

state for a brief time. This mirror formation has also been noted in the reduction by formaldehyde (Loew's method), and in the reduction with sodium formate. Magnesium and iron also give very finely divided precipitates of platinum black, but the action does not appear to be so violent as with aluminium, and the blacks obtained are denser and more coherent. That from iron appeared to be badly contaminated with carbon, even though a so-called pure iron wire was used. No analysis of it was made.

When heated in the air the following effect upon the weight of the platinum black prepared by precipitation with aluminium was observed: Weight before heating, 0.2661 gram; weight after heating to 300° , 0.2657 gram; weight after heating to redness, 0.2630 gram; or a total loss on heating to redness of about 1.2 per cent., probably representing carbon in the aluminium. Other specimens gave similar figures.

It was also observed that while the platinum black prepared by the use of zinc becomes the gray, "spongy" platinum upon being heated to redness, that precipitated by means of aluminium changes but slightly in color, although it becomes somewhat more coherent.

It therefore appears that by this method one may obtain a quite pure, finely divided platinum black, which will prove useful where this preparation is needed in chemical work.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

A RELATION BETWEEN THE CHEMICAL CONSTITUTION AND THE OPTICAL ROTATORY POWER OF THE SUGAR LACTONES.¹

By C. S. HUDSON.

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The Hypothesis.

The numerous sugars are strongly rotatory. On the other hand the alcohols which result from their reduction and the acids which are formed by their oxidation are only feebly rotatory; but the glucosidic compounds of the sugars and the lactones of these acids are as strongly rotatory as the sugars themselves. Thus for example the specific rotations of the two forms of glucose are 109° and 20° , of the methyl glucosides 157° and -32° , of gluconic acid lactone 68° , but the rotation of gluconic acid is only -2° , and sorbitol, which is the alcohol that results from the reduction of glucose, shows no rotation. Is there any other property of these substances which varies in the same manner as the rotatory power?

The constitutional chemical formulas now in use for these compounds have been chosen step by step to express their chemical reactivities,

¹ Read at the Boston meeting of the American Chemical Society, Dec., 1909.

and it is now generally agreed that the sugars, the glucosides and the lactones possess a lactonic ring, but that this is absent from the structure of the alcohols and acids. Here then is a property—the chemical constitution—which runs exactly parallel with the physical property of optical rotation, in the case of the sugar glucose. Does the same parallelism hold for the other sugars?

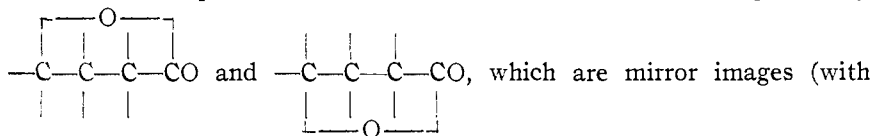
To answer this question reference may be made to Table I, which gives the specific rotations of the principal aldose sugars, and their glucosidic, lactonic, acidic, and alcoholic derivatives, so far as they are known; the numerical values are in all cases quoted from the literature.

TABLE I.—SPECIFIC ROTATIONS OF ALDOSE SUGAR DERIVATIVES.

