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### ON SOME RECENT ADVANCES IN OUR KNOWLEDGE OF THE SUGAR GROUP.

BY WALTER J. SYKES, M.D., D.P.H., F.C.S., ETC.

(*Read at Meeting, June, 1890.*)

THE synthesis of the sugar group, a process so intimately connected as it is with the physiology of plant life, has naturally formed an attractive subject of investigation amongst chemists. Numerous attempts have been made from time to time to form these bodies synthetically, but hitherto only a small measure of success has attended the efforts made in this direction. Quite recently, Dr. Emil Fischer has solved this problem in a most brilliant and satisfactory manner, since he has not only synthesised from the elements glucose and the whole mannitol group of sugars, but has also discovered new members of this group, of the existence of which we previously knew nothing. His labours throw considerable light on the molecular constitution of the individual members of the group as well. My paper of this evening is a brief *resume* of his important work in this direction.

The ordinary hexa-hydric alcohol mannitol  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{CH}_2\text{OH}$ , obtained by extraction with alcohol from ordinary manna, yields upon limited oxidation with  $\text{HNO}_3$  a body very similar in its properties to glucose. It reduces Fehling, ferments in contact with beer yeast, and rotates the polarised ray to the right, though not to such a wide angle as glucose. This body mannose is the aldehyde of mannitol, and has the following constitution :— $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{COH}$ . Upon further oxidation with Br it yields the corresponding mannonic acid  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot \text{COOH}$ . If a solution of this

acid be evaporated to a syrupy consistence, a molecule of water is disengaged, and the lactone or anhydride of the acid produced  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}\cdot\text{2}(\text{CHOH})\cdot\text{CO}$ .

This body crystallises in stellate groups of colourless needles, melts at 149 to 153° C., and has a specific rotary power of  $[\alpha]_D + 53.81$ . Its solution has a neutral reaction; it, however, readily decomposes carbonates, and forms the corresponding mannonates.

Killiani some years since obtained by boiling certain gums with dilute  $\text{H}_2\text{SO}_4$  a penta-hydric aldehyde (sugar) to which he gave the name arabinose. This sugar upon treatment with HCN yields the cyan-hydrin, and this in its turn upon treatment with  $\text{Ba}(\text{HO})_2$  yields the acid of the alcohol of the next degree higher in the series. This he called arabinose-carboxylic acid; it has the same composition as the mannonic acid mentioned above. On evaporation the arabinose-carboxylic acid yields its lactone.

In this method of Killiani's we have obviously a method of passing up the alcohol series, from lower to higher, and to which I shall have to revert further on.

The lactones of the mannonic and arabinose-carboxylic acids have obviously the same structural formulæ, and are so similar in other respects that they must have been considered identical, had not their optical properties differed. Mannonic acid lactone polarises  $[\alpha]_D + 53.81$ , the other lactone  $- 54.8$ ; in other words, making allowance for experimental error, these two bodies possess equal and opposite optical activities, and may, therefore, be looked upon as two optically opposed isomerides like the dextro and lævo-tartaric acids. This is the first instance observed of the occurrence of such a relation in the sugar group. If such be the case, it is obvious that in a solution of equal quantities of the optically opposed lactones, combination ought to take place, and an inactive lactone be produced, as in the parallel case of the two tartaric acids, which under similar conditions unite and form racemic acid. The experiment was tried, and found perfectly successful; an inactive lactone was produced which could only be split up again into its optically opposed components under special conditions.

All these lactones by reduction with sodium amalgam can be converted first into their aldehydes (sugars), and by further reduction into the corresponding alcohols. Upon dissolving  $\text{BaCO}_3$  in a solution of the lactones, the Ba salt of the corresponding acid is produced, and from this salt the acid can be liberated. In this manner we obtain by reduction from mannonic acid lactone, the corresponding aldehyde (mannose), and the alcohol. These and the acid all polarise to the right. From arabinose-carboxylic acid lactone we obtain a similar series, all polarising to the left, from a mixture of the two lactones a series optically inactive. Hence there can be no doubt that arabinose-carboxylic acid lactone is left mannonic acid lactone, and for the remainder of the paper I shall designate it as such, and also the mixed lactone as inactive mannonic acid lactone.

