14}$. In other words, the β isomer is more acidic than the α, and presumably should be more ready to react with alkali.

The case of sucrose must now be considered.

From the previous results it would be expected that sucrose, which is a glucoside containing no reducing groups, would not unite with the alkaline earths. That sucrose does so is perhaps its best known/

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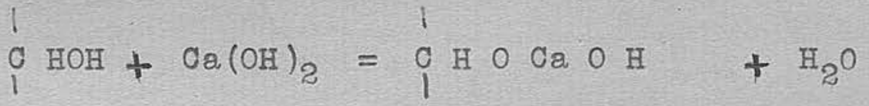
1. J.C.S., 1918, 113, 188; 1919, 115, 813.
2. Ber., 1914, 46, 3683-3693.

known and most important property, which is verified daily in the manufacture of sugar.

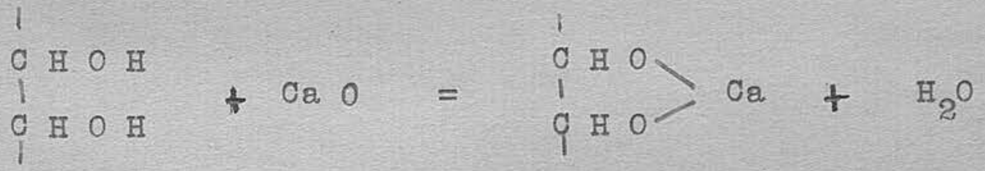
The previous explanations of this reaction are now considered.

The early school of sugar chemists, men such as Peligot, Soubeyran, Herzfeld knew little of the structure of sucrose except that it was the product of a molecule of glucose uniting with a molecule of fructose to give a non-reducing disaccharide containing eight hydroxyl groups. There are therefore small temptation to assign any definite structure to the alkaline earth sucroses. It became generally accepted[1] however, that the alkaline hydroxide interacted with sucrose splitting of one molecule of water to give an alcoholate, viz.



$$\mathrm{C\,HOH} + \mathrm{Ca(OH)_2} = \mathrm{C\,H\,O\,Ca\,O\,H} + \mathrm{H_2O}$$

Sometimes the action was regarded as taking place between a molecule of oxide and a molecule of sucrose viz.



$$\begin{matrix}\mathrm{C\,H\,O\,H}\\ |\\ \mathrm{C\,H\,O\,H}\end{matrix} + \mathrm{Ca\,O} = \begin{matrix}\mathrm{C\,H\,O}\\ |\\ \mathrm{C\,H\,O}\end{matrix}\!\!>\mathrm{Ca} + \mathrm{H_2O}$$

and Compounds of the type $C_{12}H_{20}O_{11}$ were obtained. The position of the hydroxyl groups which took part in the reaction was not known, but there seemed no reason why they should not all interact with the alkaline/

[1] Herzfeld. Z. Ver. deut. Zuckerind., 44, 293.

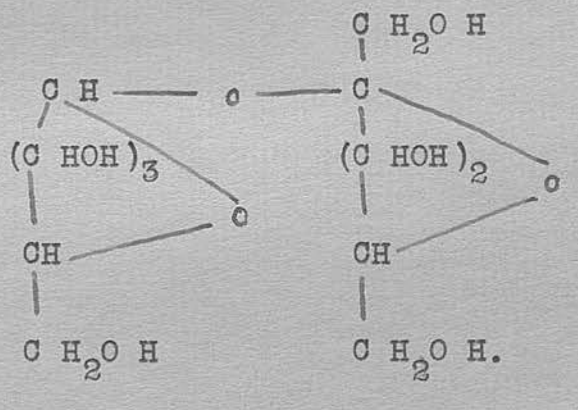
alkaline earths, to give compounds containing from one to eight molecules of alkali. A number of supposed compounds formed in this way have been mentioned in the introduction.

This theory appeared to supersede the earlier views of Peligot and Stromeyer, which will be considered later.

A modern development doubts true combination between sucrose and lime, and implies the formation of a colloid.

These two theories will now be dealt with in turn.