Sugar.	Glucosidic compound.	Lactone.	Acid.	Alcohol.	
<i>l</i> -Glucose	$\left\{ \begin{array}{l} \alpha \ 109^\circ \\ \beta \ 52^\circ \end{array} \right.$ Methyl	$\left\{ \begin{array}{l} \alpha \ 157^\circ \\ \beta \ -32^\circ \end{array} \right.$	Gluconic	68° —2° Sorbitol	0
<i>l</i> -Galactose	$\left\{ \begin{array}{l} \alpha \ 140^\circ \\ \beta \ 53^\circ \end{array} \right.$ Methyl	$\left\{ \begin{array}{l} \alpha \ 196^\circ \\ \beta \ 0^\circ \end{array} \right.$	Galactonic	—72° —11° Dulcitol	0
<i>-</i> Arabinose	$\left\{ \begin{array}{l} \alpha \ 76^\circ \\ \beta \ 184^\circ \end{array} \right.$ Benzyl	215°	Arabonic	—74° —8° Arabitol	0
<i>l</i> -Mannose	$\left\{ \begin{array}{l} \alpha \ 76^\circ \\ \beta \ -14^\circ \end{array} \right.$ Methyl	—79°	Mannonic	54° ? Mannitol	0
<i>l</i> -Xylose	$\left\{ \begin{array}{l} \alpha \ 100^\circ \\ \beta \ -8^\circ \end{array} \right.$ Methyl	$\left\{ \begin{array}{l} \alpha \ 152^\circ \\ \beta \ -66^\circ \end{array} \right.$	Xylopic	83° —7° Xylitol	0
<i>-</i> Rhamnose	$\left\{ \begin{array}{l} \alpha < -7^\circ \\ \beta > 31^\circ \end{array} \right.$ Methyl	—62°	Rhammonic	—35° —8° Rhamnitol	11°
<i>l</i> -Ribose	? ?		Ribonic	—18° ? Adonitol	0
<i>l</i> -Mannoheptose	85° ?		Mannoheptonic	—74° ? Mannoheptitol	—1°
Rhodeose	86° Ethyl	30°	Rhodeonic	—76° ?	?
<i>d</i> -Talose	? ?		Talonic —(strong)	? Talitol	0.2°
<i>d</i> -Gulose	? ?		Gulonic	—55° ? Sorbitol	0
α -Galaheptose	? ?		α -Galaheptonic	—52° ? α -Galaheptitol	0
β -Galaheptose	—22° ?		β -Galaheptonic	? ?	?
α -Gluco-octose	—51° ?		α -Gluco-octonic	46° ? α -Gluco-octitol	2°
<i>d</i> -Mannononose	50° ?		Mannonononic	—41° ?	?
<i>d</i> -Gala-octose	—40° ?		Gala-octonic	64° ?	?

The above data from the literature show that the sugars, the glucosidic compounds and the lactones, all of which contain the lactonic ring, have strong rotatory powers. There are three apparent exceptions, β -methyl galactoside, β -xylose and α -rhamnose, but for each of these the corresponding α or β isomer is strongly rotatory, proving that the slight rotations of the three compounds are due to internal compensations, and that they contain strongly active carbon atoms. On the other hand the alcohols and acids are of feeble rotatory powers, which are in general not comparable with the strong rotations of the sugars, glucosidic compounds and lactones. There is thus satisfactory proof that the lactonic ring structure causes a strong rotatory power.

The rotations of the alcohols and acids recorded are so small in comparison with those of the lactones that the rotations of the latter may be assumed to be due, as a first approximation, entirely to the lactonic ring. There are two possible stereo structures for the lactonic ring, namely



the mirror placed horizontally).¹ If the rotation of the lactone is due entirely to this ring the position of the ring must determine the sign of the rotation of the lactone. The position of the ring is determined by the position which the OH group had on the γ -carbon atom before the ring was formed. These ideas thus lead to the following hypothesis: *Lactones of dextrorotation have the lactonic ring on one side of the structure, lactones of levorotation have it on the other, and the position of the ring shows the former position of the OH group on the γ -carbon atom.*

Test of the Hypothesis.

This hypothesis will now be tested. In Table II there are collected the structural formulas and specific rotations of twenty-four lactones of the monobasic sugar acids, including every such lactone for which the structure and specific rotation have been determined. The first column gives the name and the second the stereo configuration of the lactone, the discovery of which is due in all cases to the immortal researches of Emil Fischer. In the third column is the statement, for convenience, of the position of the lactonic ring, whether "above" or "below" the chain, and in column four are the specific rotations of the lactones, which are quoted from the references given in the foot-notes. In most cases they were measured by Emil Fischer or his students.

TABLE II.—PARALLELISM BETWEEN THE SIGN OF THE ROTATION AND THE CONFIGURATION OF THE SUGAR LACTONES.

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
<i>l</i> -Arabonic	$\begin{array}{c} \text{O} \\ \text{---} \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{CO} \\ \quad \quad \\ \text{OH} \text{ H} \\ \text{H} \text{ H} \text{ OH} \end{array}$	Above	$-74^{\circ 2}$
<i>l</i> -Ribonic	$\begin{array}{c} \text{O} \\ \text{---} \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{CO} \\ \quad \quad \\ \text{OH} \text{ OH} \\ \text{H} \text{ H} \text{ H} \end{array}$	Above	$-18^{\circ 3}$

¹ The stereo formulas will be written horizontally to save space.

² E. Fischer and Piloty, *Ber.*, 24, 4219 (1891).

³ *Ibid.*, 24, 4217 (1891).

TABLE II—(Continued).

