

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  $0.90^\circ$  to the right at  $20^\circ$  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  $\alpha$ -*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 <sup>1</sup> rotation.
$\alpha$ - <i>d</i> -Mannoheptonic....	$\begin{array}{ccccccc} & H & H & OH & OH & H & O \\ CH_2OH & . & C & . & C & . & C & . & C & . & C & . & CNH_2 \\ & OH & OH & H & H & OH & \end{array}$	+28.0	+63.0(10) <sup>2</sup>
<i>d</i> -Galactonic.....	$\begin{array}{ccccccc} & H & OH & OH & H & O \\ CH_2OH & . & C & . & C & . & C & . & C & . & CNH_2 \\ & OH & H & H & OH & \end{array}$	+30.2	+58.9(10) <sup>2</sup>
<i>l</i> -Arabonic.....	$\begin{array}{ccccccc} & OH & OH & H & O \\ CH_2OH & . & C & . & C & . & C & . & CNH_2 \\ & H & H & OH & \end{array}$	+37.9	+62.5(10) <sup>2</sup>

The cause of this agreement evidently lies in the fact that the three structures have the same configurations for the  $\alpha$ -,  $\beta$ - and  $\gamma$ -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  $\alpha$ - and  $\beta$ -carbon atoms are the only ones that have much influence on the rotation.

WASHINGTON, D. C.

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

## THE ROTATORY POWERS OF THE AMIDES OF SEVERAL $\alpha$ -HYDROXY ACIDS OF THE SUGAR GROUP.

By C. S. HUDSON AND SHIGERU KOMATSU.

Received May 15, 1919.

In a recent article<sup>2</sup> it was shown that Weerman's measurements of the rotatory powers of the amides of 7  $\alpha$ -hydroxy acids of the sugar group lead to the generalization that the  $\alpha$ -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

<sup>1</sup> The molecular weights of the 3 amides are 225, 195 and 165.

<sup>2</sup> THIS JOURNAL, 40, 813 (1918).

further by the known configurations and rotations of tartraminc acid, tartramide and the amides of malic and glyceric acids. By its application to the amide of mandelic acid the configurations of the active forms of this acid were placed in the system that Fischer originated for the sugar group, which will doubtless in time grow to include most optically active substances. In that article it was stated that Weerman's measurements seemed to lack the precision that would be required in a quantitative study of the rotations of the other active carbon atoms of the amides of the sugar acids. At present we wish to treat this subject quantitatively, basing the study upon measurements that one of us (S. K.) has made during the past year. These measurements confirm the generalization already mentioned, but they differ in some instances from Weerman's data and lead to some interesting conclusions that are not apparent from his measurements.

Consider first the molecular rotations (m. w. 195) in aqueous solution of the amides of the group of acids that are related to the hexoses, the so-called hexonic acids, namely, gluconic, mannonic, gulonic and galactonic acids.

TABLE I.—CONFIGURATIONS AND ROTATIONS OF HEXONIC AMIDES.

Amide.	Fischer's configuration.	Specific rotation.	Molecular rotation.
<i>d</i> -Gluconic amide.....	$\begin{array}{cccccc} & \text{H} & \text{H} & \text{OH} & \text{H} & \text{O} \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{OH} & \text{H} & \text{OH} & \end{array}$	+31.2	+60.8(10) <sup>2</sup>
<i>d</i> -Mannonic amide.....	$\begin{array}{cccccc} & \text{H} & \text{H} & \text{OH} & \text{OH} & \text{O} \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{OH} & \text{H} & \text{H} & \end{array}$	-17.3	-33.7(10) <sup>2</sup>
<i>d</i> -Gulonic amide.....	$\begin{array}{cccccc} & \text{H} & \text{OH} & \text{H} & \text{H} & \text{O} \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{H} & \text{OH} & \text{OH} & \end{array}$	+15.2	+29.6(10) <sup>2</sup>
<i>d</i> -Galactonic amide.....	$\begin{array}{cccccc} & \text{H} & \text{OH} & \text{OH} & \text{H} & \text{O} \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{H} & \text{H} & \text{OH} & \end{array}$	+30.2	+58.9(10) <sup>2</sup>

Since there are 4 asymmetric carbon atoms in these structures the rotation of each of them can be calculated from the rotations of the 4 amides on the assumption of the principle of optical superposition. The details of the method of calculation have already been published.<sup>1</sup> It is found in this way that the molecular rotations for the 4 carbon atoms, calling the active atom next the amide end the  $\alpha$ -carbon, have the following values when the hydroxyl group is on the lower side of its carbon atom (or is on its right when the formula is written vertically with the amide group at the top):  $\alpha$ -carbon = +47.25(10)<sup>2</sup>,  $\beta$ -carbon = -14.65(10)<sup>2</sup>,

<sup>1</sup> THIS JOURNAL, 39, 465 (1917).

