[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

A RELATION BETWEEN THE CHEMICAL CONSTITUTION AND THE OPTICAL ROTATORY POWER OF THE PHENYLHYDRAZIDES OF CERTAIN ACIDS OF THE SUGAR GROUP.

BY C. S. HUDSON.

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In a previous article[1] it was shown that the lactones of the monobasic acids of the sugar group rotate polarized light to the right or to the left according as the lactonic ring upon the γ-carbon atom is on the right or the left of the configuration. That conclusion resulted from a comparison of the space-formulas and recorded rotations of twenty-four such lactones. Anderson[2] has shown that the same relation holds for eleven lactones of the saccharinic acid group.[3]

That the extensive data upon which this generalization rests could be found recorded in the literature is to be attributed to the fact that the lactones as a class crystallize very readily and rotate polarized light powerfully.

It is the purpose of the present article to call attention to a similar

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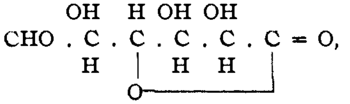
[1] THIS JOURNAL, **31**, 338 (1910).

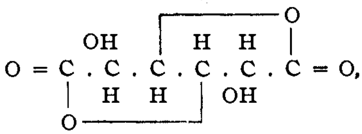
[2] *Ibid.*, **34**, 51 (1912).

[3] Occasion is taken here to record several developments of this relation which have appeared since its publication in 1910. Anderson (*Loc. cit.*) has shown that the rotation (+19°) of *d*-glucuronic lactone,



$$\mathrm{CHO}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\underset{|}{\mathrm{C}} = \mathrm{O},$$

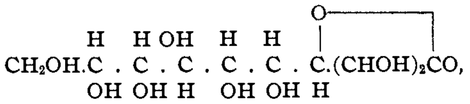
agrees with it, likewise the rotation (—201°) of *l*-mannosaccharic lactone,



$$\mathrm{O} = \underset{|}{\mathrm{C}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{|}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{|}{\mathrm{C}} = \mathrm{O},$$

since both rings of the latter substance are to be considered as on the left of the structure. The lactones of α-hydroxymethyl *d*-lyxonic and α-hydroxymethyl *d*-arabonic acids that were mentioned by Anderson have been shown by later work (Nef, *Ann.*, **403**, 205 (1914)) to be the well-known lactones of *d*-lyxonic and *d*-arabonic acids which were mentioned in my first article.

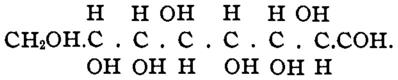
By the cyanhydrin synthesis, Philippe (*Ann. chim. phys.*, [8] **26**, 369 (1912)) has prepared from glucononose two glucodeconic acids and has found the specific rotations of their lactones to be —35 and —40, respectively. The levorotation of these lactones indicates that the lactonic ring is on the left,



$$\mathrm{CH_2OH.}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\,.\,\overset{|}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{.(CHOH)_2CO},$$

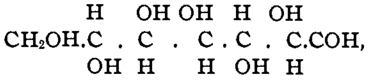
and while the configurations of the α- and β-carbons remain unknown, this determinarelationship between configuration and rotation in the case of another class of derivatives of the monobasic acids of the sugar group, namely, the

tion of the position of the hydroxyl group on the γ-carbon shows the structure of *d*-gluco-octose, which has heretofore been undecided, to be



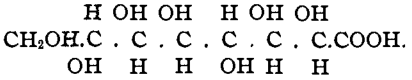
$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}.COH. \qquad (I)$$

By the addition of HCN to β-galaheptose, which has been shown by Peirce (*J. Biol. Chem.*, **23**, 327 (1915)) to be



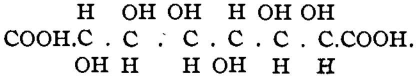
$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}.COH,$$

it should be possible to produce two gala-octonic acids, one of which would have the structure