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
<i>d</i> -Galactonic	$\begin{array}{c} \text{H} \quad \text{OH H} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH H} \quad \text{H} \quad \text{OH} \end{array}$	Above	$-78^{\circ 1}$
<i>d</i> -Talonic	$\begin{array}{c} \text{H} \quad \text{OH OH} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH H} \quad \text{H} \quad \text{H} \end{array}$	Above	$-?^2$ (large)
<i>l</i> -Rhammonic	$\begin{array}{c} \text{H H} \\ \text{CH}_3\text{CHOH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{H} \quad \text{OH OH} \end{array}$	Above	$-39^{\circ 3}$
<i>l</i> -Isorhammonic	$\begin{array}{c} \text{H OH} \\ \text{CH}_3\text{CHOH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{H} \quad \text{OH H} \end{array}$	Above	$-62^{\circ 4}$
<i>d</i> - α -Glucoheptonic	$\begin{array}{c} \text{H H} \quad \text{H H} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH OH H} \quad \text{OH OH} \end{array}$	Above	$-55^{\circ 5}$
<i>d</i> - β -Glucoheptonic	$\begin{array}{c} \text{H H} \quad \text{H OH} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH OH H} \quad \text{OH H} \end{array}$	Above	$-68^{\circ 6}$
<i>d</i> -Mannoheptonic	$\begin{array}{c} \text{H H} \quad \text{OH ?} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH OH H} \quad \text{H} \quad ? \end{array}$	Above	$-74^{\circ 7}$
<i>d</i> -Galaheptonic	$\begin{array}{c} \text{H OH} \quad \text{H ?} \\ \text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{OH H} \quad \text{H} \quad \text{OH} \quad ? \end{array}$	Above	$-52^{\circ 8}$
<i>l</i> -Rhamno-octonic	$\begin{array}{c} \text{OH H H} \quad \text{? ?} \\ \text{CH}_3\text{CHOH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CO} \\ \text{H} \quad \text{OH OH H} \quad ? \quad ? \end{array}$	Above	$-51^{\circ 9}$

¹ Ruff and Franz, *Ber.*, 35, 948 (1902).² E. Fischer, *Ibid.*, 24, 3624 (1891).³ Rayman, *Ibid.*, 21, 2048 (1888).⁴ E. Fischer and Herborn, *Ibid.*, 29, 1964 (1891).⁵ Kiliani, *Ibid.*, 19, 770 (1886).⁶ E. Fischer, *Ann.*, 270, 85 (1892).⁷ E. Fischer and Passmore, *Ber.*, 23, 2228.⁸ E. Fischer, *Ann.*, 288, 143 (1895).⁹ E. Fischer and Piloty, *Ber.*, 23, 3109 (1890).

TABLE II—(Continued).

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
<i>d</i> -Manno-octonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{H} & \text{H} & \text{OH} & \text{?} & \text{?} & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} & . & \text{C} & . & \text{CO} \\ & \text{OH} & \text{OH} & \text{H} & \text{H} & \text{?} & \text{?} & & & & & & \end{array}$	Above	-44^{01}
<i>d</i> -Xylopic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{H} & \text{OH} & \text{H} & & & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & & \text{H} & \text{OH} & & & & \\ & & \text{---} & \text{---} & \text{O} & \text{---} & \text{---} & \end{array}$	Below	$+83^{02}$
<i>d</i> -Lyxonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{H} & \text{OH} & \text{OH} & & & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & & \text{H} & \text{H} & & & & \\ & & \text{---} & \text{---} & \text{O} & \text{---} & \text{---} & \end{array}$	Below	$+82^{03}$
<i>d</i> -Gluconic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{H} & \text{H} & \text{OH} & \text{H} & & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{OH} & & \text{H} & \text{OH} & & & \\ & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+68^{04}$
<i>d</i> -Mannonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{H} & \text{H} & \text{OH} & \text{OH} & & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{OH} & & \text{H} & \text{H} & & & \\ & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+54^{05}$
<i>l</i> -Gulonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{OH} & \text{H} & \text{OH} & \text{OH} & & & \\ \text{CH}_2\text{OH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{H} & & \text{H} & \text{H} & & & \\ & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+56^{06}$
<i>l</i> - α -Rhamnohexonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{OH} & \text{H} & \text{H} & \text{OH} & & & \\ \text{CH}_2\text{CHOH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{H} & & \text{OH} & \text{H} & & & \\ & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+84^{07}$
<i>l</i> - β -Rhamnohexonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{OH} & \text{H} & \text{H} & \text{H} & & & \\ \text{CH}_2\text{CHOH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{H} & & \text{OH} & \text{OH} & & & \\ & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+43^{08}$
<i>l</i> - α -Rhamnoheptonic	$\begin{array}{cccccccc} & & & & \text{O} & & & \\ & & & & \text{---} & & & \\ & \text{OH} & \text{H} & \text{H} & \text{H} & \text{?} & & \\ \text{CH}_2\text{CHOH.C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{C} & . & \text{CO} \\ & \text{H} & \text{OH} & & \text{OH} & \text{?} & & \\ & & & & \text{---} & \text{---} & \text{O} & \text{---} & \end{array}$	Below	$+56^9$

