The analysis indicates that the substance which was isolated is the carbinol and not the corresponding ether. When a gram of the carbinol was boiled for half an hour with acetic anhydride and the reaction mixture was poured into alcohol, the original substance was recovered unchanged. It, therefore, does not form a stable acetate under these conditions. This fact, however, is quite in harmony with the conduct of other tertiary alcohols of this type.

SOMERVILLE, MASS.

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

THE AMIDE OF α-*d*-MANNOHEPTONIC ACID.

BY C. S. HUDSON AND K. P. MONROE.

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This substance was first noted by Fischer[1] as a precipitate settling from the reaction mixture of hydrogen cyanide and *d*-mannose in aqueous solution. He identified the substance as an amide by its behavior towards alkalies and iron salts, found its m. p. to be 182–3°, but published no analysis or record of its purification. Its specific rotation was not measured. As we desired to know its rotatory power we prepared it in similar manner but soon reached the conclusion that it was by no means a pure compound because on successive recrystallizations its m. p. rose to 193–4° and its specific rotation increased from +4 to +28°. These higher values were found only after the substance had been recrystallized 6 times but further recrystallization did not change them. As the substance was difficult to purify and there seeemed a possibility of the presence in it of the isomeric β-*d*-mannoheptonic amide, or some other impurity, a second method for preparing it was studied. Ten g. of pure crystalline α-*d*-mannoheptonic lactone was dissolved in 100 cc. of 50% alcohol, the solution was cooled with ice and ammonia was passed into it to saturation. A fine, white, granular precipitate formed, which was filtered off and washed with cold 50% alcohol. Its m. p. was 184–5° and $[\alpha]_D^{20} = +14$. After only two recrystallizations from hot water its m. p. was 193–4° and $[\alpha]_D^{20} = +27.8°$, both of which agree with the values found for the other preparation of this amide.

The purified amide from the hydrogen cyanide reaction was found to contain 6.1% and 5.9% N in two analyses by the Kjeldahl method, which agree with the theoretical value for $CH_2OH.CHOH.CHOH.CHOH.CHOH.CHOH.CONH_2$, 6.2%. The purified amide made by the action of ammonia on the lactone gave 5.9% and 6.1% N. An aqueous solution of the purified amide from the HCN reaction, containing 0.542 g. substance in 50 cc. solution rotated 1.21° to the right at 20° in a 4 dcm. tube

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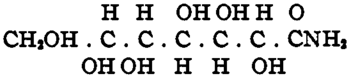
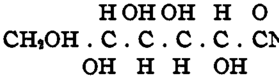
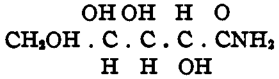
[1] *Untersuchungen über Kohlenhydrate und Fermente*, p. 300.

with sodium light; hence $[\alpha]_D^{20} = +28.0$. A second measurement gave $+28.1$. A solution of the purified amide that had been made from the lactone, containing 0.405 g. in 50 cc. solution, rotated 0.90° to the right at 20° in a 4 dcm. tube with sodium light; hence $[\alpha]_D^{20} = +27.8$. The average of the 3 measurements, $+28.0$, is taken as the specific rotation of the pure amide.

It is interesting to observe that the molecular rotations of the amides of *α-d*-mannoheptonic, *d*-galactonic and *l*-arabonic acids have the same sign and nearly the same numerical values.

TABLE I.

Rotation of Three Amides of Similar Terminal Configuration.

Amide.	Configuration.	Specific rotation.	Molecular[1] rotation.
α-d-Mannoheptonic....	 $CH_2OH\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{O}{C}NH_2$	$+28.0$	$+63.0(10)$[2]
d-Galactonic.........	 $CH_2OH\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{O}{C}NH_2$	$+30.2$	$+58.9(10)$[2]
l-Arabonic...........	 $CH_2OH\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{OH}{\underset{H}{C}}\,.\,\overset{H}{\underset{OH}{C}}\,.\,\overset{O}{C}NH_2$	$+37.9$	$+62.5(10)$[2]

The cause of this agreement evidently lies in the fact that the three structures have the same configurations for the α-, β- and γ-carbon atoms near the amide groups. In an accompanying article by Hudson and Komatsu it is shown that the principle of optical superposition holds fairly closely for such amides as these and that the α- and β-carbon atoms are the only ones that have much influence on the rotation.

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

THE ROTATORY POWERS OF THE AMIDES OF SEVERAL α-HYDROXY ACIDS OF THE SUGAR GROUP.

BY C. S. HUDSON AND SHIGERU KOMATSU.

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In a recent article[2] it was shown that Weerman's measurements of the rotatory powers of the amides of 7 α-hydroxy acids of the sugar group lead to the generalization that the α-carbon atom is principally responsible for the rotation of these substances and that *when the hydroxyl group is on the right of this carbon atom, in the configurations of Fischer's, the amide rotates to the right and vice versa.* This conclusion was borne out

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[1] The molecular weights of the 3 amides are 225, 195 and 165.

[2] THIS JOURNAL, 40, 813 (1918).