On Anhydrosugars, Part I.
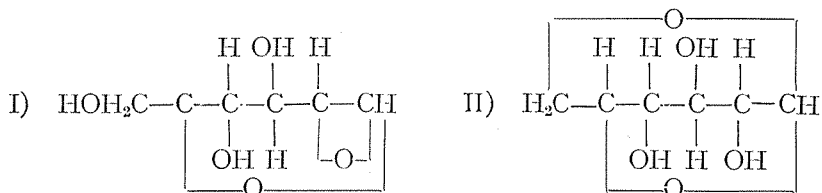# The Constitutions of Anhydrosugars

By

Choji Tanaka

It has long been known that the polysaccharides such as starch[1] and inulin[2] having the composition $(C_5H_{10}O_5)_n$ by hydrolysis with mineral acids are broken down almost quantitatively into glucose or fructose. Recently Prof. Pictet[3] has succeeded in isolating a crystalline compound of the composition of $C_6H_{10}O_5$ from starch by distillation under reduced pressure, and confirmed it to be the same substance as the compound hitherto known as laevoglucosane which had been previously obtained by Tanret[4] from certain glucosides by the action of alkali. According to Karrer[5], laevoglucosane, which is also formed from β-glucose by dehydration under reduced pressure, is on the one hand hydrolysed by the action of mineral acids almost quantitatively into glucose, and on the other polymerised by heating into higher molecular compounds[6].

The formation of anhydrosugars is given rise to by depolymerisation of polysaccharides or by dehydration of simple sugars, and the depolymerisation of polysaccharides is usually performed by heating them alone or with glycerol[7] or naphthalene[8]. The modes by which the hexose-molecule may be deprived of one molecule of water are so

1. Karrer. P.: Polymere Kohlenhydrate (1925), 37.
2. Armstrong. E. F.: The Simple Carbohydrates and the Glucosides (1924) 168.
3. Pictet. A. & Sarasin: Hel., 1 (1918), 87.
4. Tanret: Bl. (3), 11 (1894), 949.
5. Karrer: Hel., 3 (1920), 258.
6. Pictet: Hel., 1 (1918), 226.
7. Pictet. A. & John. R.: Hel., 5 (1922), 640.
8. Pringsheim. H., Leibowitz. J. & Schreiber. A.: Ann., 448 (1926), 163.

numerous as to give rise to a number of isomers, i. e. laevulosane, laevane and heterolaevulosane are known as anhydrosugar derived from d-fructose by dehydration, and in the same manner d-glucose yields such anhydrosugars as α-glucosane, laevoglucosane and chitose.

The constitution of an anhydrosugar, therefore, depends not only on the mother hexose from which the anhyrosugar originates, but also on the method of the preparation. According to Prof. Pictet, α-glucosane which is obtained from α-glucose by heating under reduced pressure, is said to have 1—2 ethylen oxide & 1—5 oxide linkings in the molecule, as will be shown later (I). This view was supported by treating α-glucosane with sodium methylate; and has been confirmed by Cramer and Cox[2], who converted it into trimethylglucosane which, by means of dilute mineral acids, gives 3, 4, 6 trimethyl glucose and also treated it with methyl iodide 2-iod-methyl glucoside,

$$\text{I)} \quad HOH_2C-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle -O-}{|}}{C}}-CH$$

$$\text{II)} \quad H_2C-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH$$

which converts it into 2-desoxymethyl glucoside. When β-glucose[3] is subjected to dry distillation under diminished pressure, it yields laevoglucosane, to which is assigned the chemical structure shown in (II), based on the facts that laevoglucosane synthesized from aceto-bromoglucose and trimethyl amine[4] is converted by methylation into trimethyl laevoglucosane[5] which gives 2, 3, 4 trimethylglucose on hydrolysis and also into aceto-1 —6-dibromoglucose when treated with acetic acid anhydride and acetyl bromide. Chitose, which is formed actually from glucosamine-hydrochloride and silver nitrite,[6] is claimed by Fischer and Andrae[7] to be 2 —5 anhydrosugar, (III), taking into consideration the chemical relationship of chitose to chitaric acid and chitonic acid. Irvine and Hynd[8] have formulated the anhydro-

1. Pictet & Castan: Hel., 3 (1920), 645.
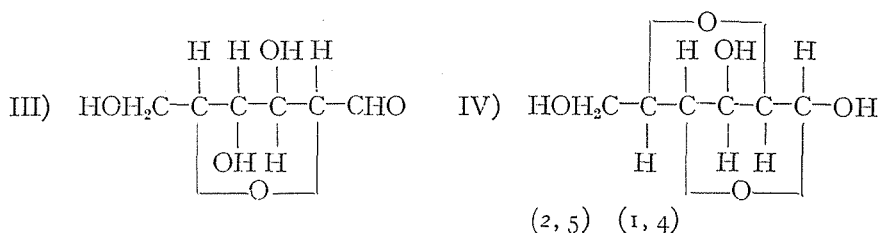2. Cramer & Cox: Hel., 5 (1922), 884.
3. Karrer: loc. cit.
4. Karrer & Smirnoff: Hel., 4 (1921), 817.
5. Irvine & Oldham: J. Chem. Soc., 120 (1921), 1744.
6. Tiemann: Ber. D. Chem. Ges., 17 (1884), 241.
7. Fischer. E. & Andrae: Ber. D. Chem. Ges., 36 (1903), 2587.
8. Irvine & Hynd: J. Chem. Soc., 101 (1912), 1128.

III)
$$H OH H$$
$$HOH_2C-C-C-C-C-CHO$$
H H
OH H
O

IV)
$$O$$
$$H OH H$$
$$HOH_2C-C-C-C-C-OH$$
H H H
O

(2, 5)   (1, 4)

glucose with the butylen oxide form (IV), but Levene and La Forge[1] consider it to be 2—5 anhydromannose from the chemical study of the 2—5 dicarboxylic acid derived from this sugar.

As to the constitution of laevulosane.[2] Prof. Pictet has proposed the ethylen oxide formula (V) or (VI), the sugar being formed by dehydration of fructose under reduced pressure, and very easily hydrolysed into the hexose by mineral acids.
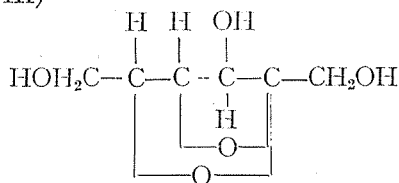
V)
$$H H$$
$$-O-$$
$$H_2C-C-C-C-C-CH_2OH$$
OH OH H
O