$\gamma$ -carbon =  $+0.95(10)^2$ , and  $\delta$ -carbon =  $-2.05(10)^2$ . It will be noticed that the numerical values decrease as the carbon atom is further removed from the amide end (the difference between the values for the  $\gamma$ - and  $\delta$ -atoms, both of which are very small, are probably near the limit of accuracy of the data). The alternation in the sign of the rotation of the successive carbon atoms is also noteworthy, suggesting the alternation in positive and negative affinity that is often ascribed to the carbons in a chain.

Consider next the amides of several of the acids of the heptose group.

TABLE II.—CONFIGURATIONS AND ROTATIONS OF HEPTONIC AMIDES.

Amide.	Fischer's configuration.	Specific rotation.	Molecular rotation. (Mol. wt. 225.)
$\alpha$ -Glucoheptonic.....	H H OH H H O $\text{CH}_2\text{OH.C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{CNH}_2$ OH OH H OH OH	+10.6	+23.8(10) <sup>2</sup>
$\beta$ -Glucoheptonic.....	H H OH H OH O $\text{CH}_2\text{OH.C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{CNH}_2$ OH OH H OH H	-30.2	-67.9(10) <sup>2</sup>
$\alpha$ -Mannoheptonic <sup>1</sup> .....	H H OH OH H O $\text{CH}_2\text{OH.C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{CNH}_2$ OH OH H H OH	+28.0	+63.0(10) <sup>2</sup>
$\alpha$ -Galaheptonic.....	H OH OH H H O $\text{CH}_2\text{OH.C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{C} . \text{CNH}_2$ OH H H OH OH	+14.3	+32.2(10) <sup>2</sup>

Although it is not possible to calculate the rotations of all 5 of the active carbon atoms in these chains, because only 4 observations are at hand, nevertheless the following molecular rotations may be determined:  $\alpha$ -carbon =  $+45.85(10)^2$ ,  $\beta$ -carbon =  $-19.6(10)^2$ ,  $\delta$ -carbon =  $-4.2(10)^2$ ,  $\epsilon$ -carbon —  $\gamma$ -carbon =  $+1.75(10)^2$ . It is noticeable again that the sign alternates from carbon to carbon. The numerical value for the  $\alpha$ -carbon is almost the same as was found for the hexonic amides, showing that the principle of optical superposition holds at least closely in passing from one of these groups to the other. Also the values for the other carbons correspond very well within the two groups. It seems highly probable, therefore, that the principle holds closely among the members of each group. One could, of course, calculate with fair approximation the rotation of the amides of several of the hexonic and heptonic acid amides that have not yet been measured, such as allonic amide or guloheptonic amide, but the mention of this may suffice at present.

Consider next the amides of the pentonic acids.

<sup>1</sup> The rotation of this substance is quoted from the accompanying article by Hudson and Monroe.

TABLE III.—CONFIGURATIONS AND ROTATIONS OF PENTONIC AMIDES.

Amide.	Fischer's configuration.	Specific rotation.	Molecular rotation. (Mol. wt. 165.)
<i>l</i> -Arabonic amide.....	$\begin{array}{ccccccc} & \text{OH} & \text{OH} & \text{H} & \text{O} & & \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 & & \\ & \text{H} & \text{H} & \text{OH} & & & \end{array}$	+37.5	+61.9(10) <sup>2</sup>
<i>l</i> -Ribonic amide.....	$\begin{array}{ccccccc} & \text{OH} & \text{OH} & \text{OH} & \text{O} & & \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 & & \\ & \text{H} & \text{H} & \text{H} & & & \end{array}$	-16.4	-27.1(10) <sup>2</sup>
<i>d</i> -Xylonic amide.....	$\begin{array}{ccccccc} & \text{H} & \text{OH} & \text{H} & \text{O} & & \\ \text{CH}_2\text{OH} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 & & \\ & \text{OH} & \text{H} & \text{OH} & & & \end{array}$	+44.5	+73.4(10) <sup>2</sup>