Although it was found that methyl glucoside and methyl fructoside did not unite with the alkaline earths, it might be expected that when the methyl group of a glucoside was replaced by a much larger molecule of the type of another sugar, then the properties of the glucoside would so be changed as to admit such interaction. From a consideration of the present day formula of sucrose



the formation of mono, di, and tri compounds could be/

be regarded as due to the substitution of the three primary hydroxyl groups. However, Purdie and Irvine[1] found that on alkylation of sugars by means of silver oxide and methyl iodide, the primary groups probably proved most difficult to methylate, and therefore must be considered as least prone to unite with a metallic oxide. The existence of compounds of the type $C_{12}H_{20}O_{11}$ Ca. is not in harmony with the experimental results obtained for the composition of such compounds, even after drying long periods.

If the replacement of the methyl group of a glucoside with a larger molecule, brings about a change in properties, then glucosides of the type of maltose and lactose, which are 6 glucose α glucoside and 5 glucose β galactoside respectively, should unite with the alkaline earths.

They were found to do so, but the reaction is due solely to the introduction of a reducing group with the glucoside, and not to any alteration in the properties of the original glucose residue, for when the reducing group is masked as in methyl maltoside and methyl lactoside the power to unite with the alkaline earths was found to disappear.

We are now reduced to the supposition that the abnormal properties of sucrose are due to the fact that/

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[1] J.C.S., 1903, 83, 1024.

that it contains labile fructose, but it is doubtful whether this can explain the formation of these compounds.

Trehalose, which has a normal structure, was found by Schukow[1] to unite with lime.

As the "alcoholate" theory was proved unsatisfactory, the colloidal theory will now be considered.

It has already been mentioned that Petit's[2] work on heat of formation gave no indication of the existence of trilime-monosucrose, and that the experiments of Dedek[3] on the influence of sucrose on aqueous solutions of calcium hydroxide was in agreement with this. Sen and Dhar[4] suggested that various colloidal metallic hydroxides were peptised by sucrose and Waterman and Aken[5] applied this to lime. It is well known that of a given substance in molecular solution, at a given temperature and in a given solvent, a fixed quantity is dissolved, which is independent of the quantity of substance at the bottom. This does not hold with colloids, and Von Buzagh[6] pointed out that the solubility increased with the quantity of gel to a maximum, so that with very large quantities of gel, the peptisability of the colloidal substance decreased.

Waterman and Aken produced results showing that/

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[1] Z. Ver. deut. Zuckerind., 50, 818.
[2] Compt. rend., 1893, 116, 823.
[3] Z. Zuckerind, Czechoslov., 1925, 26, 349.
[4] Kolloid Zeit., 1923, 33, 193.
[5] J.C.S.I., 1927, 46, 411.T.
[6] Kolloid Zeit., 1927, 41, 169.

that this effect may be observed by the action of sucrose solution on lime.

There is absolutely no reason to suspect that the compounds which sucrose forms with lime in any way differ from those of sucrose with strontia or baryta. Now both strontia sucrose and baryta sucrose are definite crystalline compounds, so there is really no inherent reason why lime should not act on sucrose in the same way to give true compounds, even though these have not yet been obtained in a crystalline form. The fact that lime and sucrose unite in molecular proportions also supports this.

The difficulty with which trilime, monosucrose and dilime-monosucrose were dehydrated was precisely what would be expected from colloids; but it must be remembered that the process was carried out at 100°C, while copper sulphate crystals only lose their final molecule of water at 200°C, and sugars like maltose and lactose give up their water of crystallisation very slowly.

On the other hand, physical data favours the colloidal theory, and the work of both Petit and Dedek pointed to the non-existence of trilime-monosucrose. It may be, however, that this compound is not formed under the conditions of their experiments. Compare distrontia-monosucrose, which was found to decompose in cold water.

In/

In the experiments of Waterman and Aken lime was added to a sucrose solution with stirring, samples of the solution being removed periodically and filtered, while now and then fresh portions of lime were added. The effects of the quantity of lime added on the lime content as well as the sucrose content of the filtrate were found, and the results were in agreement with the maximum solubility phenomenon.