VI)
$$H H OH$$
$$-O-$$
$$H_2C-C-C-C-C-CH_2$$
OH OH H
O
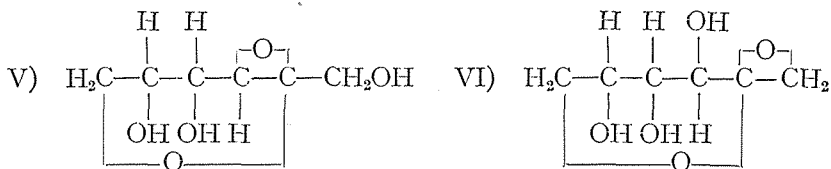
Laevane, which was prepared by Schlubach[3] from fructose by treatment with acetone containing dilute hydrochloric acid at ordinary temperature, was given an ethylene oxide formula (VII), this being based on the fact that 3, 4, 6 trimethyl fructose can be obtained by hydrolysis of hexamethyldilaevane.
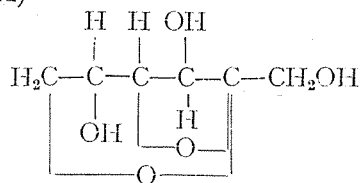
VII)
$$H H OH$$
$$-O-$$
$$HOH_2C-C-C-C-C-CH_2$$
OH H
O
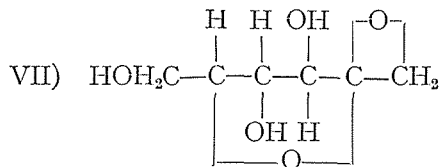
For Heterolaevulosane, obtained from fructose by treating it with conc. hydrochloric acid at o°C, Prof. Pictet[4] proposes one of the following three formulae: (2,5) (2,4) (VIII); (2,6) (2,4) (IX); (2,6 2,5) (X).

1. Levene & La Forge: J. Biol. Chem., **59** (1924), 135.
2. Gelis: A. ch. (3) **57** (1857), 234; Pictet & Reilly: Hel., **4** (1921), 613.
3. Schlubach. H. & Elsner. H.: Ber. D. Chem. Ges., **61** (1928), 2362.
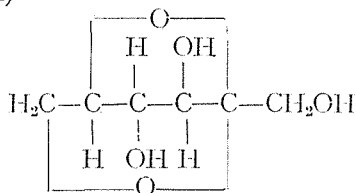4. Pictet. A. & Chavan: Hel. **9** (1926), 809.

VIII)

$$\text{HOH}_2\text{C}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\overset{\overset{\displaystyle OH}{|}}{\text{C}}-\text{C}-\text{CH}_2\text{OH}$$

IX)

$$\text{H}_2\text{C}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\overset{\overset{\displaystyle OH}{|}}{\text{C}}-\text{C}-\text{CH}_2\text{OH}$$

X)

$$\text{H}_2\text{C}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\overset{\overset{\displaystyle OH}{|}}{\text{C}}-\overset{\overset{\displaystyle OH}{|}}{\text{C}}-\overset{\overset{\displaystyle H}{|}}{\text{C}}-\text{CH}_2\text{OH}$$

The present investigation has been undertaken to confirm the constitution of these anhydrosugars by the study of their absorption spectra with ultra-violet rays, of their heat of combustion and of their chemical behaviour towards superheated water.

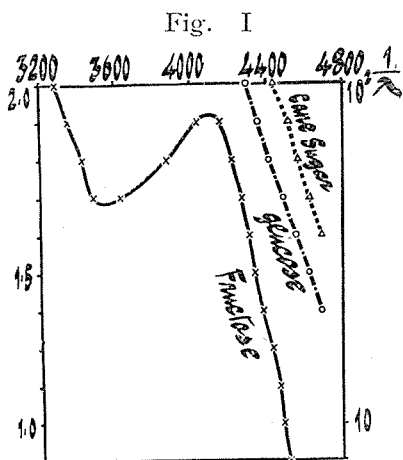## I. Absorption spectrum of some simple sugars

The absorption spectrum of some simple sugars was examined by Niederhoff[1] in the case of 2 mol. aqueous solution in a thickness of 2.5—10 mm. and he stated that they show a selective absorption band at 2800 Å, which he attributed to the occurrence of the keto-enol forms of sugars in their aqueous solution, owing to the fact that the selective absorption band almost coincides in position with that of aliphatic aldehydes or ketones as observed previously by Henri and Bielecki.[2] However, Kwiecinski[3] has opposed the above opinion and argues that the absorption band shown by the sugar solutions should be ascribed to the impurities contained in those sugars, and the fact that the intensity of the light absorption of the sugar solutions is decreased greatly by purifying the sugars is in favour of this view.

In the writer's examination of the light absorption of aqueous solutions of sugars, an iron spark is used for the light source, and the photographs are taken with an Adam Hilger quartz spectrograph

1. Niederhoff. P.: Z. physiol. Chem., **165** (1927), 130.

2. Henri. V. & Bielecki. L.: Ber. D. Chem. Ges., **46** (1914), 3627.

3. Kwiecinski. L. & Marchlenski. L.: Z. physiol. Chem., **169** (1927), 300; Kwiecinski. L., Meyer. J. & Marchlenski. L., ibid., **176** (1928), 292.

E. 2. Ilford rapid process pancromatic plates being used. The absorption curve is plotted from the photograph in the usual way.

Glucose, fructose and cane sugar were purified as much as possible and their $\frac{1}{100}$ mol. aqueous solutions, 4—100 mm. in thickness, were examined. They exhibit no selective absorption band in the region of ultra-violet. However, in a 1 mol. aqueous solution, fructose only gives a selective absorption band at a frequency of 3600, as will be seen in Fig. I. Nevertheless, the writer hesitates to decide that this selective absorption band is due to the free carbonyl group existing in the fructose molecule; it seems more reasonable to ascribe the origin of it to the presence of impurities, since the preparation of fructose in a highly pure state is very difficult on account of the decomposition of the sugar which occurs in the course of the recrystalliza-

Fig. I

tion. Glucose shows no selective absorption band, and it is interesting to compare this fact with the result obtained with cane sugar, which gives an end absorption in the ultra-violet region. Other simple sugars such as galactose, rhamnose and arabinose, as will be seen in Fig. II, give no selective absorption band, but an end absorption in the ultra-violet region.

These spectro-chemical investigations

Fig. II
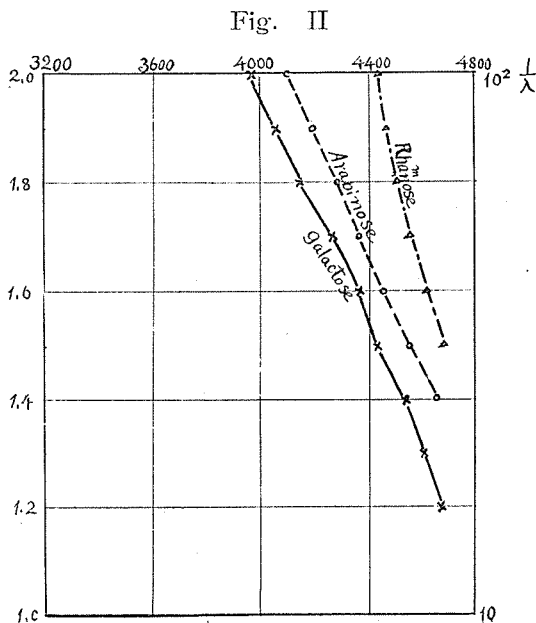
of the sugars will afford evidence for the idea that the behaviour of the carbonyl group of the sugar molecule towards chemical actions is different from that of other fatty and aromatic carbonyl compounds.