¹ Fischer and Passmore, *Ber.*, 23, 2234 (1890).² Tollens and Weber, *Z. Ver. Zuckerind.*, 49, 953.³ E. Fischer and Bromberg, *Ber.*, 29, 583 (1896).⁴ Schnelle and Tollens, *Ann.*, 271, 74.⁵ Fischer and Hirschberger, *Ber.*, 22, 3222 (1889).⁶ Thierfelder, *Z. physiol. Chem.*, 15, 75 (1891); E. Fischer, *Ber.*, 24, 526 (1891).⁷ E. Fischer and Piloty, *Ber.*, 23, 3104 (1890).⁸ E. Fischer and Morrell, *Ibid.*, 27, 389 (1894).⁹ E. Fischer and Piloty, *Ibid.*, 23, 3107 (1890).

TABLE II—(Continued)

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
<i>d</i> - α -Gluco-octonic	$\begin{array}{cccccccc} \text{H} & \text{H} & \text{OH} & \text{H} & \text{H} & ? & & \\ \text{CH}_2\text{OH} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{CO} \\ & & & & & & & \\ & \text{OH} & \text{OH} & \text{H} & & \text{OH} & ? & \\ & & & & & \text{---} & \text{O} & \text{---} \end{array}$	Below	+46° ¹
<i>d</i> - β -Gluco-octonic	$\begin{array}{cccccccc} \text{H} & \text{H} & \text{OH} & \text{H} & \text{H} & ? & & \\ \text{CH}_2\text{OH} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{CO} \\ & & & & & & & \\ & \text{OH} & \text{OH} & \text{H} & & \text{OH} & ? & \\ & & & & & \text{---} & \text{O} & \text{---} \end{array}$	Below	+24° ²
<i>d</i> - α -Gala-octonic	$\begin{array}{cccccccc} \text{H} & \text{OH} & \text{OH} & \text{H} & ? & ? & & \\ \text{CH}_2\text{OH} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{CO} \\ & & & & & & & \\ & \text{OH} & \text{H} & \text{H} & & ? & ? & \\ & & & & & \text{---} & \text{O} & \text{---} \end{array}$	Below	+64° ³
<i>d</i> - α -Gluco-nononic	$\begin{array}{cccccccc} \text{H} & \text{H} & \text{OH} & \text{H} & \text{H} & ? & ? & \\ \text{CH}_2\text{OH} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{CO} \\ & & & & & & & \\ & \text{OH} & \text{OH} & \text{H} & \text{OH} & & ? & ? \\ & & & & & & \text{---} & \text{O} & \text{---} \end{array}$	Below	+ (?) ⁴ (large)

The table shows that among these twenty-four sugar lactones (which include all the known substances upon which there is sufficient data known to test the hypothesis) there is not a single exception to the theory; all the lactones which have the ring "above" the chain are levorotatory and all having it "below" the chain are dextrorotatory.

Application of the Theory to Determine the Constitution of the Sugars.

As this relation between the stereo position of the lactonic ring and the sign of the rotation of the lactone is well founded it may be used in determining the constitution of the sugars. For some of the sugars such a determination is only a tracing backward of the steps of the above experimental proof of the hypothesis, but for certain others (*e. g.*, rhamnose) this method gives entirely new data on the constitution, as will be shown. In determining the constitutions of the sugars Emil Fischer has used most ingeniously a mass of chemical data of various kinds, nearly all of which he worked out in his own laboratory; in what follows it will be shown that the constitutions of the monose aldehyde sugars can be independently determined from two kinds of experimental data, (1) a knowledge of the sugars which result from the cyanide synthesis or its reverse, and (2) a knowledge of the signs of the rotations of the lactones of the monobasic sugar acids. This second kind of data cannot be obtained for the ketone sugars because they do not yield acids and lactones, and their structure cannot be found by this method alone.