It has been found that phenyl-hydrazine forms an important series of compounds with several members of the sugar group, and as one of these combinations has proved the key to the solution of the problem of the synthetical formation of the sugar group, it will be advisable to devote a few minutes to a description of these compounds.

Phenyl-hydrazine is a body having the composition  $\text{Ph}^* - \text{NH} - \text{NH}_2$ ; it possesses

\*  $\text{Ph} = \text{C}_6\text{H}_5$ , the symbol for the radical of benzene.

basic properties, and readily unites with HCl and acetic acids. It forms with aldehydes and ketones a class of stable bodies [thus with aldehyde the following reaction takes place:  $-\text{CH}_3\text{COH} + \text{Ph} - \text{NH} - \text{NH}_2 = \text{Ph} - \text{NH} - \text{NCH}(\text{CH}_3) + \text{H}_2\text{O}$ .] When added to an aldehyde member of the sugar group in the proportion of one molecule to one molecule, an exactly similar reaction takes place. Thus, if one molecule of the aldehyde mannose be added to one of phenyl-hydrazine, the compound  $\text{C}_{12}\text{H N}_2\text{O}_5$  is formed. To this series of bodies Fischer gives the name phenyl-hydrazones or more shortly hydrazones. They are for the most part colourless bodies, mostly soluble in water, and are occasionally of diagnostic value. Under the influence of strong HCl they split up into phenyl-hydrazine and the original aldehyde (sugar).

When, however, three molecules of phenyl-hydrazine are added to one molecule of an aldehyde or ketone sugar, the following reaction takes place:  $3\text{C}_6\text{H N}_2\text{H} + \text{C}_6\text{H O}_6 = \text{C}_1\text{H}_{22}\text{N O}_4 + \text{C}_6\text{H} \cdot \text{NH}_2 + \text{NH}_3 + 2(\text{H}_2\text{O})$ . In this reaction phenyl-hydrazine plays the part of an oxidiser, two atoms of H being removed; these are not evolved as gas, but react upon the third phenyl-hydrazine molecule, forming aniline and  $\text{NH}_3$ . To this series the name phenyl-glucosazone or shortly glucosazone has been given. They are difficultly soluble bodies, and are extremely useful in the isolation and recognition of the various members of the sugar group, their melting points, solubility, and crystalline forms, differing. They rotate the polarised ray in the reverse direction to that which the aldehyde of the same series does, and may in this way be used for the purposes of discrimination.

Thus if 0.1 gram. of R. mannose-glucosazone be dissolved in 1 c.c. of strong HC, immediately added to 5 c.c. water and tested in a 10 decimetre tube, it will turn the ray 1.20 to the left.\*

A phenyl-glucosazone treated with strong HCl is resolved into phenyl-hydrazine and a body having the composition  $\text{C}_6\text{H}_{10}\text{O}_6$ , that is, containing two atoms less H than the original sugar. For this class the name glucosone, or, more shortly, osone, has been proposed. They polarise weakly in an opposite direction to the aldehyde sugar of the series to which they belong.

Upon acting on an osone with Zn dust and acetic acid, two atoms of H are attached, and the lævulose belonging to the series is formed. The lævuloses have the formula  $\text{CH}_2\text{OH} \cdot 3(\text{CHOH}) \cdot \text{CO} \cdot \text{CH}_2\text{OH}$ , and are therefore ketonic bodies. They polarise strongly in the opposite direction to the aldehyde of the same series.

Phenyl-hydrazine also gives a series of very insoluble compounds with the acids of the group; these are distinguished as hydrazides.

Seeing that in one series we have members some of which polarise to the right, some to the left, it is obviously impossible to use the old terms dextro and lævo any longer, as confusion must unavoidably arise. To obviate this, Fischer proposes to name all the series according to the rotation of the aldehyde (sugar) member of the series, and for this purpose use the letters R. L. I. to the compounds in it, just in the same manner as we use O. M. P. in the benzene ring compounds. It is extremely awkward to speak of R. lævulose, and the name "fructose" is proposed instead, which is simply fruit sugar latinised.

\* The observation must be taken quickly, as HCl, even in the cold, decomposes the compound in three or four hours completely.