$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}.COOH. \qquad (II)$$

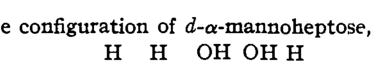
The oxidation of I and II should give the same dibasic acid,



$$COOH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}.COOH.$$

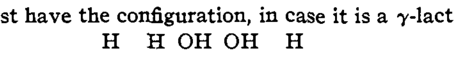
Anderson (*Loc. cit.*) has shown that β-dextrosaccharonic lactone rotates slightly to the left (—4.7°) and is in disagreement therefore with the relation between rotation and structure because its γ-ring is to the right of the structure. As Anderson points out, however, β-saccharonic acid is strongly levorotatory, the specific rotation of its sodium salt being —35°, and the change of rotation due to lactone formation is in the direction called for by theory. The same explanation probably holds for the small levorotation of *d*-allonic lactone (—6.8°) (Levene and Jacobs, *Ber.*, **43**, 3146 (1910)), which is in the opposite direction to that indicated by theory. The direction of the rotation of the sirupy *d*-altronic lactone (+35), prepared by Levene and Jacobs, agrees with the theory. In doubtful cases where the lactone rotates only slightly, it would be well to consider the direction of the change in rotation due to lactone formation in applying the theory.

Peirce's proof of the configuration of *d*-α-mannoheptose,



$$CH_2OH\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,CHO,$$

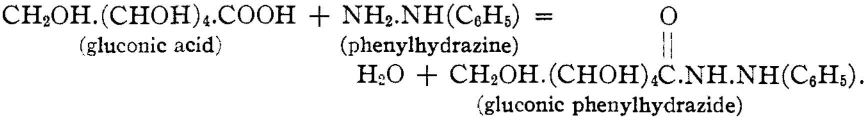
shows that the lactone of *d*-manno-nononic acid, which Fischer and Passmore (*Ber.*, **23**, 2226 (1890)) prepared from this heptose by the cyanhydrin reaction through *d*-manno-octose, must have the configuration, in case it is a γ-lactone,



$$CH_2OH\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{\llcorner O}{\overset{H}{C}}.(CHOH)_2.\underset{\lrcorner}{CO}.$$

This structure of the lactone would lead one to expect that the substance would rotate polarized light to the right, but Fischer and Passmore record a left-handed specific rotation, —41.0°. This large negative value is in complete opposition to the lactone rule; however, it should be taken into consideration that Fischer, in 1909 ("Untersuchungen über Kohlenhydrate und Fermente," p. 582) mentioned that a repetition of the synthesis of higher carbon sugars from mannose had given different products from the first experiments, beyond the octose.

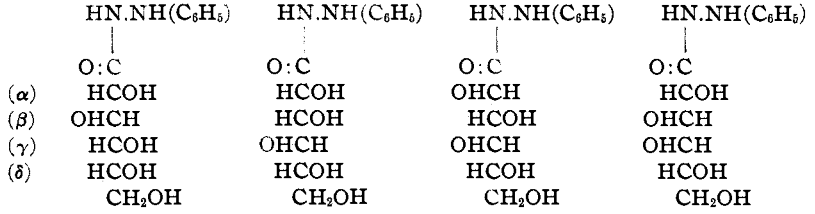
phenylhydrazides. The typical reaction by which they are formed, is for example,



$$\underset{\text{(gluconic acid)}}{CH_2OH.(CHOH)_4.COOH} + \underset{\text{(phenylhydrazine)}}{NH_2.NH(C_6H_5)} = H_2O + \underset{\text{(gluconic phenylhydrazide)}}{CH_2OH.(CHOH)_4\overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5)}.$$