II. Absorption Spectrum of Some Anhydrosugars

In this study, anhydrosugars from glucose such as chitose, laevoglucosane and α-glucosane, and laevulosane, heterolaevulosane and laevane from fructose were used, and their physical constants are shown in the following table.

· Table I

Mother Sugar	Glucose			Fructose		
Anhydro-sugar	Chitose	Laevo-glucosane	α-Gluco-sane	Laevu-losane	Hetero-laevulo-sane	Laevane
M.p.	95 - 97°	178°	110°—120°	140—147°	ca. 160°	
Reducing Power.	57.5% of Glucose	—	46.8% of Glucose	45.1% of Fructose	—	10% of Fructose
Rotatory Power [α]$_D$	22.°8	−66.°3	+50.°5	+18°	−65.°0	−11.°0
Hygros-copicity	+	—	+	+	+	+
Taste	tasteless	bitter	bitter	bitter	tasteless	tasteless

In the experiments, the anhydrosugars are examined in $\frac{1}{100}$ mol. aqueous solutions. The anhydrofructoses such as laevulosane, laevane and heterolaevulosane, as is shown in Fig. III, show only the end absorption at frequencies of 4200—4300, and α-glucosane gives the same light absorption as laevane, but laevoglucosane shows no end absorption in the ultra-violet region even in a $\frac{1}{50}$ mol. aqueous solution. These experimental results indicate that these anhydrosugars contain no carbonyl group in their molecules, but two oxide linkings as ascertained by other chemists from their chemical properties.

Chitose, however, as will be seen in Fig. IV, shows a selective absorption band at 3600 due to the presence of a carbonyl group combined with the hydrofuran ring in its molecule, as might be anticipated from its chemical behavior. Calcium chitonate, on the

Fig. III   Fig. IV
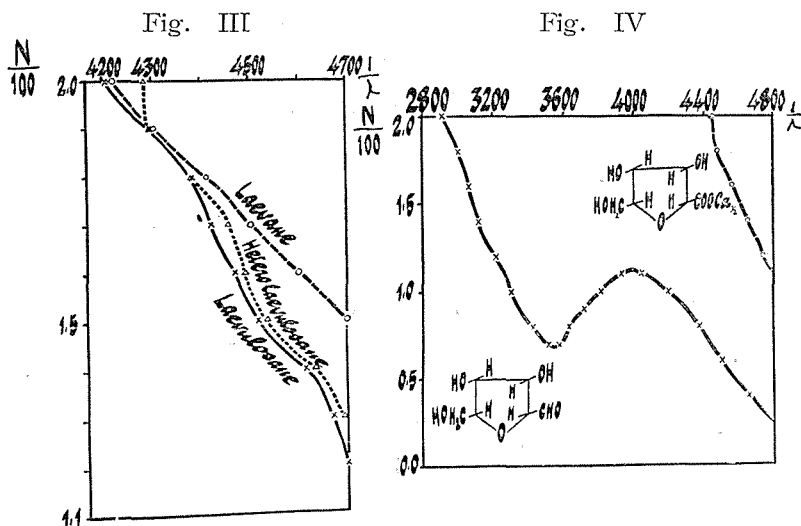
other hand, when the light absorption of its $\dfrac{1}{1000}$ mol. aqueous solution is examined, shows only an end absorption in the ultra-violet region but no such selective absorption band as noticed in chitose.

Thus, the anhydrosugars derived from glucose or fructose, except chitose, exhibit only an end absorption in the ultra-violet region, the position of which when compared with that of their mother sugars, is seen to be shifted towards the region of longer wave length. These anhydrosugars can be classified from the study of absorption spectra into two groups; the one group, to which α-glucosane, laevoglucosane, laevulosane, heterolaevulosane and laevane belong, shows only an end absorption in the ultra-violet region, and the other exhibits a selective absorption band in the ultra-violet region, chitose being one of the typical examples.

III. The Heat of Combustion of Some Simple Sugars and Anhydrosugars.

The heat of combustion of sugars was determined with the Berthelot-Mahler Bomb calorimeter, 0.5—0.7 gms. of sugar in a tablet form being taken, as in the usual way. The experimental results are shown in Table II.

In this table, the heat of combustion of starch[1] and inulin[2] is cited

1. Vielle: Ann. chim. phys., (6), **10** (1895), 455.
2. Langbein: J. prak. Chem., (2), **45** (1892), 305.

Table II

	Heat of Combustion for 1 gm. cal.	Molecular Heat of Combustion. K.	ΔK	
			to Fructose	to Glucose
Inulin	4187			
Laevane	4300	696.6	+21.2	
Heterolaevulosane	4183	677.6	+ 2.2	
Laevulosane	4173	676.8	+ 1.4	
Fructose	3752	675.4		
Glucose	3740	673.2		+4.9
α Glucosane	4186	678.1		+4.6
Laevo-glucosane	4184	677.8		— 1.2
Chitose	4148	672.0		
Starch	4183			

from the literature for the purpose of comparison with that of an-hydrosugars   The value for 1 gm. of the anhydrosugars is very similar to that of these polysaccharides, but differs from that for the hexoses.   The idea was obtained from these experimental results that these polysaccharides are probably formed from anhydrosugar by polymerization or association, on which account no apparent effect on the heat toning of their molecules would be seen.

The molecular heat of combustion of the anhydrosugars is com-pared with that of the hexoses from which the anhydrosugars are derived.
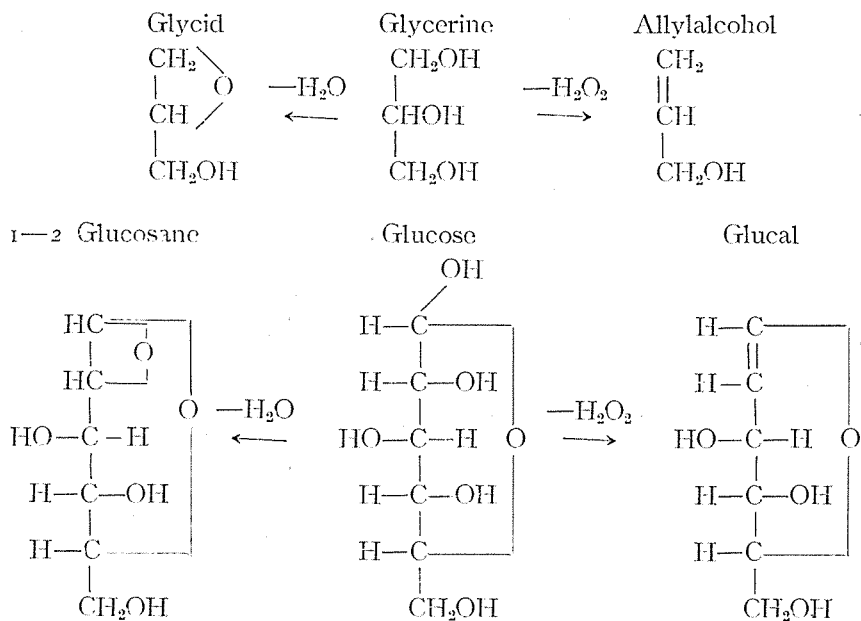
As will be seen from ΔK shown in Table II, the transformation of the simple sugars into the anhydrosugars will occur with the absorption of heat, while chitose is derived from glucose with evolu-tion of heat.   Chitose shows a smaller molecular heat of combustion than the other anhydrosugars examined ; .this is owing to the fact that chitose has only one oxide linking in its molecule whereas all of the others have two oxide linkings.