The accompanying table gives a summary of the group and its various compounds and derivatives :—

CH <sub>2</sub> OH — Evaporation.				
CH <sub>2</sub> OH		CH <sub>2</sub> OH	Oxidation	CH <sub>2</sub> OH
CH—	Conversion into a salt with a carbonate	CHOH	with Br.	CHOH
CHOH		CHOH	Reduction	CHOH
CHOH		CHOH	with Na	CHOH
CO—		CHOH	Amalgam	CHOH
		COOH		COH
R. Lactose.		Mannonic acid.		Mannose.
				Mannitol (with borax.)
Polarise right.				
I. Do.	Do.		Do.	Do.
Inactive.				
L. Do.	Arabinose-carboxylic acid.		Do.	Do.
Polarise left.				
With one molecule of Ph-hzin.	CH <sub>2</sub> OH 3(CHOH) CHOH CH-N-HN-Ph. Ph-hydrazone.	Two molecules Ph-hydrazine.	CH <sub>2</sub> OH Strong HCl 3(CHOH) C-N-HN-Ph. CH-N-HN-Ph. Ph-glucosazone.	CH <sub>2</sub> OH 3(CHOH) Zn. and Δ. CO CHO Glucosone. Lævulose.
R. Mannose.				
Polarise left.				
I. Do.	Do.	Do.	Do.	Do.
Inactive.				
L. Do.	Do.	Do.	Do.	Do.
Polarise right.				

It is evident that if we could form any one of the bodies of the inactive series synthetically from the elements, we could transform it into all the members of that series; and if it were possible to split up any one of these inactive bodies so formed into its optically opposed components, the synthesis of the whole of the members of the group could be accomplished. This has been found possible.

So long since as 1861, Butlerow had observed that formaldehyde in aqueous solution by contact with various bases yielded, by condensation, a sugar-like body, to which he gave the name methylenitan. Loew pursued this investigation further, and found that the various bases differed very much in their power of causing the condensation of formaldehyde. Lead oxide was found to have a remarkably powerful action at a moderately high temperature, even when present in very small quantity. The method which he found to give the best results is as follows :—To four litres of water, containing in solution 40 grams. of formaldehyde, are added half a gram. of magnesium oxide, two or three grams. of magnesium sulphate, and 350 to 360 grams. of granulated lead. The whole is to be kept at a temperature of 60° C. for twelve hours. On evaporation of the fluid, a sweet neutral syrup is left behind, which reduces Fehling, and is capable of undergoing alcoholic fermentation. To this substance Loew gave the name formose.

Fischer obtained, by acting upon acrolein bromide with barium hydrate,\* a sugar-

\*  $2C_3H_4Br_2O + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2$ .

like body, which he named *a. acrose*. More recently he was able to form the same body from glycerose obtained in the following manner :—500 grams. of plumbic hydroxide are stirred intimately into 1,000 grams. of 85 per cent. glycerol; to this is added, with constant stirring, two and a half litres of ice-cold alcohol. The lead glyceroxide thus formed is spread in thin layers, placed under a bell glass in proximity with a shallow vessel containing a quantity of Br equal to half the weight of the lead salt. After the Br is absorbed, the product is extracted with alcohol and concentrated in a partial vacuum, when the glycerose remains as a syrup. The syrup is diluted with water and KHO added until the solution contains about one per cent. of the base, on standing for some days, polymerisation takes place, and amongst other compounds *a. acrose* is formed.

