

soils are not rare, but very common and widely distributed in the United States.

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

THE ROTATORY POWERS OF THE AMIDES OF ACTIVE α -HYDROXY ACIDS.

By C. S. HUDSON.

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Weerman¹ has recently published measurements of the rotatory powers in water of the amides of seven monobasic acids of the sugar group. A comparison of the configurations that have been established for these acids or their amides by Fischer with their rotations is shown in the following table:

TABLE I.—CONFIGURATIONS AND SPECIFIC ROTATIONS.

Amide.	Fischer's configuration.	α -Carbon OH position.	Specific rotation.
<i>d</i> -Gluconic amide.....	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{OH} & \text{H} & \text{O} & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{cccc} \text{OH} & \text{OH} & \text{H} & \text{OH} \end{array}$	Below	+33.8°
<i>d</i> -Galactonic amide.....	$\begin{array}{ccccccc} & \text{H} & \text{OH} & \text{OH} & \text{H} & \text{O} & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{cccc} \text{OH} & \text{H} & \text{H} & \text{OH} \end{array}$	Below	+36.7°
<i>l</i> -Mannonic amide.....	$\begin{array}{ccccccc} & \text{OH} & \text{OH} & \text{H} & \text{H} & \text{O} & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{cccc} \text{H} & \text{H} & \text{OH} & \text{OH} \end{array}$	Below	+29.9°
<i>d</i> -Gulonic amide.....	$\begin{array}{ccccccc} & \text{H} & \text{OH} & \text{H} & \text{H} & \text{O} & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{cccc} \text{OH} & \text{H} & \text{OH} & \text{OH} \end{array}$	Below	+16.1°
<i>l</i> -Arabonic amide.....	$\begin{array}{ccccccc} & \text{OH} & \text{OH} & \text{H} & \text{O} & & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{ccc} \text{H} & \text{H} & \text{OH} \end{array}$	Below	+38.4°
<i>l</i> -Ribonic amide.....	$\begin{array}{ccccccc} & \text{OH} & \text{OH} & \text{OH} & \text{O} & & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{ccc} \text{H} & \text{H} & \text{H} \end{array}$	Above	-15.7°
<i>d</i> -Xylonic amide.....	$\begin{array}{ccccccc} & \text{H} & \text{OH} & \text{H} & \text{O} & & \\ & & & & & & \\ \text{CH}_2\text{OH} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{C} & \cdot & \text{CNH}_2 \end{array}$ $\begin{array}{ccc} \text{OH} & \text{H} & \text{OH} \end{array}$	Below	+44.5°

It will be seen that the *dextrorotary amides have the hydroxyl group below the asymmetric α -carbon atom, while the levorotary ones have it above.* Recently Dr. E. Yanovsky has measured for me the rotation of *d*- α -glucoheptonic

amide, $\text{CH}_2\text{OH} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{CNH}_2$, and Dr. L. H. Chernoff

¹ Dissertation "Over de Inwerking van Natriumhypochloriet op Amiden van Onverzadigde Zuren en Oxyzuren," published by A. H. Kruyt, Amsterdam, 1916.

OH OH H H O
 that of *l*-rhammonic amide, CH₃ . C . C . C . C . CNH₂. Both sub-
 H H OH OH

stances were dextrorotary in agreement with the above relation. This relation is the same one that has been noted previously by Levene¹ for the direction of rotation of the salts and the phenylhydrazides of such acids. It is analogous to the relation that I have shown to hold between the direction of rotation and the position of the hydroxyl group on the γ -carbon atom of the lactones of these acids.² These rules for the direction of rotation may be easily remembered if the formulas are looked upon as placed vertically with the carboxyl group at the top, since a hydroxyl group on the right of the γ -carbon atom indicates that the lactone will rotate to the right and *vice versa*, and a hydroxyl on the right of the α -carbon indicates that the amide, the phenylhydrazide and the salts will rotate to the right. It is not surprising that the rotations of the amides are found to follow the same rule as do those of the phenylhydrazides because the latter compounds may be looked upon as substituted amides, R.CHOH.CONH₂ becoming R.CHOH.CONH.NH(C₆H₅). Probably other substituted amides of these acids, such as the anilides R.CHOH.CONH.C₆H₅, follow the same rule.

