TABLE IV.—SOLUBILITY BY WEIGHT.

Temperature.	Chloride. Grams in 100 cc. solution.	Chloride. Grams in 100 grams water	Bromide. Grams in 100 cc. solution.	Bromide. Grams in 100 grams water.	Iodide. Grams in 100 cc. solution.	Iodide. Grams in 100 grams water.
0°	0.6728	0.6728	0.4554	0.4554	0.0442	0.0442
15°	0.9070	0.9090	0.7285	0.7305	0.0613	0.0613
25°	1.0786	1.0842	0.9701	0.9744	0.0762	0.0764
35°	1.315	1.3244	1.3124	1.3220	0.1035	0.1042
45°	1.5498	1.5673	1.7259	1.7457	0.1440	0.1453
55°	1.8019	1.8263	2.1024	2.1376	0.1726	0.1755
65°	2.0810	2.1265	2.5161	2.5736	0.2140	0.2183
80°	2.5420	2.6224	3.2350	3.3430	0.2937	0.3023
95°	3.0358	3.1654	4.1767	4.3613	0.3814	0.3960
100°[1]	3.208	3.342	4.550	4.751	0.420	0.436

At 0° the solubility of the chloride by weight is about one and one-half times that of the bromide; at 35°, their solubilities are practically equal and at 95° that of the chloride is about three-fourths of that of the bromide.

DEPARTMENT OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH., March, 1903.

THE CARBOHYDRATE GROUP IN THE PROTEIN MOLECULE.[2]

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IT HAS been known for some time that certain complex substances found in animal organisms, when decomposed with acids, yielded protein and carbohydrate bodies, together with other products. These substances, known as mucins, mucoids, chondroproteids, nucleins, hyalogen substances, etc., are generally regarded as compounds in which the protein is united with some other complex organic group of which this carbohydrate is a part. Although several investigators long ago suggested the possible presence of a carbohydrate group in the protein molecule proper, no evidence of weight supported this view until Pavy,[3] by hydrolyzing coagulated ovalbumin, obtained a solution from which he prepared an osazone with a melting-point near that of glucosazone. In consequence of this discovery, Pavy concluded that his investigations brought "the extensive group of proteids of both the animal and vegetable kingdoms of nature into the class of glucosides."

This announcement of Pavy's led to numerous investigations

[1] By extrapolation, see Fig. 2.

[2] From the laboratory of the Connecticut Agricultural Experiment Station.

[3] "Physiology of the Carbohydrates."

followed by many contradictory statements respecting the presence of the carbohydrate group in the protein molecule proper. It has, however, been definitely proved that several of the animal proteins which are not, at present, considered to be compounds of protein with non-protein substances, yield carbohydrate which has been identified with chitosamine, conalbumin, the globulins of egg white and of egg yolk. Chitosamine has been obtained from crystallized ovalbumin, serum albumin, and an osazone from the mixed globulins of the blood serum. From no other "simple" protein, so far as we can find, is it certain that carbohydrate has been directly obtained.

The presence of a carbohydate group in the protein molecule is, however, generally assumed, because it is commonly supposed that all proteins, casein excepted, give Molisch's reaction. This is a furfurol reaction of great delicacy and is given by minute quantities of all carbohydrates when decomposed with strong sulphuric acid, even though they, like the hexoses, yield but a small proportion of furfurol. As Molisch's reaction has been applied to only a few of the vegetable proteins, we have tested a series of them in order to see if they, like the animal proteins, would all give this reaction.

We have also attempted to determine quantitatively the amount of furfurol which these proteins yield, by boiling them with hydrochloric acid (sp. gr. 1.06), collecting the distillate and precipitating with phloroglucin in the usual way. The aniline acetate test was also applied to the distillate, in order to detect any minute quantities of furfurol which it might contain. The results of these experiments are given in the following table, in which the proteins are arranged as far as possible in the order of the intensity of the Molisch reaction which they gave under practically the same conditions, which were the following:

Ten milligrams of the protein were suspended in 1 cc. of water, 2 drops of a 15 per cent. alcoholic solution of α-naphthol were added, and then 3 cc. of concentrated sulphuric acid.

This method yields only approximately comparative results but is sufficient to show, in a general way, the relative intensity of the reaction.

Those proteins which gave no Molisch reaction were also tested in larger quantity, but with perfectly negative results.

The outcome of these experiments was as follows:

FURFUROL REACTIONS GIVEN BY VARIOUS PROTEINS.