A great objection to their work is that the experiments extended over a period less than 300 hrs. The interaction of lime and sucrose is not rapid, so that in the short time allotted for the work no true equilibrium was reached, and variations would appear in the solubility, which would depend on the concentrations of the components of the solution.

Similarly, the lime sucrose precipitate was obtained by allowing lime sucrose solutions to rise in temperature from 0°C. to 25°C. This is not comparable with the usual practice, where precipitation is brought about by boiling.

If the action is one of peptisation, then the passing of lime into sucrose solution should result in the formation of a sol.

Aten, Ginneken, and Engelhard[1] found that the conductivity of such solutions was consistent with complete/

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[1] Rec. trac. Chim., 1926, 45, 753.

complete dissociation when dilute, though more concentrated solutions, especially of calcium hydroxide, gave low values. The effect of sucrose on the conductivity of calcium hydroxide solutions was determined in the present research, and results agreeing with those of the above mentioned experimenters were found. The decrease in the conductivity may be due to the presence of undissociated molecules of mono, di, or tri lime sucroses, or alternatively to the existence of colloidal particles; but if the action is one of peptisation it is strange that a colloidal solution should not be obtained in all cases.

Lime sucrose compounds were also found to dialyse readily through collodion membranes. Thus their solutions cannot be colloidal unless it is stipulated that a mixture of crystalloid and colloid exist in equilibrium, which is improbable.

The acceptance of the colloidal theory, however, would go far to explain the divergences met with in the work of previous investigators.

It is probable that lime sucrose may exist in colloidal form; that it must do so has yet to be proved.

Both the colloidal theory and the theory of alcoholate formation have now been considered, and both seem unsatisfactory. But there is another possibility which cannot be neglected.

It is well known that in the manufacture of sucrose/

sucrose from plant juice a residue of molasses is obtained, from which finally no more sugar can be extracted. The exhausted molasses, however, contains considerable quantities of sucrose which cannot be extracted in the usual way as it is fixed, i.e. combined with the potassium salts of organic acids to give compounds not readily decomposed.

Sucrose potassium chloride[1] $C_{12}H_{22}O_{11}$ Kcl $2H_2O$ is of the same type, and is a definite crystalline salt. Maumené[2] pointed out that no replacement of the hydroxyl groups occurs, and that the compound is one of addition and not substitution. The union is therefore of a different type from that of the hexoses with the alkaline earths, and is probably due to residual affinity.

As has already been said, sucrose contains no reducing groups and therefore should not unite with the alkaline earths. It is therefore suggested that the combination which does take place is of an entirely different nature from that which occurs when a reducing sugar interacts with bases, and is of the same type as the union of sucrose and a salt such as potassium chloride.

That this is the case was maintained by Peligot and Stromeyer[3], who, however, regarded some of the compounds of sucrose with bases as substitution compounds./

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1. Compt. rend., 1873, 76, 485.
2. Bull. Soc. Chim., 1873, II, 19, 289.
3. Z. Ver. deut. Zuckerind., 37, 959.

compounds. Other Chemists grouped all compounds of the alkaline earths with both monosaccharides and disaccharides together as purely additive. Little experimental evidence was produced to support their views, and the theory appears to have been superseded to a great extent by that of alcoholate formation.

It should be noted that the properties of the alkaline earth sucroses and the sucrose double salts are very similar. The ease with which sucrose may be obtained from its alkaline earth derivatives, as compared with the difficulty of preparation from the double salts, may be ascribed to the ease with which the base is converted into a salt which does not unite the sugar. Yet attention must be drawn to the fact that during the decomposition of lime sucrose solutions with carbon dioxide, partially carbonated compounds, containing sucrose, lime, and calcium carbonate are obtained.[1]

It was generally assumed that the carbon dioxide was replacing the vacant hydroxyl group of the lime sucrose, viz.

$$\overset{|}{\underset{|}{C}}\,H\,O\,Ca\,O\,H \;+\; C\,O_2 \;=\; \overset{|}{\underset{|}{C}}\,H\,O\,Ca.\;C\,O_3\,H.$$

There is no reason, however, why the action should not be supposed to proceed as though the only change is the conversion of the lime to calcium carbonate, and/

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1. Barreswill and Dubrunfaut, Annalen, 1851, 80, 344.

and this calcium carbonate forms with the sucrose a compound of exactly the same type as the original sucrose, which continues to exist as a double salt, notwithstanding the small tendency of these two substances to unite.