Such phenylhydrazides as a rule crystallize very readily and are very useful derivatives for identifying the monobasic acids of the sugar group. They have generally been characterized by their melting points and solubilities, and it is indeed unfortunate, from the standpoint of the matters that are to be discussed in the present article, that in only three instances has the optical rotatory power in water of a phenylhydrazide been recorded by the discoverer of the substance. These exceptions are β-galaheptonic phenylhydrazide, which was found by Fischer[1] to rotate to the left, —6.32°, *d*-erythronic phenylhydrazide, which was found by Ruff[2] to rotate to the right, +17.5°, and β-mannoheptonic phenylhydrazide, which was found by Peirce[3] to rotate to the left, —25.8°. Probably the reason why the rotations of the phenylhydrazides have not been measured in as extensive a way as have those of the lactones is because many of the phenylhydrazides are of low solubility in all solvents. However, in a recent article by the late J. U. Nef[4] measurements are recorded for the specific rotations in water of the phenylhydrazides of *d*-erythronic (+12.0°), *d*-threonic (—28.8°), *d*-lyxonic (—11.2°), *d*-gluconic (+12.0°), *d*-gulonic (+13.7°), *d*-idonic (—12.4°) and *d*-galactonic (+11.0°) acids; a consideration of the rotations of these substances leads directly to a very simple generalization which bears promise of being quite useful in the development of the chemistry of the sugars.

Referring to the configuration of the four hexonic phenylhydrazides that were measured by Nef



	$HN.NH(C_6H_5)$	$HN.NH(C_6H_5)$	$HN.NH(C_6H_5)$	$HN.NH(C_6H_5)$
	|	|	|	|
	O:C	O:C	O:C	O:C
(α)	HCOH	HCOH	OHCH	HCOH
(β)	OHCH	HCOH	HCOH	OHCH
(γ)	HCOH	OHCH	OHCH	OHCH
(δ)	HCOH	HCOH	HCOH	HCOH
	CH_2OH	CH_2OH	CH_2OH	CH_2OH
	d-gluconic	*d*-gulonic	*d*-idonic	*d*-galactonic

it will be observed that each structure contains the four asymmetric carbon atoms α, β, γ and δ. Let it be assumed that the principle of

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[1] *Ann.*, **288**, 152 (1895).

[2] *Ber.*, **32**, 3680 (1899).

[3] *Loc. cit.*, p. 331.

[4] *Ann.*, **403**, 204 (1914). The values used are taken from pages 249, 271, 273, 295, 296, 298, 303.

optical superposition holds among the members of this group, and that therefore the rotation due to the α-carbon atom is $-\alpha$ when the OH group is on the left, as in the idonic derivative, and $+\alpha$ when it is on the right, as in the other three structures. Similarly, let the values of the rotations of the other asymmetric carbon atoms be $\pm\beta$, $\pm\gamma$ and $\pm\delta$, respectively. Then the molecular rotations of the four phenylhydrazides, of molecular weight 286, may be written:

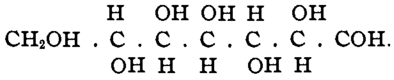
Phenylhydrazide.	Molecular rotation.
(1) *d*-Gluconic acid.............	$+\alpha - \beta + \gamma + \delta = (+\ 12)(286) = +34.3(10)^2$
(2) *d*-Gulonic acid..............	$+\alpha + \beta - \gamma + \delta = (+13.7)(286) = +39.2(10)^2$
(3) *d*-Idonic acid...............	$-\alpha + \beta - \gamma + \delta = (-12.4)(286) = -35.5(10)^2$
(4) *d*-Galactonic acid...........	$+\alpha - \beta - \gamma + \delta = (+11.0)(286) = +31.5(10)^2$

Solving these four equations gives the values

$$\alpha = +37.3(10)^2,\ \beta = +3.9(10)^2,\ \gamma = +1.4(10)^2,\ \delta = -0.6(10)^2.$$

It will be observed at once that *the value of α, which is the rotation of the α-carbon atom, is so very much larger than the values of the rotations of the other three carbons, that its sign determines the direction of the rotation of the hexonic phenylhydrazides.* This conclusion is emphasized by the rotations of the phenylhydrazides of gulonic and idonic acids, which differ only in the configuration of the α-carbon atom, its hydroxyl being on the right in the gulonic, and on the left in the idonic compound; for the former the specific rotation is to the right, +13.7, and for the latter nearly an equal amount to the left, —12.4, showing that the α-carbon atom is responsible for nearly all the rotation. The conclusion may be expressed in the converse form, namely, that *the direction of rotation of the phenylhydrazide indicates the configuration of the hydroxyl on the α-carbon atom. If the phenylhydrazide rotates to the right, the hydroxyl on the α-carbon is on the right and vice versa.*