He also repeated the above-mentioned Loew's process, and found that Loew's formose was a mixture of various aldehyde and ketone sugars. Upon treating formose with excess of Ph-hydrazine, a mixture of Ph-glucosazones were formed, all of which were, *with one exception, soluble in alcohol or ether*. The insoluble one, on being treated with strong HCl, yielded the osone, which with Zn and A gave *a. acrose*. This body, formed by either of the three processes, afforded, upon reduction with Na amalgam, a body to which he gave the name *a. acritol*, and which only differed from mannitol\* in its optical inactivity. It struck him that this might be inactive mannitol and *a. acrose* inactive mannose. The first conjecture was undoubtedly true, but the second a little removed from the truth, since *a. acrose* turned out to be a lævulose. The purified *a. acrose* must naturally, from the mode of its formation, viz., the reduction of the osone, be a lævulose; but the original sugar might be either an aldehyde or a ketone. Its formation from glycerose led to the view being entertained that it was an aldehyde. Placing two molecules of glycerose together,  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{COH} + \text{CH OH}\cdot\text{CHOH}\cdot\text{COH}$ , it would seem most probable that one of the H atoms in the second  $\text{CH}_2\text{OH}$  would simply step back and unite with the COH group of the first molecule, yielding the aldehyde sugar,  $\text{CH}_2\text{OH}\cdot 4(\text{CHOH})\cdot\text{COH}$ . It was found that on treating the original solution in which the sugar had been synthesised with Ph-hydrazine in the cold, no crystalline hydrazone was formed, as is the case with mannose, and that only on heating is a glucosazone yielded. This reaction is characteristic for lævulose.

The formation of a sugar allied to grape sugar, by the condensation of formaldehyde, is of great interest, since it has been assumed by several botanico-physiologists that this is the first step in the process of assimilation. By the agency of the chlorophyll cells, the  $\text{H}_2\text{CO}_3$  lost two atoms of O, forming formaldehyde  $\text{HCOH}$ ; three molecules of this polymerise to form a molecule of grape sugar  $\text{C H}_1 \text{O}_6$ , which by some occult process loses another molecule of  $\text{H}_2\text{O}$  and becomes starch. The synthesis recently described gives considerable confirmation to this view.

If then *a. acrose* be identical with I. lævulose, either it or one of its derivatives ought to be able to be split up into their optically active components.† Fermentation with beer yeast was found to ferment away the R. portion and leave the L., but here,

\* In polarising mannitol and its isomerides, borax was invariably added, which considerably heightens their optical activity.

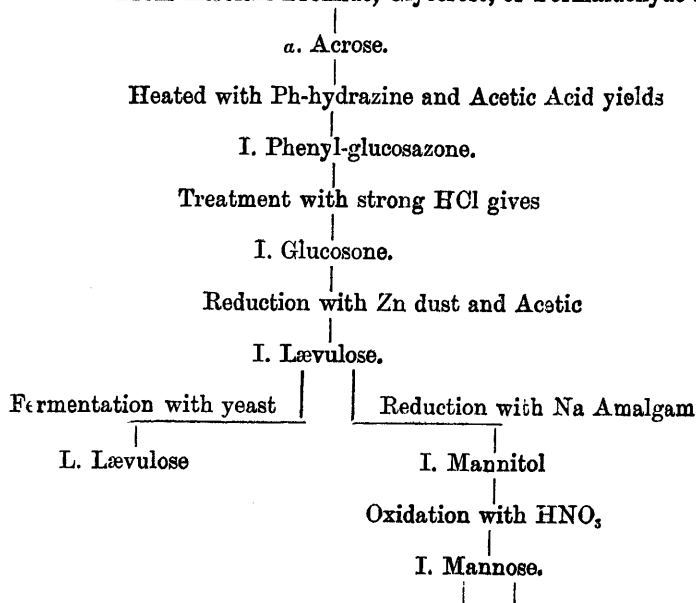
† Lævulose, on reduction with Na amalgam, yields the alcohol of the series, mannitol. From this the other members of the series can be obtained in the manner before described.

obviously, the R. mannose is lost, so far as further experimentation with it is concerned. In order to effect the splitting up, the acid was subjected to investigation. The mannonic acid salts of various organic bases were tried, such as cinchonine and cinchonidine, etc., but all these were found to be too soluble. Strychnine was found to form a mannonate which, upon evaporation of its aqueous solution, deposited itself as a mass of fine crystalline needles. If these be dissolved in absolute alcohol, a clear solution forms for a moment, but almost immediately, at a boiling heat, the difficultly soluble L. mannonate of strychnine falls. This precipitate, upon purification and removal of the strychnine, yields pure L. mannonic acid, and from this all the L. members of the series can be formed.