It would be interesting to consider in a quantitative way the rotations of the amides that are mentioned in the table, but Weerman's actual readings are so small, in most cases less than two degrees, that the recorded specific rotations may be uncertain to the extent of several per cent. It seems possible, however, to draw at least one quantitative conclusion from them. By the same method of calculation that was used for the phenylhydrazides³ the individual specific rotations of the 4 asymmetric carbon atoms of the hexonic amides may be found from the rotations of gluconic, mannonic, gulonic and galectonic amides to be, for the α -carbon +32, β -carbon -10, γ -carbon -1, and the δ -carbon -7. Although these values may be changed somewhat by more accurate measurements they clearly show that the α -carbon is so strongly rotatory in these compounds that its influence determines the direction of rotation for the whole structure.

The Rotatory Powers of Tartaric and Tartraminic Acids and Tartramide.—It has been shown by Fischer⁴ that dextrorotary tartaric acid ($[\alpha]_D^{20} = +14^\circ$ in 5% aqueous solution⁵) has the configuration

¹ *J. Biol. Chem.*, 23, 145 (1915); Levene and Meyer, *Ibid.*, 26, 355 (1916); 31, 623 (1917). Regarding the phenylhydrazides, see also Hudson, *THIS JOURNAL*, 39, 462 (1917).

² *THIS JOURNAL*, 31, 338 (1910).

³ *Ibid.*, 39, 465 (1917).

⁴ *Ber.*, 29, 1377 (1896).

⁵ Landolt, *Ibid.*, 6, 1073 (1873).

OH H
 CHO . H . C . C . COOH, hence its mono-amide, tartraminic acid, must
 H OH

OH H
 have the configuration CONH₂ . C . C . COOH and its di-amide, tar-
 H OH
 OH H
 tramide, the structure CONH₂ . C . C . CONH₂. In the last formula
 H OH

the position of the hydroxyl group on each of the two α -carbons is to be considered as on the right, the carbon chain being written vertically and the two amide groups placed successively at the top. Both asymmetric carbon atoms, therefore, rotate to the right and it is to be expected that tartramide has a high dextrorotation; in agreement with this conclusion its specific rotation in water has been found by Frankland and Sutor¹ to be +106.5. Walden² found the value 109°. Since the configuration of tartraminic acid may be regarded as consisting of half that of tartramide and half that of tartaric acid, the rotation of tartraminic acid may be expected to be the mean of +14 and +106.5 or +60°. In satisfactory agreement with this calculation Weerman³ has found the value +64, and the last unit is uncertain because the actual reading that he observed was only about 4°. If Walden's value of 109 is used in the calculation the agreement is still better. Both tartramide and tartraminic acid, therefore, conform to the general relation for the direction of rotation of the amides.

The Configurations of the Active Malic Acids.—Naturally occurring malic acid is of levorotation in dilute aqueous solution. Its antipode has been produced by the reduction of natural (dextrorotary) tartaric acid⁴ with hydriodic acid, hence Fischer has assigned to levorotatory malic acid

OH
 the configuration COOH.CH₂.C.CO₂H. The di-amide of this acid
 H

OH
 must accordingly be assigned the configuration CONH₂.CH₂.C.CONH₂.
 H

Since this formula contains only one asymmetric carbon atom and the hydroxyl group is on the left of this carbon, it is to be expected that the

¹ *J. Chem. Soc.*, 83, 1354 (1903). Regarding the dextrorotation of a large number of substituted di-amides of dextro tartaric acid, which agree with the relation, see Frankland and Twiss, *J. Chem. Soc.*, 89, 1853 (1906).

² *Z. physik. Chem.*, 17, 707 (1895).

³ Dissertation, p. 109.

⁴ Bremer, *Ber.*, 8, 861 (1875).

di-amide of natural malic acid will be levorotary in case the above configuration is correct. Such is the fact, the specific rotation in water having been observed by Walden¹ to be -38° . This agreement is supported by Walden's further observation that the di-anilide, di-*o*-toluide, and di-*p*-toluide of natural malic acid are all strongly levorotary substances. A number of other substituted malamides that have been measured by Frankland and his pupils² also agree with the relation. This confirmation of the configuration of the active malic acids is of theoretical value just now because Freudenberg³ has recently passed from active malic to active lactic and active glyceric acids, and has obtained the configurations of the latter two in terms of the configuration of malic acid. As Freudenberg remarks, however, the yield of active malic acid from the reduction of dextrorotary tartaric acid is only 2% which, of course, is so low that the selected configuration of malic acid is rendered doubtful. The present new proof, however, shows that the hitherto accepted configuration of Fischer's is correct and that the configurations which Freudenberg has assigned to lactic and glyceric acids are in consequence also correct. The configurations of active lactic, glyceric and α -hydroxy butyric acids could doubtless be obtained directly, without reference to syntheses from other substances if the rotations of the corresponding amides were known, which is not the case at present.⁴