From these 3 values the molecular rotations of the 3 active carbon atoms in the pentonic amides may be calculated to be,  $\alpha$ -carbon = +44.5(10)<sup>2</sup>,  $\beta$ -carbon = -23.15(10)<sup>2</sup>,  $\gamma$ -carbon = +5.75(10)<sup>2</sup>. The value for *d*-xylonic amide is taken from Weerman's article, as we have not been able to crystallize this substance. The value for the  $\alpha$ -carbon is obtained by the use only of our own data for the amides of arabonic and ribonic acids, both of which have been prepared in very pure crystalline condition. A change in the value for the amide of xylonic acid would not affect the value of the rotation of the  $\alpha$ -carbon atom but would alter those of the  $\beta$ - and  $\gamma$ -carbons. The alternation in sign of the successive carbon atoms is again apparent, and likewise the decrease in the rotation as the carbon atom is further removed from the amide end. The numerical value for the  $\alpha$ -carbon, 44.5(10)<sup>2</sup>, is quite near those that have been found for this carbon in the hexonic and heptonic acids, showing that the principle of optical superposition holds fairly closely for these amides.

Lastly, mention is made of the diamides of 3 of the dibasic acids of the sugar group, *d*-mannosaccharic and *d*-saccharic acids and tartaric acid.

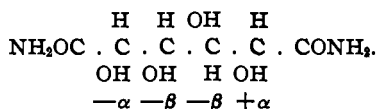
TABLE IV.—CONFIGURATIONS AND ROTATIONS OF THREE DIAMIDES.

Diamide.	Fischer's configuration.	Specific rotation.	Molecular rotation.
<i>d</i> -Saccharic diamide.....	$\begin{array}{ccccccc} & \text{O} & \text{H} & \text{H} & \text{OH} & \text{H} & \text{O} \\ \text{NH}_2\text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{OH} & \text{H} & \text{OH} & & \end{array}$	+13.3	+27.7(10) <sup>2</sup>
<i>d</i> -Mannosaccharic diamide..	$\begin{array}{ccccccc} & \text{O} & \text{H} & \text{H} & \text{OH} & \text{OH} & \text{O} \\ \text{NH}_2\text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 \\ & \text{OH} & \text{OH} & \text{H} & \text{H} & & \end{array}$	-24.4	-50.8(10) <sup>2</sup>
Tartaric diamide.....	$\begin{array}{ccccccc} & \text{O} & \text{OH} & \text{H} & \text{O} & & \\ \text{NH}_2\text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{C} & \cdot \text{CNH}_2 & & \\ & \text{H} & \text{OH} & & & & \end{array}$	+106.5 <sup>1</sup>	+157.6(10) <sup>2</sup>

If the active carbon atoms in these structures be named in the manner that has been followed for the monoamides one must name from each

<sup>1</sup> Measurement by Frankland and Slaton, *J. Chem. Soc.*, 83, 1354 (1903).

end towards the center and in giving a sign to the rotations of the carbons of the left half must consider the structure to be turned through  $180^\circ$  in the plane of the paper, so as to put the left hand amide group around to the right end. Thus the 4 asymmetric carbons in *d*-saccharic diamide would be given the following signs and designations:



Two equations may now be set up for the molecular rotations of the diamides of *d*-saccharic and *d*-mannosaccharic acids, respectively.

$$d\text{-Saccharic diamide } -\alpha - \beta - \beta + \alpha = +27.7(10)^2.$$

$$d\text{-Mannosaccharic diamide } -\alpha - \beta - \beta - \alpha = -50.8(10)^2.$$

Solving these two equations for the two unknown quantities gives  $\alpha = +39.25(10)^2$  and  $\beta = -13.85(10)^2$ .

In the case of tartramide there are two  $\alpha$ -carbons, both to be considered positive, and no  $\beta$ -carbons, hence  $2\alpha = +157.6$  and  $\alpha = +78.8(10)^2$ .

The values for the carbons of the hexaric diamides are near those for the hexonic monoamides and are of the same sign. In the case of the tartaric diamide the sign is the same for the  $\alpha$ -carbon but its numerical value is much larger, possibly because the two  $\alpha$ -carbons, of strong rotation are not separated in this structure by any intervening carbon atoms.

It would be desirable to extend this study to the amides of other optically active dibasic acids. The present data are sufficient to allow the calculation, of the rotatory powers of the diamides of all the hexaric acids.

TABLE V.—MOLECULAR ROTATIONS OF THE ACTIVE CARBON ATOMS OF AMIDES FROM THE SUGAR GROUP.