Thus, the anhydrosugars are classified into two groups from the view point of the molecular heat of combustion ; α-glucosane, laevoglu-cosane, laevulosane, heterolaevulosane and laevane belong to the one group, which is considered to be formed from the corresponding hexose with absorption of heat, and the other group, of which chitose is an example, must be derived from hexose with evolution

of heat, and such a classification of the sugars is in harmony with that obtained from the study of the absorption spectra mentioned above.

It is noteworthy that of the anhydrosugars examined laevane has the greatest molecular heat of combustion. The height of the heat of combustion of laevane above the mean value for the anhydrosugars should be attributed to the occurrence of an ethylen oxide linking in the molecule, since the linking, which is under stress, will be exceedingly retentive of energy, as may be supposed from the Baeyer strain theory. If this assumption as to the relation between the chemical structure and heat toning is accepted as correct, however, one cannot explain the fact that the molecule of α-glucosane and laevulosane shows a small heat toning, although it also is regarded as having an ethylen oxide linking in it. In order to settle the relation between the constitution of the sugars and the heat of combustion, the derivatives of glucose and glycerine were investigated.

Glycid, which is derived from glycerine by elimination of one molecule of water, is regarded as being similar to 1—2 glucosane in the relation of its properties and constitution. And allyl-alcohol and glucal stand in the same relation to their mother substances, as is illustrated in the table.

Glycid		Glycerine		Allylalcohol
CH$_2$\		CH$_2$OH		CH$_2$
| O —H$_2$O		| —H$_2$O$_2$		||
CH / ←		CHOH →		CH
|		|		|
CH$_2$OH		CH$_2$OH		CH$_2$OH

1—2 Glucosane   Glucose   Glucal

The materials used for the investigation were glycerine, glycid, allylalcohol and their acetyl compounds, and acetyl derivatives of glucose, 1—2 glucosane, laevoglucosane, glucal, fructose and tetracetyl glucosen; their physical properties are shown in Tables III and IV.

Table III

Acetyl Sugar	M. p.	$[\alpha]_D$
α-Pentacetyl glucose	112—113°	+101.°9 in Chloroform
β-Pentacetyl glucose	131—132°	+ 4.°0 „
β-Pentacetyl fructose	108—109°	−121.°3 „
Triacetyl 1—2 glucosane	56—57°	+106.°8 in Benzene
Tetracetyl 1—2 glucosen	64—65°	− 19.°8 „
Triacetyl glucal	54—55°	− 15.°4 „
Laevoglucosane triacetate	111°	−51.°4 in Absolute alcohol

Table IV

Sample	B. p.	d_{25}^{25}	n_D^{25}
Glycid	64—65°/12 −13 mm.	1.1110	1.4358
Glycid-acetate	77—79°/26.5 mm.	1.1050	1.4210
Allyl-alcohol	97°	0.8707	1.4073
Allyl-acetate	102°	0.9094	1.4040

The absorption spectra of all the acetyl compounds were studied in $\frac{1}{100}$ mol. alcohol solutions and $\frac{1}{100}$ mol. aqueous solutions and those of glucose and laevoglucosane in $\frac{1}{100}$ mol. aqueous solutions. All of these compounds exhibit the end absorptions in the ultra-violet region, as will be seen in Figs. IV, V, VI, and the forms of their absorption curves are very similar. Although α-pentacetyl glucose shows an absorption spectrum similar in form and position to that of β-pentacet 1 compound, the end absorption of ultra-violet rays by β-pentacetyl fructose is shifted more towards the region of longer wave length than that of β-pentacetyl glucose, and the same relation
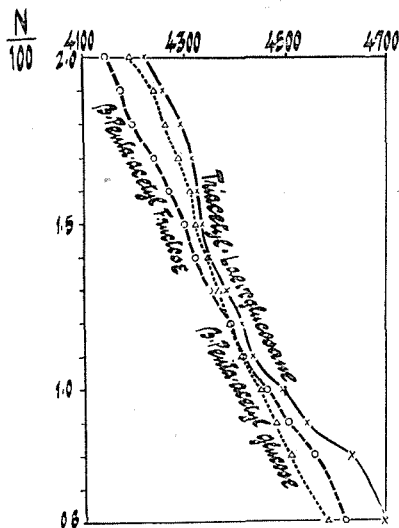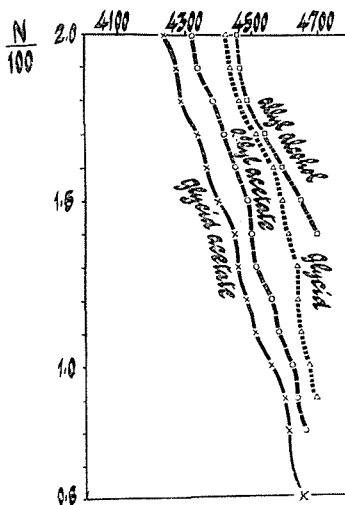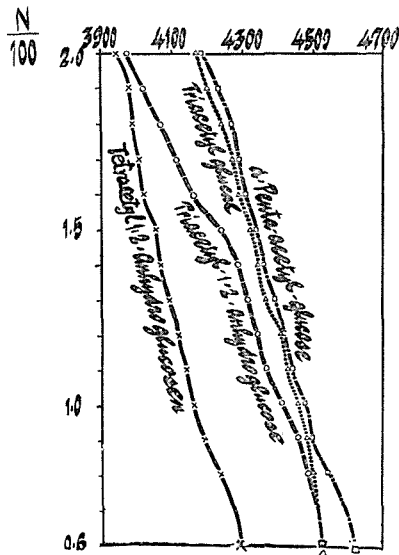
Fig. IV

Fig. V

Fig. VI

holds in the case of glycid and allyl alcohol, as will be seen in Table V. The introduction of an acetyl group into the molecule of sugars and of alcohols causes the displacement of the absorption end of the ultra-violet rays towards the region of longer wave length.

Glycid and its derivatives, compared with allyl alcohol and its derivatives, show the end absorptions in the region of longer wave length. The same relation is observed between glucose and its derivatives. With regard to the position of the absorption end, of solutions of the same concentration arrange themselves in the order of glucal, 1—2-anhydroglucose and 1—2-glucosen, and the absorption spectra seem to maintain some relation with the chemical structures.

Such an intimate relation between the chemical constitution of sugars and alcohols and their absorption spectra will also be noticed between their constitutions and thermal data.