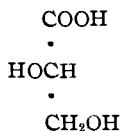
The Configurations of the Active Mandelic Acids.—The mandelic acid which is obtained from amygdalin has a specific rotation⁵ to the left, $[\alpha]_D^{22} = -153^\circ$ in water and -148° in acetone. Its amide has been found by Walden to rotate to the left, $[\alpha]_D^{22} = -67$ in acetone and without doubt it would be strongly levorotary in water. The configurations of the active mandelic acids are accordingly considered to be

¹ *Z. physik. Chem.*, **17**, 249 (1895).

² McCrae, *J. Chem. Soc.*, **83**, 1324 (1903).

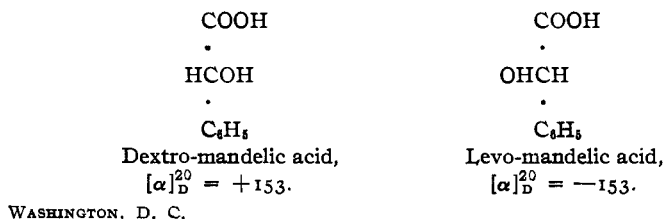
³ *Ber.*, **47**, 2027 (1914).

⁴ After sending in this article for publication I have fortunately found that Frankland, Wharton and Aston (*J. Chem. Soc.*, **79**, 266 (1901)) have measured the rotation of the amide of one of the active forms of glyceric acid. Their acid rotated to the right, its calcium salt rotated to the left and its amide rotated strongly to the left ($[\alpha]_D^{20} = -46^\circ$ for the liquid amide without any solvent and $[\alpha]_D^{20} = -66^\circ$ in methyl alcohol). There can hardly be any doubt that the amide would rotate to the left in water. Consequently dextrorotary glyceric acid is to be assigned the configuration



This confirms Freudenberg's proof for glyceric acid.

⁵ Walden, *Z. physik. Chem.*, **17**, 706 (1895).



[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF PHYSIOLOGICAL CHEMISTRY,
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THE EDIBLE LITCHI NUT (*Litchi Chinensis*).

By B. E. READ.

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The so-called Chinese hazel nut, *Litchi Chinensis* Sonner, (syn. *Nephelium litchi*, *Litchi* Sonn.), together with the allied species of the *Nephelium* occurs in the tropical countries of the far east where it is cultivated for medicinal and edible purposes. The litchi belongs to the genus *Alectryon* of the natural order *Sapindaceae*, which genus consists of more than 16 species, all of which are arborescent and are distributed over the Malayan, Papuan and Pacific Islands, being represented in the latter 2 groups by this particular species *Nephelium*. The type of this genus is the Titaki of New Zealand, *Alectryon excelsus*, which like the Hawaiian Mahoe has edible fruits.¹ It is singular that while the leaves and branches of many of these trees are unquestionably poisonous the fruit of others is valuable as an article of diet. The litchi nut and the longan and rambutan fruits as such are greatly appreciated for their excellent flavor and are used in "inflammatory and bilious fevers."

Of these many useful fruits only one, the litchi nut, has established itself through Chinese sources on the American market. There are said to be 8 varieties of this nut, which may account for varying reports about them. Those imported here from Canton are nearly globose with a dull brick-red pericarp which when ruptured exposes a sweet, brown, fleshy arillus surrounding a glossy chestnut-brown, orbicular seed, described in detail by Engler and Prantl.²

The litchi nut has long been used by the Chinese in medicine, the following paragraph from the Chinese Materia Medica giving a good idea of how highly it is esteemed by them.³

Nephelium Litchi.—Many of the sapindaceous plants are poisonous but the nephelium fruits are an exception, being much esteemed both in the fresh and dry

¹ J. F. Rock, "The Indigenous Trees of the Hawaiian Islands" (1913).

² Engler und Prantl, "Die Natürlichen Pflanzen-familien," Wilhelm Engelmann, Leipzig (1896).

³ Stuart, G., "Chinese Materia Medica." Published by Presbyterian Mission Press, Shanghai (1911).