Car- bon.	4-Carbon series, diamide.	Pentonic amides.	Hexonic amides.	Heptonic amides.	Hexaric diamides.
$\alpha^1$ .....	+78.8(10) <sup>2</sup>	+44.5(10) <sup>2</sup>	+47.25(10) <sup>2</sup>	-45.85(10) <sup>2</sup>	+39.25(10) <sup>2</sup>
$\beta$ .....	.....	-23.15(10) <sup>2</sup>	-14.65(10) <sup>2</sup>	-19.6 (10) <sup>2</sup>	-13.85(10) <sup>2</sup>
$\gamma$ .....	.....	+ 5.75(10) <sup>2</sup>	+ 0.95(10) <sup>2</sup>	?	.....
$\delta$ .....	.....	.....	- 2.05(10) <sup>2</sup>	- 4.2 (10) <sup>2</sup>	.....
$\epsilon$ .....	.....	.....	.....	?	.....

In Table V are recorded the values that have been adduced for the molecular rotations of the different carbon atoms in these various amides. The values for the  $\beta$ - and  $\gamma$ -carbons of the pentonic amides depend upon Weerman's value for xylonic amide. We suspect that his value is slightly too high. If the rotation of the  $\gamma$ -carbon may be neglected in the pentonic amides, as seems probable from its low values in the hexonic series, the value of the rotation of the  $\beta$ -carbon can be calculated without using Weerman's determination. It is found to be  $-17.4(10)^2$ , which is near

<sup>1</sup> With the formula of the compound written vertically and the amide group placed at the top, if the OH group of the particular carbon atom is on the right of the structure the sign of rotation of the carbon is that given in the table.

the average of the values that have been found in the hexonic and hepatic series. Using this value and neglecting that of the  $\gamma$ -carbon, gives for xylonic amide the rotation of arabonic amide,  $+37.5^\circ$ , in place of Weerman's measurement,  $+44.5^\circ$ .

### Experimental.

*d*-Galactonic Amide was prepared by passing dry ammonia gas into an absolute alcoholic solution of pure galactonic lactone, as described by Weerman. It was recrystallized 4 times from water and dried at  $70^\circ$  for 15 hours, and in another case at  $100^\circ$  for 7 hours. The two products showed the same specific rotation. 2,500 g. of substance dissolved to 50 cc. in water rotated at  $20^\circ$  in a 4 dcm. tube in sodium light  $6.04$  circular degrees to the right, hence  $[\alpha]_D^{20} = +30.2^\circ$ . Its melting point was  $172-172.5^\circ$ .

*d*-Gluconic amide was prepared similarly, crystallized 3 times from 90% alcohol and dried at  $70^\circ$  for 25 hours. Its m. p. was  $143-4^\circ$ . 2,500 g. of substance, made up to 50 cc. in water, rotated  $6.24^\circ$  to the right in a 4 dcm. tube; hence  $[\alpha]_D^{20} = +31.2$ . A second measurement gave the same value.

*d*-Gulonic amide was prepared by adding alcohol to a solution of 10 g. of gulonic lactone in strong ammonia water. The crystals were recrystallized from alcoholic solution twice and dried at  $70^\circ$  for 20 hours. M. p.  $122-3^\circ$ ; yield 10 g. 2,500 g. of substance, dissolved to 50 cc. in water rotated  $3.03^\circ$  to the right in a 4 dcm. tube; hence  $[\alpha]_D^{20} = +15.2$ .

*d*-Mannonic amide was prepared by passing dry ammonia into an alcoholic solution of mannonic lactone. It was recrystallized from aqueous alcohol twice and dried at  $70^\circ$  for 20 hours. M. p.  $172-3^\circ$ . 0.4710 g. of substance in 50 cc. aqueous solution rotated  $0.65^\circ$  to the left in a 4 dcm. tube; hence  $[\alpha]_D^{20} = -17.2$ . A second determination gave  $-17.4^\circ$ , and the average is  $-17.3^\circ$ .

$\alpha$ -*d*-Glucoheptonic amide was prepared by passing dry ammonia into an alcoholic solution of the lactone, was recrystallized from alcohol twice and dried at  $70^\circ$  for 10 hours. M. p.  $134.5^\circ$ . 0.3668 g. of substance in 25 cc. aqueous solution rotated  $0.31^\circ$  to the right in a 2 dcm. tube; hence  $[\alpha]_D^{20} = +10.6$ .

$\beta$ -*d*-Glucoheptonic amide was prepared by passing dry ammonia into an alcoholic solution of the pure lactone. The lactone showed a specific rotation of  $-66.0^\circ$  and m. p.  $152-3^\circ$ , in agreement with the values ( $-67.7^\circ$  and m. p.  $151-2^\circ$ ) that have been found by Fischer.<sup>1</sup> The amide was recrystallized twice from aqueous alcohol and dried at  $70^\circ$  for 24 hours. M. p.  $158^\circ$ . From 17.5 g. lactone 7.5 g. pure amide was obtained. 2,500 g. of substance in 50 cc. aqueous solution rotated  $6.00^\circ$  to the left in a 4 dcm. tube; hence  $[\alpha]_D^{20} = -30.0^\circ$ . A second measurement showed  $-30.3$ , and the average  $-30.2$  is taken.