¹ E. Fischer, *Ann.*, 270, 94 (1892).

² *Ibid.*, 270, 101 (1892).

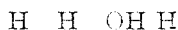
³ *Ibid.*, 288, 149 (1895).

⁴ *Ibid.*, 270, 103 (1892).

The Stereo Configuration of d-Glucose.—The cyanide synthesis or its reverse has shown the steps of the following series: *d*-erythrose \longrightarrow *d*-arabinose \longrightarrow *d*-glucose \longrightarrow *d*-glucoheptose \longrightarrow *d*-gluco-octose. The specific rotations of the lactones of the monobasic acids derived from these sugars are (see Table II), *d*-arabonic $+74^\circ$, *d*-gluconic $+68^\circ$, *d*-glucoheptonic -68° , *d*-gluco-octonic $+46^\circ$. Writing the carbon chain of the octose $\text{CH}_2\text{OH.C.C.C.C.C.C.C}$, it is first noticed that as its lactone

(1)(2)(3)(4)(5)(6)(7)

rotates positive ($+46$) its ring is to be considered below the chain and joining atom 7 to its γ -carbon 4. This shows that the H atom on 4 is above the chain. Passing next to the heptose, since its lactone rotates negative (-68°) the H atom on the new γ -carbon 3 by the same reasoning is below the chain. Similarly the signs of the rotations of the other two lactones show that the H atom is above 2 and above 1. This determines the stereo constitution of the carbons 1, 2, 3, and 4, and as these are all the asymmetric carbons which occur in the aldehyde formula of glucose,



this may be written $\text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{COH}$. This formula is



identical with the one which Emil Fischer has chosen from chemical data alone. The steps of the above proof of the structure of *d*-glucose give also the structures of *d*-arabinose and *d*-erythrose.

The Stereo Configuration of d-Galactose.—The cyanide synthesis or its reverse has shown the following series: *d*-lyxose \longrightarrow *d*-galactose \longrightarrow *d*-galaheptose \longrightarrow *d*-galaactose, and the rotations of the lactones of the corresponding monobasic acids have been found to be (Table II) *d*-lyxonic $+82^\circ$, *d*-galactonic -78° , *d*-galaheptonic -52° , *d*-galaactonic $+64^\circ$. By the same reasoning as given above these rotations show that in the stereo formula of galactose the H atom is above carbons 1 and 4

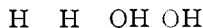


and below 2 and 3, giving $\text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{COH}$. This formula is



identical with the one which Fischer has chosen for galactose. The stereo configuration of *d*-lyxose follows from that of *d*-galactose.

The Stereo Configuration of d-Mannose.—The cyanide reaction has shown the following series: *d*-arabinose \longrightarrow *d*-mannose \longrightarrow *d*-mannoheptose \longrightarrow *d*-manno-octose, and the rotations of the lactones of the corresponding monobasic acids have been found to be (Table II) *d*-arabonic $+74^\circ$, *d*-mannonic $+54^\circ$, *d*-mannoheptonic -74° , *d*-manno-octonic -44° . In the configuration of mannose therefore the H atom

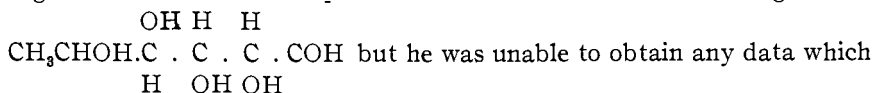


is below 3 and 4 and above 1 and 2, giving $\text{CH}_2\text{OH.C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{COH}$.



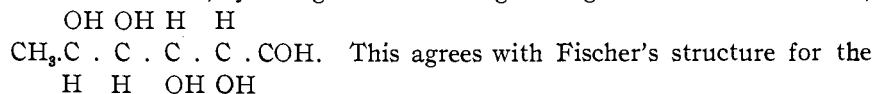
This is also identical with the structure which Fischer has established for mannose.