If it should be that this simple relation holds throughout the sugar group, or even holds in most instances, it would be quite a useful aid in the determination of structure. Thus, for example, the cyanhydrin synthesis yields two heptonic acids (α and β) from galactose because the symmetric carbonyl carbon of the sugar becomes the asymmetric α-carbon of the heptonic acids. Since Fischer has found, as mentioned, the specific rotation of β-galaheptonic phenylhydrazide to be towards the left, —6.32°, it is to be concluded that the OH group is on the left of the α-carbon, which indicates that the structure of the corresponding sugar, β-galaheptose, is



$$\begin{array}{cccccc} & \mathrm{H} & \mathrm{OH} & \mathrm{OH} & \mathrm{H} & \mathrm{OH} \\ \mathrm{CH_2OH}\ . & \mathrm{C}\ . & \mathrm{C}\ . & \mathrm{C}\ . & \mathrm{C}\ . & \mathrm{C}\ .\ \mathrm{COH.} \\ & \mathrm{OH} & \mathrm{H} & \mathrm{H} & \mathrm{OH} & \mathrm{H} \end{array}$$

This is indeed the structure which Peirce[1] has recently conclusively estab-

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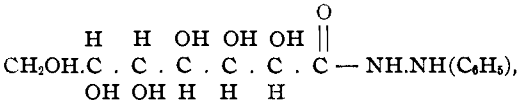
[1] *Loc. cit.*

lished for β-galaheptose by showing that the alcohol from the epimeric α-galaheptose is the antipode of that from α-mannoheptose.

Since the structure of β-mannoheptonic phenylhydrazide has been shown by Peirce to be

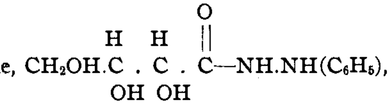


$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\overset{\overset{O}{\|}}{C}-NH.NH(C_6H_5),$$

it is to be expected that its rotation is to the left, a conclusion which is confirmed by Peirce's measurement, $[\alpha]_D^{27} = -25.8°$.

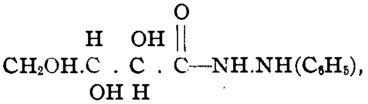
There remain Nef's measurements of the rotations of the phenylhydrazides of *d*-erythronic, *d*-threonic and *d*-lyxonic acids, which have the configurations:

d-erythronic pheuylhydrazide,



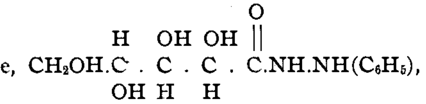
$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\overset{\overset{O}{\|}}{C}-NH.NH(C_6H_5),\quad [\alpha]_D^{20} = +12.0$$

d-threonic phenylhydrazide,



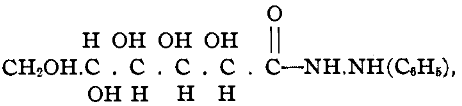
$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\overset{\overset{O}{\|}}{C}-NH.NH(C_6H_5),\quad [\alpha]_D^{20} = -28.8$$

d-lyxonic phenylhydrazide,



$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\quad [\alpha]_D^{20} = -11.2$$

In the second and third of these the hydroxyl is on the left of the α-carbon and the rotation is to the left, while for *d*-erythronic phenylhydrazide the right-hand position of the hydroxyl corresponds with the observed right-hand rotation. Nef[1] states that the specific rotation of pure *d*-talonic phenylhydrazide,

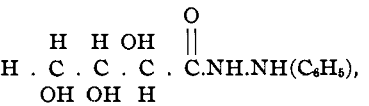


$$CH_2OH.\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\overset{\overset{O}{\|}}{C}-NH.NH(C_6H_5),$$

which he prepared in only a small quantity, was −25.1° in cold water. The direction of this rotation agrees with theory, but its value is larger than would be expected for a hexonic phenylhydrazide. All of the recorded rotations of the phenylhydrazides, ten in number, thus agree with the relation.