$\alpha$ -*d*-Galactoheptonic amide was prepared according to Fischer's<sup>2</sup> directions, recrystallized twice from alcohol and dried at  $70^\circ$  for several hours. M. p.  $206^\circ$ . 0.2159 g. of substance in 50 cc. aqueous solution rotated  $0.25^\circ$  to the right in a 4 dcm. tube; hence  $[\alpha]_D^{20} = +14.5$ . A second measurement showed  $+14.1$  and the mean is taken,  $+14.3^\circ$ .

*l*-Arabonic amide was prepared from ammonia and the lactone and was recrystallized twice from 90% alcohol, and dried at  $70^\circ$  for 18 hours. M. p.  $135-6^\circ$ . 2,500 g. of substance in 50 cc. aqueous solution rotated  $7.43^\circ$  to the right in a 4 dcm. tube; hence  $[\alpha]_D^{20} = +37.2$ . A second estimation gave  $+37.9$  and the mean is taken,  $+37.5^\circ$ .

<sup>1</sup> *Ann.*, 270, 64 (1892).

<sup>2</sup> *Ibid.*, 288, 139 (1895).

*l*-Ribonic amide was prepared from ammonia and the lactone. The latter was prepared from arabonic acid by rearrangement on heating with pyridine, according to Fischer<sup>1</sup> and Piloty's directions. The amide was recrystallized twice from 90% alcohol and dried at 70° for several hours. M. p. 137–8°. 0.8450 g. of substance in 25 cc. aqueous solution rotated 1.11° to the left in a 2 dcm. tube; hence  $[\alpha]_D^{20} = -16.4$ . Weerman found m. p. 136–7° and  $[\alpha]_D^{20} = -15.7$ .

*d*-Mannosaccharic diamide was prepared according to Fischer's<sup>2</sup> directions by dissolving pure *d*-mannosaccharic dilactone in strong ammonia water, filtering off the crystalline precipitate and washing it with alcohol and ether. It was recrystallized once from water and dried at 70° for 14 hours. M. p. 188–189.5° with decomposition. 0.1765 g. of substance in 50 cc. aqueous solution rotated 0.36° to the left in a 4 dcm. tube; hence  $[\alpha]_D^{20} = -24.4$ . A second estimation gave –24.5. Fischer found m. p. 189°.

*d*-Saccharic diamide was prepared by the interaction of diethyl *d*-saccharic ester and ammonia, following Heintz's<sup>3</sup> directions. It was recrystallized twice from alcohol and dried at 100° for 5 hours. M. p. 172–3°. 0.8572 g. of substance in 50 cc. aqueous solution rotated 0.91° to the right in a 4 dcm. tube; hence  $[\alpha]_D^{20} = +13.3$ °.

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[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

## RESEARCHES ON PROTEINS. VI. THE DESTRUCTIVE DISTILLATION OF FIBROIN.

[PRELIMINARY PAPER.]

BY TREAT B. JOHNSON AND PETER G. DASCHAVSKY.

Received June 7, 1919.

This preliminary report of an investigation, now in progress in this laboratory, is made in order to announce our intention of incorporating in our Researches on Proteins the study of the products of decomposition when silk fibroin is subjected to destructive distillation *in vacuo*. The research will not be completed for several months, but in the light of the recent work of Pictet and Cramer<sup>4</sup> on the destructive distillation of ovalbumin it seems necessary to make known at this time our activity in this same field of research.

Very little is known regarding the nature of the products of decomposition which are formed by the distillation of protein material. While much attention has been paid to the chemistry of coal distillation and also destructive distillation of wood and cellulose material, so far as the writers are aware, no important literature has been contributed dealing with the dry distillation of proteins outside of that bearing on the production of Dippel's oil by distillation of bones. The only publications available to us which contribute any data on this subject are those of

<sup>1</sup> *Ber.*, 24, 4214 (1891).

<sup>2</sup> *Ibid.*, 24, 539 (1891).

<sup>3</sup> *Pogg. Ann.*, 105, 211 (1858).

<sup>4</sup> *Helv. Chim. Acte*, 2, 188–195 (1919); *C. A.*, 10, 1076 (1919).