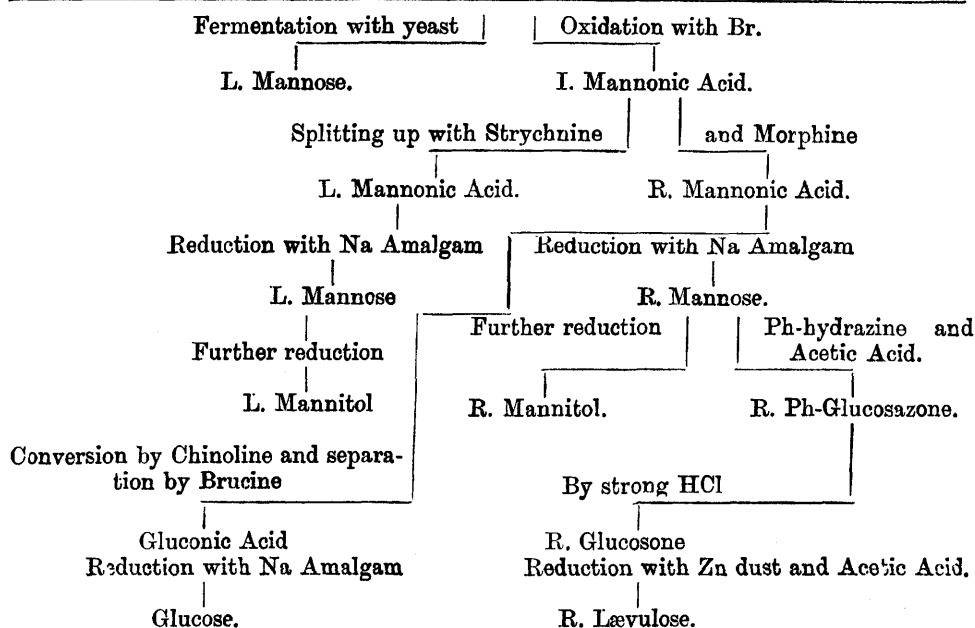
The separation is, however, by no means complete, the alcoholic mother liquor containing besides all the R. mannonate of strychnine about a third of the L. salt. In order to obtain the R. acid pure, the strychnine is removed from the mixed salts left by the last experiment, and the solution of the mixed acids treated with morphine. From this liquid there separates after long standing crystals in large quantity of R. mannonate of morphine. These on purification and removal of the morphine yield R. mannonic acid, agreeing in every particular with the acid obtained from ordinary mannitol. From this acid can obviously be produced all the members of the R. series.

Here then the synthesis of the whole group from formaldehyde is complete, and as this body can be made from methylic alcohol, and the alcohol in its turn be built up from the elements, the synthesis of the whole mannitol group from the elements follows as a natural consequence. The series of reactions involved in this process are grouped in the accompanying table. The way is long and tedious at present, and the percentages of the compound formed in some of the processes very small, but no doubt better and simpler modifications will be discovered hereafter.

From Acrolein Bromide, Glycerose, or Formaldehyde arises,







I may mention in passing that Fischer found that by boiling ivory-nuts having with dilute  $\text{H}_2\text{SO}_4$ , they yield about 30 per cent. of R. mannose, and as this ferments readily, he suggests these, which are, at the present time, a waste article, as a source of alcohol.

So far nothing has been said about glucose. This body is much akin to mannose. It possesses the same structural formula, forms with phenyl-hydrazine the same glucosazone, which yields the same osone and lævulose. Upon reduction, both aldehydes yield the same alcohol mannitol. Their polarising activities are, however, different. Dextrose turns much further to the right than mannose. The hydrazones are also different; that of the former being soluble, that of the latter being comparatively insoluble. By oxidation with Br both yield acids and corresponding salts. Gluconic acid forms with calcium a salt which separates from a concentrated solution in fine needles, which gradually grow in the fluid into cauliflower-shaped aggregates. This form is characteristic for gluconate of calcium.