In order to test the matter further, I have prepared the following phenylhydrazides and measured their specific rotations in water:

d-arabonic,



$$CH_2OH\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\quad [\alpha]_D^{20} = -14.5°$$

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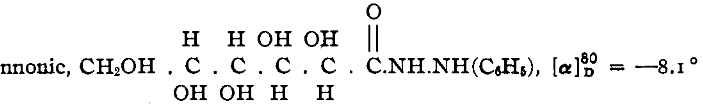
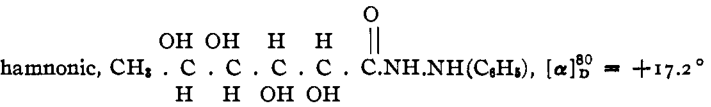
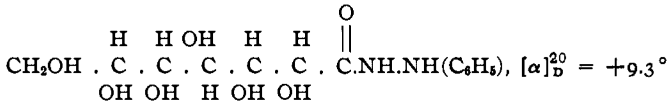
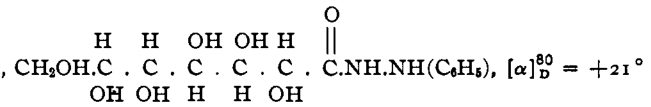
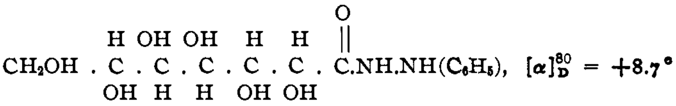
[1] *Loc. cit.*, p. 281.

d-mannonic,

$$CH_2OH\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\ [\alpha]^{80}_{D} = -8.1°$$

l-rhamnonic,

$$CH_3\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\ [\alpha]^{80}_{D} = +17.2°$$

d-α-glucoheptonic,

$$CH_2OH\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\ [\alpha]^{20}_{D} = +9.3°$$

d-α-mannoheptonic,

$$CH_2OH.\underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\ [\alpha]^{80}_{D} = +21°$$

d-α-galaheptonic,

$$CH_2OH\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{H}{\overset{OH}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \underset{OH}{\overset{H}{C}}\ .\ \overset{\overset{O}{\|}}{C}.NH.NH(C_6H_5),\ [\alpha]^{80}_{D} = +8.7°$$

A comparison of the position of the hydroxyl on the α-carbon with the direction of rotation of the phenylhydrazide shows that the rule holds for these six additional substances, making sixteen phenylhydrazides upon which the correlation has been tested. The experimental data of the measurements follow.

For *d-arabonic phenylhydrazide*, an aqueous solution containing 0.266 g. in 29.7 g. solution rotated to the left in a 400 mm. tube 0.52 circular degrees at 20°, hence $[\alpha]^{20}_{D}$ = —14.5°. In a second experiment, 0.972 g. substance in 100 cc. aqueous solution rotated to the left at 20° in a 400 mm. tube 0.56°, hence $[\alpha]^{20}_{D}$ = —14.4°. In a 200 mm. tube at 20° this solution rotated 0.28° to the left, and on warming to 80° the solution read at that temperature 0.49° to the left, which corresponds to $[\alpha]^{80}_{D}$ = —25°. On cooling this solution to 20° its reading returned to the former value, —0.28°, showing that the specific rotation of *d*-arabonic phenylhydrazide changes from —14 at 20° to —25 at 80° and that the change is reversible and is not due to hydrolysis, because in that case the change would be irreversible. This conclusion is confirmed by the observation that the reading does not slowly change on keeping the solution one hour at 80°, as would be the case if a slow hydrolysis were in progress. The rotations of the various other phenylhydrazides that were measured at 80° on account of their low solubilities in cold water also did not change with the time, showing that hydrolysis did not occur. All the samples of the phenylhydrazides were carefully purified by several recrystallizations.

For *d-mannonic phenylhydrazide*, which is one of the most insoluble compounds of this class, a solution containing 1.21 g. substance in 43.5

cc. water was prepared on the steam bath, and at 80° it read to the left in a 200 mm. tube 0.45°, hence $[\alpha]_D^{80} = -8.1°$.