Karrer[1] has observed from the thermal investigations of the acetyl sugars that the molecular heat of combustion is additive and the value for the molecule of sugars calculated from that of the acetyl derivatives agrees well with that estimated directly. Owing to the difficulty of getting the anhydrosugars in a pure state,[2] the molecular heat of combustion of triacetyl 1—2-glucosane, tetracetyl 1—2-glucosen and triacetyl glucal were estimated, and from these the value for the anhydrosugars was calculated, 209.53 K^3 being taken as the molecular heat of combustion for the acetyl group. The molecular heat of combustion for glycid and allyl alcohol, which was estimated directly, coincides distinctly with that calculated from the data of glycid acetate and allyl acetate.

Table V

Sample	Constitution	Heat of Combustion for 1 gm. cal.	Molecular Heat of Combustion K.	Molecular Heat of Combustion. As Acetyl Free.	ΔK to Glycerine
Glycerine	CH₂OH CHOH CH₂OH	4312	397.3		
Glycid.	CH²⟍ CH ╱ O CH₂OH	5610	425.1		+27.8
Allyl-alcohol	CH₂ ‖ CH CH₂OH	7626	442.3		+44.8
Glycid-acetate	CH₂⟍ CH ╱ O CH₂OCOCH₃	5490	636.8	427.3	
Allyl-acetate	CH² ‖ CH CH₂OCOCH₃	6549	654.9	445.4	

1. Karrer. P. & Fioroni. W.: Hel., **6** (1926), 396.
2. Brigl. P.: loc. cit; Maurer, K. loc. cit; Bergmann & Schotte: Ber. D. Chem. Ges., **54** (1921), 440.
3. Karrer. P.: loc. cit.

Table VI

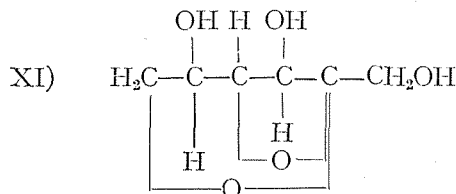| Sample	Constitution	Heat of Combustion for 1 gm. cal.	Molecular Heat of Combustion K.	Molecular Heat of Combustion. As Acetyl Free. K.	ΔK to Glucose
Tetracetyl 1—2-glucosen	O⌐CH ‖ COAC │ CHOAC │ CHOAC │ └CH │ CH₂OAC	4647	1533.5	703.5	+30.3
Triacetyl 1—2-glucosane	O⌐CH╲ │ O │ CH╱ │ CHOAC │ CHOAC │ └CH │ CH₂OAC	4593	1322.8	694.2	+21.0
Triacetyl-glucal	O⌐CH ‖ CH │ CHOAC │ CHOAC │ └CH │ CH₂OAC	4949	1358.1	729.6	+46.4
Triacetyl-laevo-glucosane	O⌐CH─┐ │ CHOAC O │ CHOAC │ CHOAC │ └CH─┘ │ CH₂─	4527	1303.8	675.2	+2.0

And thus, the relation of glucose to glucal in the molecular heat of combustion, and as well as in the chemical constitution is quite analogous to that of glycerine to allyl alcohol, and also the heat toning between glucose and 1—2-glucosane is also noticed to be similar with that of glycerine and glycid. From the comparative

study of the heat of formation of glucose, 1—2-glucosane and 1—6-glucosane, we have learned that 1—2-glucosane contains more energy than the isomer, owing to the occurrence of an ethylene oxide linking in the sugar molecule.

### V. The Constitutions of the Anhydrosugars

In the study of the molecular heat of combustion of anhydrosugars, the writer has stated laevane shows the exaltation of 21 K which harmonizes with the assumption that an ethylene oxide linking occurs in its molecule.

While, laevulosane to which Prof. Pictet has already proposed a structural formula of an ethylen oxide linking but the calorimetric investigation contradicts to this opinion.   The fact that the sugar hydrolysed very easily by the action of superheated water, will be explained by assuming the occurrence of a propylen oxide linking (XI) in it.

$$\text{XI)} \qquad \underset{\substack{|\\ \text{H}\\ \text{---}\text{O}\text{---}}}{\text{H}_2\text{C}}\text{---}\underset{}{\text{C}}\overset{\overset{\text{OH}}{|}}{}\text{---}\underset{}{\text{C}}\overset{\overset{\text{H}}{|}}{}\text{---}\underset{}{\text{C}}\overset{\overset{\text{OH}}{|}}{}\text{---}\text{CH}_2\text{OH}$$

α-Glucosane is also supposed from its thermal data to possess a propylen oxide linking and this supposition will agree with the behavior of the sugar toward the action of superheated water, though the writer's sample does not coincide in every respect with Pictet's substance.

The spectrochemical and calorimetrical studies of chitose and also its chemical reaction with superheated water, are favour of the structural formula (III) proposed by E. Fischer for the sugar.   In the similar manner, the 1—6-oxide formula (II) is proposed to laevoglucosane, and heterolaevulosane which does not exhibit any calorimetric exaltation and resists very strongly towards the action of superheated water, is assigned to posses the formula XII.

$$\text{XII)} \qquad \text{H}_2\text{C}\text{---}\text{C}\text{---}\text{C}\text{---}\text{C}\text{---}\text{C}\text{---}\text{CH}_2\text{OH}$$
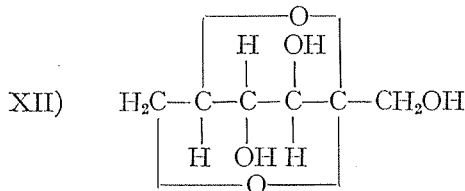
VI. The Preparation of the Materials

1. *Chitose*[1]

This anhydrosugar was first obtained by Ledderhose,[2] and then by Tiemann[3] from glucosamine and nitrite. In the preparation of this sugar, 25 gms. of glucosamine hydrochloride, $[a]_D = +73°$, prepared from lobster-shells by the action of conc. hydrochloric acid, was dissolved in 125 c.c. of water and cooled to $-2°$, and 25 gm. of freshly prepared silver nitrite was added slowly with vigorous stirring. After the reaction was ended, the silver chloride was filtered off, the trace of silver salt in the filtrate was removed by hydrochloric acid, and then the whole was evaporated to a syrup under reduced pressure. To remove completely the amino group in the compound, the syrup was dissolved again in 125 c.c. of water, and 15 c.c. of 10% hydrochloric acid and 15 gms. of silver nitrite were added; this operation was repeated several times. The 10% solution of the syrup thus prepared, which was free from some acidic substances, was mixed with 1 gm. of beer yeast and kept at 25° for 7 days to remove a fermentable hexose. After fermentation was ended the yeast was removed by filtration and the filtrate was evaporated to a small volume under diminished pressure, absolute alcohol was added and the insoluble substance was filtered off. The filtrate was evaporated to a syrup under diminished pressure, the anhydrosugar was extracted with absolute methyl alcohol, decolourized with animal charcoal and absolute ether was added, whereby a white powder was formed. After being purified by repeating the precipitation, it was dried in a vacuum desiccator with phosphorus pentoxide. The substance is very hygroscopic, melts at about 95—97°, has no taste and decolourizes potassium permangante solution when cold, reduces Fehling's solution and its reducing power is 57.5% of glucose. It is soluble in water, absolute methyl alcohol but slightly in ethyl alcohol, and insoluble in ether and acetone.