Sucrose double salts and sucrose bases show similar behaviour during dialysis.

It is now evident why methyl maltoside and methyl lactoside should fail to unite with the alkaline earths, for neither maltose[2] or lactose[3] form double salts themselves, and it is very unlikely that their methyl derivatives would do so.

The indecisive results of the methylation of alkaline earth sucroses may perhaps be attributed to the fact that the alkali does not replace any definite hydrogen group of the molecule.

On the other hand, it must not be thought that reducing sugars, such as the hexoses, cannot form double salts. In the case of sucrose the formation of the double salt may be regarded as due to the residual affinity of the entire molecule, while with the monosaccharides it may be regarded as due to the reactivity of the so-called aldehydic group. Where the combination is due to one reactive hydroxyl group, as/

[1] Boivin and Loiseau, Compt. rend., 1883, 97, 1139. (see previous page)
[2] Herzfeld, Annalen, 1883, 220; 210.
[3] Lambert. Compt. rend., 1889, 108, 1016.

as in the hexoses, the resulting compound might be distinguished from double salt formation brought about by the residual affinity of an entire molecule by being looked on as a salt containing glucose of crystallisation, just as it might contain alcohol of crystallisation. Such glucated salts should be more stable than those formed by the weak residual valency of sucrose. Geerlings[1] found this to be so, and was able to obtain crystalline sucrose from a solution of sucrose potassium acetate by the addition of glucose, which displaced the sucrose and combined with the acetate.

It is strange that maltose and lactose do not give double salts for it would be expected that, even if the residual affinity of the molecule did not enable them to do so, the reducing group would be called into play as in glucose. But no such action could be observed.

A number of solubilities and rotations of alkaline earth sugars have been determined. In the case of the reducing sugars, the compounds are not merely decomposed by carbon dioxide, but also by the alkali they themselves contain, so great accuracy cannot be claimed, while the smallness of the crystals of the sucrose derivatives appeared to cause variation in/

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1. Z. Ver. deut. Zuckerind., 45, 320.

in the solubility. With the exception of fructose, the rotation of the pure compound was found to be very similar to that obtained when the theoretical amount of alkaline earth was added to a sugar solution. In the case of fructose, concentration probably produces very marked effects, so that rotations obtained by extrapolation are of little value. Hence it is not possible to compare the rotation of the compound with previous results obtained at different concentrations.

SUMMARY.

1. Lime unites with glucose, fructose, maltose and lactose respectively to give one Compound only, consisting of one molecule of lime combined with one molecule of the sugar.

2. Lime fructose exists as a hexahydrate and dihydrate, lime glucose as a dihydrate, while lime maltose and lime lactose give only a monohydrate. When apparently completely dehydrated, these compounds retain from a half to one molecule of water.

3. As methyl glucoside, methyl fructoside, methyl maltoside and methyl lactoside do not unite with the alkaline earths, it is probably that the above lime sugars are formed by the interaction of the reducing group of the sugar with lime to give a 'lime glucoside' and water.

4. No trace of α and β forms can be encountered in the lime glucosides.

5. Sucrose unites with lime to give a monolime-monosucrose which exists as a hexahydrate and a dihydrate, but which may not be a true compound, and dilime-monosucrose and trilime monosucrose, which are probably hexahydrates.

Strontia/

Strontia and sucrose give monostrontia-monosucrose which is probably a hexahydrate, and distrontia-monosucrose which is anhydrous.
Baryta and sucrose yield only anhydrous mono-baryta-monosucrose.

6. It is suggested that the compounds of sucrose with the alkaline earths are neither alcoholates nor colloids, but of the same type as the double salts obtained when sucrose unites with potassium chloride.

The author wishes to express his indebtedness to Dr J.E. Mackenzie for his helpful suggestions and advice during the course of this work.