For *l-rhamnonic phenylhydrazide*, an aqueous solution containing 1.23 g. substance in 30.5 cc. water read to the right in a 200 mm. tube at 80°, 1.39°, hence $[\alpha]_D^{80} = +17.2°$.

For *d-α-glucoheptonic phenylhydrazide*, a solution containing 0.713 g. substance in 20 cc. water read to the right in a 200 mm. tube at 20°, 0.66°, hence $[\alpha]_D^{20} = +9.3°$.

For *d-α-mannoheptonic phenylhydrazide*, a solution containing 1.48 g. substance in 44.8 cc. water read to the right in a 200 mm. tube 1.38° at 80°, hence $[\alpha]_D^{80} = +21°$. This rotation is opposite to that found by Peirce for the epimeric *d*-β-mannoheptonic phenylhydrazide, and of nearly the same magnitude, showing that the α-carbon causes most of the rotation.

For *d-α-galaheptonic phenylhydrazide*, a solution containing 0.214 g. substance in 17.3 cc. water read to the right in a 200 mm. tube 0.21° at 80°, hence $[\alpha]_D^{80} = +8.5°$.

Recently Levene[1] has shown that the configuration of the α-carbon atom of the monobasic acids of the sugar group has a strong influence upon the rotation of the metallic salts of these acids, and that when the hydroxyl group on this carbon atom is to the right of the structure the salt is more dextrorotatory than is the salt of the epimeric acid which has its hydroxyl on the left of the α-carbon. Thus, for example, if the specific rotations of the sodium salts of *d*-gluconic (+11.78) and *d*-mannonic (—8.82) acids are compared, it is found that the acid which has the hydroxyl group on the right of its α-carbon, namely, gluconic acid, gives the more dextrorotatory salt. Levene has shown that this relation holds in general for epimeric pairs of such acids. It should be possible, as Levene indicates, to determine the configuration of many sugars by this relation, provided the necessary epimeric pairs of acids are prepared. It seems to me, however, that the phenylhydrazides offer a preferable way of determining these configurations because, as has been shown, it does not seem necessary to prepare the pair of epimeric acids since the direction of rotation of the phenylhydrazide of either one of them indicates the configuration of the α-carbon atom in both. It is also usually the case that the phenylhydrazide is the most readily prepared crystalline derivative of the sugar acids. Levene and Meyer have measured the specific rotations of the sodium salts of all the hexonic acids, and there can be no question but that the measurements for the gluconate, mannonate, gulonate and galactonate are closely correct, because these salts were prepared by neutralizing the very pure recrystallized lactones of these acids. It is interesting to calculate from their measurements the

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[1] *J. Biol. Chem.*, **23**, 146 (1915); also Levene and Meyer, *Ibid.*, **26**, 355 (1915).

rotations of the four asymmetric carbon atoms in the configuration of the hexonic acids in order to compare them with the values that have been found for the phenylhydrazides. Since the sodium salts are largely dissociated while the phenylhydrazides are not, it is not surprising that the values derived from the salts are quite different from those found for the phenylhydrazides.

	Molecular configuration.	Molecular rotation.
Na *d*-gluconate	$+\alpha - \beta + \gamma + \delta$	$= (+11.78)(218)^{1} = +25.7(10)^{2}$
Na *d*-mannonate	$-\alpha - \beta + \gamma + \delta$	$= (-8.82)(218) = -19.2(10)^{2}$
Na *d*-gulonate	$+\alpha + \beta - \gamma + \delta$	$= (+12.68)(218) = +27.6(10)^{2}$
Na *d*-galactonate	$+\alpha - \beta - \gamma + \delta$	$= (+0.40)(218) = +0.87(10)^{2}$

[1] Molecular weight of the sodium salt.

Solving these equations

$$\alpha = +22.4(10)^2,\ \beta = +13.4(10)^2,\ \gamma = +12.4(10)^2,\ \delta = +4.2(10)^2.$$

Comparing these values with those recorded previously in this article for the asymmetric carbon atoms of the hexonic phenylhydrazides, it will be noted that the α-carbon in the salts has a larger influence upon the rotation than the β-, γ- or δ-carbon but not a larger influence than the sum for these three atoms, which shows that the direction of rotation of the salt may be conditioned in certain configurations by the β-, γ- and δ-carbons rather than by the α-carbon, which was not the case for the phenylhydrazides.