	Subst.	CO_2	H_2O	C%	H%
1.	0.1208 gm.	0.2080 gm.	0.0700 gm.	44.25	6.44
2.	0.1026 gm.	0.1665 gm.	0.0601 gm.	44.26	6.50
			Calc. for $C_6H_{10}O_5$	44.42	6.22

1. Fischer, E. & Leuchs: Ber. D. Chem. Ges., **35** (1902), 3787; Neuberg: Ber. D. Chem. Ges., **35** (1902), 4009; Levene & La Forge: loc. cit.
2. Ledderhose: Z. physiol. Chem., **2** (1878), 213; **4** (1879), 139.
3. Tiemann: Ber. D. Chem. Ges., **17** (1884), 241.

Cryoscopy.

	Subst.	Water.	Depression. Δ	Mol. wt. Found.	Calc. for $C_6H_{10}O_5$
1.	0.4506 gm.	14.7310 gm.	0.349°	163	
2.	0.4371 gm.	15.1900 gm.	0.329°	163	162

Rotatory power in aqueous solution :

$$1. \quad [a]_D^{12} = \frac{0.245 - 0.005}{2.008 \times 0.53} \times 100 = +22.°8$$

$$2. \quad [a]_D^{12} = \frac{6.15 - 0.05}{5.16 \times 0.53} \times 100 = +22.°4$$

Chitose tribenzoate.[1]......To the cold solution of 5 gms. of chitose, in the presence of 30% caustic soda solution, 12 gm. of benzoyl chloride were added with agitation, and tribenzoyl chitose thus formed was recrystallized from ethyl ester in white feathery crystals with M p. of 116°.

Subst.	CO_2	H_2O	C%	H%
0.1219 gm.	0.3040 gm.	0.0520 gm.	68.01	4.78
	Calc. for $C_{27}H_{22}O_4$		68.4	4.6

This substance is soluble in ethyl alcohol, ethyl ester, ether and amyl alcohol, but not in water.

2. *Calcium Chitonate*[2] $Ca(C_6H_{11}O_7)_2$.

55 gms. of bromine were added drop by drop to the solution of 20 gms. of chitose dissolved in 300 c.c. of distilled water and cooled to 0°. After 10 hours almost all of the bromine was consumed and the reaction product was left to stand over night at room temperature, and then was heated in an open dish to drive off the residual bromine and treated with lead carbonate and silver oxide to neutralize hydrobromic acid formed in the course of the reaction. The insoluble bromides were filtered off and hydrogen sulphide gas was passed into the solution to remove the silver and lead remaining in it. It was then filtered, and an excess of hydrogen sulphide expelled. After it had been confirmed that any trace of sulphuric acid ion occured in the solution, it was neutralized with calcium carbonate and was evaporated down to a small volume under diminished pressure, whereby calcium chitonate was separated as white crystals, the total yield being about

1. Neuberg : loc. cit.
2. Fischer & Tiemann : loc. cit.

16 gms. It was recrystallised from a hot water solution, after being decolourized with animal charcoal.

$$[\alpha]_D^{29} = \frac{+1.20 - 0.12}{0.3253 \times 1} \times 100 = +33.^{\circ}2 \text{ in aqueous solution.}$$

3. *Anhydrous Calcium Chitonate[1] Ca $(C_6H_9O_6)_2$.*

This substance was prepared by dehydration of calcium chitonate : 0.5557 gm. of calcium chitonate prepared by the above method was dried in Abderhalden's drying apparatus with phosphorus pentoxide at 140° under 3 mm. pressure for 12 hours, to constant weight. This substance shows in $\frac{1}{100}$ mol. aqueous solution the same absorption spectrum of ultra-violet rays as calcium chitonate.

4. *Laevoglucosane[2].*

This substance was prepared by dry distillation of potato starch in a vacuum : 100 gm. of potato starch were heated in a 2-litre distillation flask at 260—270° under 10 mm. pressure. First water distilled over, followed by a brownish viscous liquid solidifying to a pasty mass. The mass was recrystallised from hot absolute alcohol or aceton, and laevoglucosane was obtained in white crystals melting at 178°. It neither reduces Fehling's solution, nor decolourizes potassium permanganate solution when cold, and is not hygroscopic.

$$[\alpha]_D^{20} = \frac{-0.72 - 0.61}{1.0027 \times 2} \times 100 = -66.3° \text{ in aqueous solution.}$$

Subst.	CO_2	H_2O	C%	H%
0.1120 gm.	0.1811 gm.	0.0648 gm.	44.62	6.43
	Calc. for $C_6H_{11}O_5$		44.42	6.22

Cryoscopy.

			Mol. wt.	
Subst.	Water.	Depression. Δ	Found.	Calc. for $C_6H_{10}O_5$
0.4832 gm.	14.7300 gm.	0.347°	163	162

5. *Triacetyl laevoglucosane[3]*

20 gms. of acetic anhydride were added slowly to 30 c.c. of pyridine solution containing 5 gms. of laevoglucosane and the mixture

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1. Fischer E. & Andrae : loc. cit.
2. Pictet & Sarasin : loc. cit.
3. Tanret : loc. cit.

was stood for about 2 days at room temperature, then poured into ice water, and filtered. The filtrate was evaporated to a small volume under diminished pressure when white crystals were obtained with a yield of 7.6 gms. The pure substance recrystallized from hot 94% alcohol solution, melts at 111°C.

$$[a]_D^{29} = \frac{-1.00 - 0.09}{2.109 \times 1} \times 100 = -51.2° \text{ in absolute alcohol solution.}$$

6. *a-Glucosane*[1]

10 gms. of *a*-glucose were heated in a distillation flask at 155° under 15.5 mm. pressure, and the residue in the flask was treated with hot absolute alcohol to extract unchanged glucose. The residue was dissolved in hot methyl alcohol, decolourized with animal charcoal and poured into absolute ether, whereby a white powder was formed. The same treatment was repeated on the reaction product to remove glucose and finally the pure anhydrosugar was dried with phosphor pentoxide in a vacuum dessicater. It is very hygroscopic, has a bitter taste, decolourizes potassium permanganate solution when cold, and decomposes at about 110—120°. It reduces Fehling's solution and the reducing power is 46.8% of glucose. Its analytical results coincide with those calculated for the formula $C_6H_{10}O_5$, while the molecular weight estimated by the cryoscopic method indicates that the substance is contaminated with some polymer.

$$[a]_D^{21} = \frac{+0.95 + 0.07}{2.029 \times 1} \times 100 = +50.5° \text{ in aqueous solution.}$$

7. *Laevulosane*[2]

This anhydrosugar was prepared by dehydration of fructose following the directions given by Prof. Pictet: 20 gms. of pure fructose were heated in a distillation flask at 125—130° under 8 mm. pressure for about 2 hours. After the theoretical amount of water was distilled over, the residual mass was treated with hot absolute alcohol to extract the unchanged fructose and there remained mostly the anhydrosugar in the insoluble residue, which was extracted with hot absolute methyl alcohol. After the methyl alcohol had been distilled off under reduced pressure, it was diluted with water to make a 10% solution, some

1. Pictet & Castan: loc. cit.
2. Pictet & Reilly: loc. cit.

beer yeast was added and it was left to stand for a few days at $25°$ to ferment the fructose remaining in it. The filtrate separated by filtration from the yeast was evaporated to a syrup under diminished pressure and dissolved in absolute methyl alcohol, and the anhydrosugar was precipitated with absolute ether. By repeating the same treatment several times, a white hygroscopic powder was obtained. It melts at $140—147°$, decolourizes a cold potassium permanganate solution and reduces Fehling's solution and its reducing power is 45.1% of fructose.