It is evident the difference between glucose and mannose must be one of physical isomerism; and for an explanation of this we must turn to the Le Bel and Van't Hoff theory. We know that if a C atom becomes associated with four different groups, it

becomes optically active. Thus the molecules  $\begin{array}{ccc} \text{H} & \text{H} & \text{CH}_3 \\ \text{HCH} & \text{HCH} & \text{HCH} \end{array}$ , that is, methane,

methylic alcohol, ethylic alcohol, are all optically inactive; but so soon as we introduce a fourth group, and cause the C atom to be united with four different groups, we get an opti-

cally active molecule, as in lactic acid  $\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ \text{H-C-COOH} & & \text{COOH-C-H} \\ \text{OH} & & \text{OH} \end{array}$ . This can be also written

and as the groups are arranged in the one way or the other, so the acid polarises to the right or the left. Such a C atom surrounded by four different groups is called asymmetric. Though the arrangement of lactic acid can be shown on a level surface, some other peculiarities of the grouping round the C atom cannot be so exhibited; for instance, if the four bonds of the C atom were all in the same plane, there ought to be

$$\begin{array}{cc} \text{Cl} & \text{Cl} \\ \text{HCH} & \text{HCCl} \end{array}$$

two different dichloro-methanes, HCH and HCCl, which we know there are not. But

$$\begin{array}{cc} \text{Cl} & \text{H} \end{array}$$

if, as according to the above-mentioned theory, the four bonds of the C atom are so arranged that if the atom be placed in the centre of a regular tetrahedron, they point to the four angles of the figure, it will be easily seen that the two Cl atoms in the before-mentioned compound, in whatever position they may be placed, invariably hold the same relation to the C nucleus.

In the hexahydric aldehydes mannose and glucose, we have obviously four asymmetric C atoms, which may be designated  $\text{CHO} \cdot \underset{\text{As 1,}}{\text{CHOH}} \cdot \underset{\text{As 2,}}{\text{CHOH}} \cdot \underset{\text{As 3,}}{\text{CHOH}} \cdot \underset{\text{As 4,}}{\text{CHOH}} \cdot \text{CH}_2\text{OH}$ , and as each of these asymmetric atoms may in its turn polarise right or left—in other words, be positive or negative—sixteen modifications are possible. Fischer comes to the conclusion, on very plausible grounds, that the difference in the optical activity of mannose and glucose is caused by an alteration in the properties of the C atom marked As 1, the other three asymmetric atoms preserving the same respective relations in the two compounds; so glucose may be looked upon as the right and mannose as the left modification of the same system.

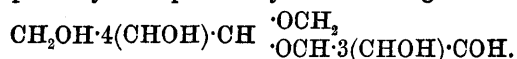
For the purpose of obtaining the gluconic series from the mannonic, the acid seemed the most suitable member to work upon. Mannonic acid may be related to gluconic either as racemic to one of the optically active tartaric acids, or as racemic to meso-tartaric acid. In the first case it should be possible to split up mannonic acid into gluconic and a second isomeride. In the second case there would be more prospect of effecting the transformation by a high temperature. After numerous failures, the conversion was effected by heating mannonic acid with chinoline to  $140^\circ \text{C}$ ., a mixture of the two acids, mannonic and gluconic, arising, just as a mixture of racemic and meso, tartaric arises upon heating cinchonine racemate to  $170^\circ \text{C}$ . After removal of the chinoline, which was liberated by  $\text{Ba}(\text{HO})_2$ , and distilled off by steam, the two acids were separated by conversion into their brucine salts, the mannonic one being insoluble and the gluconic one soluble. After removal of brucine from the gluconate, the acid is evaporated until its lactone forms. This, by reduction with Na amalgam, yields glucose, which has the same specific rotatory power and other characteristics of the natural product. Upon similar treatment the I. and L. mannonic acids should yield an I. and an L. glucose.

Fischer has also made a series of very interesting observations on the saccharons or sugars of the  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  type, which throw considerable light on the constitution of two of them, amylon and lacton.

Upon treating milk-sugar with Ph-hydrazine and acetic acid the osazone comes down, this by treatment with HCl yields the osone. If this osone be boiled with dilute HCl, inversion takes place, and a mixture of galactose and glucosone in equal molecules arises.