In concluding, it may be mentioned that the benzylphenyl hydrazones of the sugars exhibit an interesting correlation between structure and rotation. By inspection of the following table, it will be observed that the hydrazone rotates to the left when the asymmetric α-carbon atom of the configuration has its hydroxyl to the right and *vice versa:*

Benzylphenyl hydrazone.	Position of OH on α-carbon.	$[\alpha]^{20}_{D}$.	Solvent.
d-Erythrose[1]	Right	−32°	Alcohol
Methyl tetrose[2]	Right	− 6.5°	Alcohol
l-Arabinose[3]	Right	−12.1°	Methyl alcohol
Rhamnose[3]	Right	− 6.4°	Methyl alcohol
d-Glucose[3]	Right	−33°	Methyl alcohol
d-Gulose[4]	Right	−24°	Methyl alcohol
d-Galactose[3]	Right	−17.2°	Methyl alcohol
l-Erythrose[5]	Left	+32.8°	Alcohol
d-Lyxose[6]	Left	+26.4°	Alcohol
Fucose[7]	Left	+ 9.1°	Pyridine
d-Mannose[3]	Left	+29.8°	Methyl alcohol

[1] Ruff, *Ber.*, **32**, 3672 (1899).

[2] Ruff and Kohn, *Ibid.*, **35**, 2362 (1902).

[3] Lobry de Bruyn and Van Ekenstein, *Rec. trav. chim. Pays Bas.*, **15**, 226 (1896).

[4] *Ibid.*, **19**, 182 (1900).

[5] Ruff, *Ber.*, **34**, 1366 (1901).

[6] Ruff and Ollendorff, *Ibid.*, **33**, 1801 (1900).

[7] Tollens and Müther, *Ibid.*, **37**, 307 (1904).

The benzylphenyl hydrazones exhibit mutarotation and doubtless exist, therefore, in solution in isomeric forms and the rotations of their solutions refer to mixtures of such forms in equilibrium. Their structures are not as simple and as definitely known as are those of the acid phenylhydrazides, the rotations have not been measured in one solvent throughout, and the correlation between their structure and rotation is not proved in as many cases as have been shown for the phenylhydrazides. Nevertheless, the existing data indicate that such a relationship probably holds.

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THE PREPARATION OF PURE CRYSTALLINE MANNOSE AND A STUDY OF ITS MUTAROTATION.

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1. The Hydrolysis of Vegetable Ivory and the Direct Crystallization of Beta Mannose.*

Without doubt the best source from which mannose may be prepared is the waste sawdust and turnings from vegetable ivory button factories as has been pointed out by Reiss[1] and by Fischer and Hirschberger.[2] Vegetable ivory is the endosperm of the seed of the tagua palm, *phytelephas macrocarpa*, and by acid hydrolysis it yields large proportions of mannose. Hitherto, the usual method for preparing the sugar in crystalline condition has been the procedure of Fischer and Hirschberger, which consists essentially in hydrolyzing the vegetable ivory with 6% hydrochloric acid at 100° for six hours, neutralizing the solution with sodium hydroxide, decolorizing it with bone char and precipitating the mannose with phenylhydrazine as the insoluble mannose phenylhydrazone. The latter is purified by recrystallization and the mannose regenerated from it by boiling with benzaldehyde.[3] The sirup which is thus produced crystallizes slowly after being seeded with mannose crystals, which were first obtained by Van Ekenstein.[4] This method is expensive

* Our thanks are expressed to Mr. T. S. Harding for his skilful assistance in the development of this method for preparing crystalline mannose readily.

[1] *Ber.*, **22**, 609 (1889).

[2] *Ibid.*, **22**, 3218 (1889).

[3] Herzfeld and de Witt, *Z. Ver. Rübenzuckerind.*, **32**, 794 (1895).

[4] *Rec. trav. chim. Pays Bas.*, **15**, 222 (1896).