Sample.	CO_2	H_2O	C%	H%
1. 0.1114 gm.	0.1808 gm.	0.0650 gm.	44.34	6.48
2. 0.1122 gm.	0.1820 gm.	0.0660 gm.	44.24	6.18
	Calc. for $C_6H_{10}O_5$		44.42	6.22

Cryoscopy.

Subst.	Water.	Depression. $\varDelta$	Mol. wt. Found.	Calc. for $C_6H_{10}O_5$
0.4184 gm.	14.9724 gm.	$0.320°$	168	162

$$[a]_D^{14} = \frac{+0.46 \times 100}{4.600 \times 0.53} = +18° \text{ in aqueous solution.}$$

8. *Heterolaevulosane*[1]

This was prepared, also according to the directions given by Prof. Pictet, from 75 gms. of pure fructose by treating it with 300 c.c. of conc. hydrochloric acid (s g. 1.2) at $0°$ for 75 hours. The hydrochloric acid was removed first by evaporation under reduced pressure, and then with lead carbonate and silver oxide, and the silver and lead salts remaining in the solution were removed by means of hydrogen sulphide. The hexose in the solution was fermented with 3 gm. of yeast in a 10% aqueous solution, kept at $27–30°$ for about 48 hours. The solution was separated from the yeast neutralized with calcium carbonate and evaporated to syrup under reduced pressure. The anhydrosugar was then extracted with absolute methyl alcohol and was precipitated with absolute ether after being decolourized with animal charcoal, and purified by repeating the precipitation. The substance is a white, very hygroscopic powder; it decomposes at about $160°$, decolourises potassium permanganate solution very slowly when cold, does not reduce Fehling's solution and has no taste.

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1. Pictet & Chavan: loc. cit.

Sample.		CO_2	H_2O	C%	H%
1.	0.1226 gm.	0.1995 gm.	0.0712 gm.	44.38	6.45
2.	0.1102 gm.	0.1798 gm.	0.0612 gm.	44.50	6.18
		Calc. for $C_6H_{10}O_5$		44.42	6.22

Cryoscopy.

				Mol. wt.	
Subst.	Water.	Depression. Δ	Found.	Calc. for $C_6H_{10}O_5$
1.	0.4166 gm.	14.6724 gm.	0.325°	163	
2.	0.3452 gm.	13.9334 gm.	0.293°	160	162

Rotatory power in an aqueous solution:

$$1. \quad [a]_D^{13} = \frac{-1.27 - 0.05}{2.026 \times 1} \times 100 = -65.0°$$

$$2. \quad [a]_D^{12} = \frac{-1.99 - 0.03}{3.135 \times 1} \times 100 = -64.5°$$

9. *Diheterolaevulosane*[1]

The insoluble residue separated from heterolaevulosane by extraction with absolute methyl alcohol, was purified by crystallization from hot methyl alcohol and about 5 gms. of diheterolaevulosane was obtained in the form of white crystals. It melts at 268° and does not reduce Fehling's solution, and is readily soluble in water, slightly soluble in absolute methyl alcohol and ethyl alcohol.

			Mol. wt.	
Subst.	Water.	Depression. Δ	Found.	Calc. for $(C_6H_{10}O_5)_2$
0.5183 gm.	14.6083 gm.	0.203°	323	324

Subst.	CO_2	H_2O	C%	H%
0.1085 gm.	0.1764 gm.	0.0625 gm.	44.26	6.40
Calc. for $C_6H_{10}O_5$			44.42	6.22

$$[a]_D^{29} = \frac{-0.76 - 0.12}{2.0010 \times 1} \times 100 = -44.0°$$

The heat of combustion for 1 gm. of this substance is found to be 4188.0 cal. and its molecular heat of combustion is 1356.9 K. It is hydrolysed into hexose, but only with great difficulty, by the action of water heated to 150° for 24 hours.

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1. Pictet & Chavan: loc. cit.

10. *Laevane*[1]

This anhydrosugar was prepared according to the directions given by Schlubach; 125 gms. of pure fructose were added to a mixture of 1500 c.c. of absolute acetone and 20 c.c. of 10% hydrochloric acid and the mixture was shaken at room temperature for 14 days to form a homogenous solution, thereupon neutralized with lead carbonate and then filtered. The filtrate was evaporated to a syrup under reduced pressure, from which diacetone fructose was removed with ether. The residue was dissolved in about 20 times its volume of water and was treated with 10 gms. of yeast at 30° for 3 days to remove the unchanged fructose. After the fermentation had ceased, the yeast was separated by filtration and the organic acid formed in the course of the fermentation neutralized with calcium carbonate and filtered; the filtrate was evaporated down to a syrup under reduced pressure and then treated with absolute methyl alcohol. When the extract was distilled under reduced pressure to remove methyl alcohol, the anhydrosugar was obtained in a syrupy form with some diacetone fructose which was removed with ether. The insoluble residue was dissolved in absolute methyl alcohol and the sugar was precipitated with absolute ether after decolourizing with animal charcoal. By repeating the precipitation, the pure laevane was obtained in the form of a white powder, the yield being about 5 gms. It has no taste, is very hygroscopic, reduces Fehling's solution and its reducing power is 9.9% of fructose. This substance is readily soluble in water and methyl alcohol, slightly soluble in ethyl alcohol but insoluble in ether.

Subst.	CO_2	H_2O	C%	H%
0.1225 gm.	0.1981 gm.	0.0706 gm.	44.10	6.40
	Calc. for $C_6H_{10}O_5$		44 42	6.22

Cryoscopy.

			Mol. wt.	
Subst.	Water.	Depression. Δ	Found.	Calc. for $C_6H_{10}O_5$
0.5353 gm.	15.2730 gm.	0.398°	163	162

Rotatory power in aqueous solution:

$$[\alpha]_D^{20} = \frac{-0.13 - 0.09}{2.000 \times 1} \times 100 = -11.°0$$

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1. Schlubach. H. & Elsner. H.: Ber. D. Chem. Ges., **61** (1928), 2362.