The Stereo Configuration of Rhamnose.—This methyl pentose sugar has been shown by Fischer to have the stereo configuration



would establish the stereo structure of the first asymmetric group CH_3CHOH . This physico-chemical method for establishing the structure of the sugars can be applied in this case where the usual strictly chemical methods fail. Writing the carbon chain for rhamnose $\text{CH}_3\text{C.C.C.C.C.}$, and

referring to the following cyanide syntheses, methyl tetrose $\xrightarrow{(1)(2)(3)(4)(5)}$ rhamnose \rightarrow rhamnohexose \rightarrow rhamnoheptose, the specific rotations of the corresponding lactones having been found to be methyl tetronic -47° ,¹ rhammonic -35° , rhamnohexonic $+84^\circ$, and rhamnoheptonic $+56^\circ$, it is seen that the hydrogen atom is to be placed above carbons 3 and 4 and below 1 and 2, yielding the following configuration for rhamnose,



atoms 2, 3, and 4, and it also shows the configuration of the atom 1 which has been in doubt. Rhamnose is thus a reduction product from *l*-mannose. It is interesting to note that Winther² has previously selected this configuration for the first carbon, basing his selection upon the fact that Tate's bacillus attacks rhamnose.

Partial Stereo Configurations of Rhodeose and Fucose.—The methyl pentose rhodose yields a lactone with the specific rotation -76° ,³ consequently its structure can be partially determined from the above prin-

ciples to be $\text{CH}_3\text{C} \begin{array}{c} | \\ \text{OH} \\ | \end{array} \text{C} \begin{array}{c} | \\ \text{H} \\ | \end{array} \text{C} \begin{array}{c} | \\ \text{H} \\ | \end{array} \text{C} \begin{array}{c} | \\ \text{H} \\ | \end{array} \text{COH}$, and it follows that its antipode, fucose, is the mirror image of this.

Proof of the Position of the Lactonic Ring.

The foregoing relations furnish a proof of a view which organic chemists have been led to adopt by a large number of chemical facts, namely, that the formation of lactones involves the γ -carbon atom preferably to any other. The parallel relation between the position of the lactonic ring and the sign of the rotation of the lactone is based on the assumption that the ring is formed on the γ -carbon atom; if it were considered as formed on any other atom whatsoever the parallelism would no longer hold even approximately; thus, referring back to Table II, if the ring is

¹ Ruff and Kohn, *Ber.*, 35, 2362.

² *Ber.*, 28, 3000.

³ Votocek, *Z. Zuckerind. Boh.*, 25, 297 (1902).

supposed to form on the α -atom, there are then seven cases of agreement with the hypothesis of parallelism, eight disagreements and nine remaining doubtful. If the ring forms on the β -carbon there are then ten cases of agreement and ten of disagreement and four in doubt. If the ring forms on the δ -carbon there result six agreements, twelve disagreements and six doubtful. But it has been seen that if the ring forms on the γ -carbon there are twenty-four agreements, no disagreements and none in doubt. As the chances that an event which can happen in two equally probable ways will happen in exactly the same way twenty-four times out of twenty-four trials is only one in seventeen million it seems certain that the lactonic ring in these monobasic sugar lactones forms on the γ -carbon atom.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF PUMPKIN SEED.

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The seeds of the common pumpkin (*Cucurbita pepo*, Linné) have been recognized for several decades by the United States Pharmacopoeia under the title of *Pepo*, and are regarded as an efficient and harmless taenifuge. This property appears to have been generally attributed to the fatty oil contained in the seed, which is stated to have been used with success in repeated half-ounce doses.¹ On the other hand, Heckel² found that the membrane surrounding the embryo is capable of expelling tapeworms, and as the membrane contains a resin, he believed this to be the active constituent. There is, however, no indication that Heckel had in any way confirmed this supposition by the separate administration of the resin. A more definite observation regarding the activity of the resin appears to have been made by Wolff, since it is recorded³ that he found this efficient as a taenifuge in doses of 15 grams, whereas the fatty oil, when pure and free from resin, was inert. Ordinarily, however, the remedy is employed in the form of the kernels of the fresh seed, suitably prepared, in doses ranging from 30 to 200 grams.

No complete chemical examination has hitherto been made of pumpkin seeds, and the constituents of their fatty oil have been only imperfectly known. The results of an investigation by Kopylow,⁴ in 1876, showed that previous statements respecting the presence of an alkaloid or glucoside in these seeds could not be confirmed, but that they contained, be-

¹ *Lancet*, Sept. 25, 1875, p. 462.

² *Ibid.* and *Pharm. J.*, Oct., 1875, p. 308. Compare also Vigieo, *Amer. J. Pharm.*, 1876, p. 509.

³ *U. S. Dispensatory*, 18th Edit., p. 1012.

⁴ *Pharm. Zeit. für Russland*, 1876, p. 513.