If this mixture be again treated with Ph-hydrazine and acetic acid Ph-glucosazone comes down first, almost in the cold, since an osone combines more readily with this base than an aldehyde. Upon warming for some time the Ph-lactosazone comes down. This shows that the molecule of milk-sugar is built up of a molecule of glucose and one of galactose that the COH portion is only free in one group, and this the glucose one, since it is the only group modified by Ph-hydrazine in the milk-sugar molecule before inversion. The COH group of the galactose portion is evidently altered in the anhydride formation, and this change may probably be expressed by the following formula :

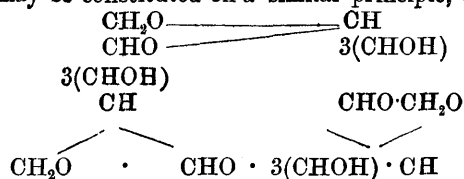


Amylon or malt-sugar upon similar treatment gives evidence of a similar anhydride formation between two molecules of glucose.

Upon treatment with Br lacton and amydon yield two acids of the composition  $\text{C}_{12}\text{H}_{22}\text{O}_{12}$ , called respectively lactobionic and maltobionic. Upon inversion lactobionic acid yields one molecule of galactose and one of gluconic acid ; maltobionic one of glucose and one of gluconic acid. This is also confirmatory of the structure given above

The constitution of cane-sugar is still a mystery, if the attempt be made to combine, a molecule of glucose and one of lævulose in a similar manner to lacton or amydon, either an aldehyde or a ketone group remains active, and this would necessarily reduce Fehling, which cane-sugar does not do. Probably the old view of its being an ether may prove to be correct.

Looking at the constitution of amydon and lacton, the idea has struck me that dextrin and starch may be constituted on a similar principle, thus,



This formula is obviously expansible into a ring of any dimensions, dextrin consisting of a smaller number of groups, starch of a much larger. Supposing such a ring of forty groups to be attacked by diastase, and broken up at one point, the ring then becomes maltodextrin, *i.e.*, a chain of dextrin groups with an amydon group at each end. The chain may then be attacked at another point and two smaller chains would arise with a higher proportion of amydon to dextrin, until at last a number of groups unite to that form of dextrin on which diastase acts with extreme difficulty.

By Killiani's cyan-hydrin process we have a method of proceeding from an aldehyde of one series to the acid of the one higher up, and in this way can be built up from the hexahydric mannose a heptahydric acid ; this can be converted into its lactone, and by reduction into the hepta-hydric aldehyde. From this, by a repetition of the process, can be formed an octohydric aldehyde, and so on. Fischer has in this manner obtained from mannose the heptahydric sugar persite. He proposes to name the aldehydes of the series similar in constitution to mannose—mannohexose, mannoheptose, etc., those akin to glucose, glucohexose, glucooctose, etc., the alcohols being expressed by changing the -ose into -itol, as mannohexitol, and the acids by changing the -ose into -onic.

On consideration of the results of these experiments, we cannot fail to be struck with some of the curious features of plant life; for instance, all the carbohydrates hitherto examined are members of the R. series; for the members of the L. we have to turn to the gums, and these are looked upon by physiologists to some extent as excretions. They also do not consist of left-handed members only, since O'Sullivan has isolated from a number of gums an arabinose which rotates powerfully to the right. Fischer is inclined to take the view that in plant life, as in artificial synthesis, the inactive series is first formed; this is then split up, the members of the R. series being used up in the formation of starch and the other carbohydrates, whilst the members of the L. serve for some other unknown purpose.

The inability of L. series to undergo alcoholic fermentation is also very curious; bacteria seem to be able to attack R. or L. equally well.

The discovery of some means of producing the levulose of the L. series (that is, the dextro-rotatory one) on a commercial scale, would be of great advantage to brewers, as it would enable them to produce a beer capable of retaining indefinitely a certain amount of sweetness, a purpose for which saccharin has been proposed. The addition of a carbohydrate sugar would be obviously much less objectionable than the use of a chemical compound, in no way allied to the sugar group except in taste.

Those desirous of pursuing the subject further are referred to the original papers in the "Berichte" of the Berlin Chemical Society, volumes xviii. to xxiii., where the fullest details will be found. Excellent abstracts have also appeared in the journal of the Chemical Society from the year 1887 up to the present time.

In conclusion, I have to thank Mr. Arthur R. Ling for much valuable assistance in the preparation of this paper.

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