11. β-*Pentacetyl glucose*[1]

A mixture of 100 gms. of glucose, 50 gms. of anhydrous sodium acetate and 1000 gms. of acetic anhydride was heated for about two hours in a water bath until it formed a homogeneous liquid, and then was poured into ice water drop by drop with vigorous agitation, whereon white crystals were precipitated and filtered.   250 gms. of pure acetyl glucose were obtained by recrystallization from hot 94% alcohol solution.   It melts at 131—132°.

$$[\alpha]_D^{29} = \frac{+0.34 - 0.12}{0.5496 \times 1} \times 100 = +4.°00 \text{ in chloroform solution.}$$

12. α-*Pentacetyl glucose*[2]

80 gms. of acetic anhydride were added drop by drop with vigorous agitation to a mixture of 18 gms. of α-glucose and 100 gms. of pyridine, which was cooled to 0°.   After all the glucose was dissolved, it was poured into ice water, whereupon pentacetyl sugar was obtained in the form of white crystals and recrystallized from hot 94% alcohol.   The yield was about 15.8 gms.   It melts at 112—113°.

$$[\alpha]_D^{29} = \frac{+2.44 - 0.09}{0.2305 \times 1} \times 100 = +101.9° \text{ in chloroform solution.}$$

13. β-*Pentacetyl fructose*

This substance was prepared according to the directions given by Hudson[3]: 15 gms. of recrystallized fructose were gradually added to a mixture of 90 c.c. of acetic anhydride and 40 c.c. of conc. sulphuric acid, which was cooled by a mixture of ice and salt.   The mixture was treated with about 500 c.c. of ice water and neutralized with sodium bicarbonate and filtered, and the residue and the filtrate were treated with chloroform separately.   The chloroform solutions were mixed together and dried with calcium chloride and concentrated in vacuo to a small volume.   The crude acetyl compound was obtained in white crystals with a yield of 7 gms.   The substance recrystallized from its ether solution melts at 108—109°.

$$[\alpha]_D^{29} = \frac{-1.36 - 0.09}{2.076 \times 1} \times 100 = -121.°3 \text{ in chloroform solution.}$$

1. König & Knorr: Ber. D. Chem. Ges., **34** (1901), 957.
2. Behrend & Roth: Ann., **331** (1904), 362.
3. Hudson & Browns: J. Am. Chem. Soc., **37** (1915), 1283.

14. *Triacetyl glucal*[1]

20 gms. of β-acetobromo-glucose[2] (M.p. 87—88°) were reduced with 40 gms. of zinc powder in 200 c.c. of 50% acetic acid at low temperature; the zinc powder was filtered off and the filtrate evaporated to a small volume at ordinary temperature in vacuo to remove acetic acid. The syrup was then diluted to 100 c.c. with water, and extracted with ether, and the ethereal solution was neutralized with sodium bicarbonate, treated with water, and dried with calcium chloride. On the ether being distilled off, there remained a colourless syrup which changed to a crystalline mass. The yield was 11.8 gms. It was purified by crystallization from absolute alcohol-petroleum ether solution, M.p. $= 54 - 55°$.

$$[\alpha]_D^{10} = \frac{-1.03 + 0.06}{6.298 \times 1} \times 100 = -15.°4 \text{ in absolute alcohol solution.}$$

This substance decolourizes bromine water immediately, shows a dark green colour by the pine shave reaction and reduces Fehling's solution when hot.

15. *Tetracetyl glucosen*[3]

10 gms. of β-acetobromo glucose warmed to about 60° were mixed with 5 gms. of dry benzene and 3 gms. of diethyl amine, and the mixture was then left to stand at room temperature for 36 hours, after which it was diluted with absolute ether, and diethylamine hydrobromide which crystallized out from the solution was separated by filtration. The ethereal solution was treated with dilute sulphuric acid to remove basic substance and then with water. The ethereal solution was then distilled to drive off ether, and acetyl glucosen which was purified by crystallization from its alcohol ether solution, was obtained in a syrupy form. The yield was about 4 gms. The pure crystals were found to melt at 64—65°.

$$[\alpha]_D^{20} = \frac{-0.28 - 0.13}{0.2097 \times 1} \times 100 = -19.6° \text{ in absolute alcohol solution.}$$

16. *Triacetyl 1—2 glucosane*[4]

This substance was prepared by the method proposed by Brigl[5]:

1. Fischer. E.: Ber. D. Chem. Ges., **47** (1914), 196.
2. Fischer. E.: Ber. D. Chem. Ges., **49** (1916), 584.
3. Maurer. K.: Ber. D. Chem. Ges., **62** (1929), 332.
4. Brigl: loc. cit.
5. Brigl: loc. cit.

dry ammonia gas was passed vigorously into 10 gms. of dry finely powdered 3, 4, 6 triacetyl glucosyl chloride[1] suspended in 80 gms. of dry benzene, and the mixture was kept in a flask at $15°$ for 3 hours, and then shaken occasionally. After 10 hours the ammonium chloride formed by the reaction was removed by filtration and the filtrate was concentrated over conc. sulphuric acid in a vacuum dessicator, and then benzene was distilled off under diminished pressure at ordinary temperature and petroleum ether was added, whereupon a crystalline product of 3, 4, 6 triacetyl 1, 2 glucosane was obtained, separated from the solvent and recrystallized from benzene-petroleum ether solution, M.p. $=56-57°$.

$$[\alpha]_D^{29} = \frac{+2.53-0.12}{0.2256 \times 1} \times 100 = +106.8° \text{ in benzene solution.}$$

17. *Allyl Alcohol*

A crude allyl alcohol was purified by distilling with calcium oxide. The physical constants were: B.p. $=97°$, $d_{25}^{25}=0.8707$, $n_D^{25}=1.4073$.

18. *Allyl Acetate*[2]

This substance was prepared from allyl iodide and silver acetate following the directions of Cahours and Hofmann[3]. The crude allyl acetate thus obtained was purified by distillation with silver acetate and then with lead oxide to remove some iodide and acidic substance. It boils at $102-103°$, $n_D^{25}=1.4040$, $d_{25}^{25}=0.9094$.

19. *Glycid*[4]

This substance was prepared by pouring epichlorohydrine (B.p. $=116°$) dissolved in alcohol into a cooled alcohol solution containing an equivalent amount of potassium hydroxide. Potassium chloride deposited in the course of the reaction was filtered and the alcohol distilled off, and the residue was subjected to fractional distillation under reduced pressure. The physical constants of glycid, thus obtained, are as follows: B.p. $=64-65°/12-13$ mm, $d_{25}^{25}=1.1110$, $n_D^{25}=1.4358$.

1. Brigl: Z. physiol. Chem., **116** (1921), 1.
2. Hofmann: Ann., **102** (1857), 295.
3. Tollens: Ann., **156** (1870), 156.
4. Nef: Ann., **335** (1906), 232.

20. *Glycid Acetate*[1]

A mixture of 20 gms. of epichlorohydrine (B.p.$=116°$) and 115 gms. of potassium acetate was heated at 110—115° for 20 hours, and then the reaction temperature was raised to 140°. After the reaction was ended the product was cooled and the acetate, separated from potassium chloride by filtration, was extracted with ether. The extract was distilled to get rid off ether and epichlorohydrine, and the glycid acetate was purified by fractional distillation under diminished pressure. It boils at 77—79°/26.5 mm., $n_D^{25}=1.4210$, $d_{25}^{25}=1.1050$.

In conclusion, the writer wishes to express his sincere thanks to Prof. Komatsu for his kind guidance throughout the experiments, and also to the Department of Education for a research grant.

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1. Breslauer: Z. prak. Chem. (2), **20** (1879), 191.