Protein.	Condition.	Source.	Molisch reaction.	Aniline acetate.	Phloroglucin.
Avenalin.	Crystals.	Oatseed.	None.	....	....
Edestin.	Crystals.	Hempseed.	None.	None.	None.
Globulin.	Crystals.	Castor-bean.	None.	....	....
Casein.	Amorphous.	Cow's milk.	None.	....	....
Globulin.	Crystals.	Flaxseed.	Trace.	None.	None.
Legumin.	Spheroids.	Vetch.	Slight.	None.	....
Legumelin.	Amorphous.	Cow-pea.	Slight.	....	....
Zein.	Amorphous.	Maize.	Slight.	None.	None.
Legumin.	Spheroids.	Horse-bean.	Slight.	None.	....
Amandin.	Spheroids.	Almonds.	Slight.	None.	None.
Globulin.	Spheroids.	Sunflower.	Slight.	None.	None.
Glycinin.	Spheroids.	Soy bean.	Slight.	None.	None.
Excelsin.	Crystals.	Brazil-nut.	Slight.	None.	None.
Legumin.	Spheroids.	Lentil.	Slight.	None.	None.
Globulin.	Spheroids.	Cottonseed.	Moderate.	None.	None.
Glutenin.	Amorphous.	Wheat flour.	Moderate.	....	....
Hordein.	Amorphous.	Barley flour.	Strong.	None.	None.
Ovalbumin.	Crystals.	Hen's egg.	Strong.	Slight trace.	Slight trace.
Gliadin.	Amorphous.	Wheat flour.	Strong.	None.	None.
Vignin.	Spheroids.	Cow-pea.	Strong.	None.	None.
Nucleovitellin.	Amorphous.	Hen's egg.	Strong.	None.	None.
Leucosin.	Amorphous.	Wheat flour.	Very strong.	....	....
Phaseolin.	Spheroids.	Adzuki bean.	Very strong.	None.	None.
Phaseolin.	Crystals.	Kidney bean.	Very strong.	....	....

It is to be noted that several of these proteins gave no reaction whatever[1] and therefore contain no carbohydrate; that a larger number gave only a slight reaction, which, in view of the great delicacy of Molisch's test, must be attributed to a slight contamination of the preparation with some carbohydrate; that the rest gave positive reactions, some even stronger than was given by ovalbumin, which is known to contain a considerable amount of carbohydrate. From this we conclude that these latter may possibly contain a carbohydrate group. None of the proteins yielded any furfurol when boiled with hydrochloric acid, except ovalbumin, which showed a trace, and none of these, therefore, contain a measurable proportion of any pentose-yielding group. After these tests had been made, Grund[2] published the results of similar attempts to obtain furfurol from animal proteins, but with the same negative results. Whether those proteins which do not yield an osazone but which give a strong Molisch reaction actually contain a carbohydrate group cannot thus be determined. Molisch's reaction is of such extreme delicacy that mere traces of carbohydrate are sufficient to cause a strong reaction, especially if these, like the pentoses and nucleic acids, yield large proportions of furfurol when hydrolyzed by acids.

In order to determine the intensity of this reaction with small quantities of carbohydrates, we tried the following experiments:

Cellulose.—0.5 milligram of filter-paper gives a very powerful reaction, much more intense than was given by any of the proteins tested.

Hexose.—0.1 milligram of dextrose gave as strong a reaction as those marked strong in the table.

Pentose.—0.1 milligram of arabinose gave a strong reaction; 0.05 milligram a decided one.

Furfurol.—0.01 milligram gave a strong pink.

Nucleic Acid.—0.5 milligram of nucleic acid gave a strong reaction, while 0.05 milligram gave one similar to those given by the proteins marked slight. 0.5 milligram of nucleic acid would correspond to a phosphorus content of 0.5 per cent., 0.05 milligram to 0.05 per cent. of the quantity of protein used in these tests—a quantity which would be readily detected. From these experiments it is evident that very small quantities of contaminating

1 Erb (*Ztschr. Biol.*, **41**, 309) has stated that edestin does not give Molisch's reaction.

2 *Ztschr. physiol. Chem.*, **35**, 111 (1902).

substances, many or all of which are liable to be present with the protein, especially in vegetable extracts, may be quite enough to cause a strong Molisch reaction.

The evidence of a carbohydrate group in the protein molecule which Molisch's reaction affords cannot, therefore, be accepted as conclusive, other evidence which shows that more than insignificant quantities of carbohydrate are present being also necessary.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 77.]

p-AMINOBENZONITRILE.[1]

BY MARSTON TAYLOR BOGERT AND LOTHAIR KOHNSTAMM.

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INTRODUCTORY.

IN the last edition of Beilstein's "Handbuch," Vol. II, p. 1273, three widely separated melting-points are recorded for *p*-aminobenzonitrile, namely, 74°, as reported by Engler;[2] 110°, reported by Fricke;[3] and 86°, reported by Griess.[4] In the recent German edition of "Roscoe and Schorlemmer," and in Richter's "Lexikon," the preference is given to the figure 110°—why, we do not know, unless it is due to the usual inclination on the part of compilers of reference works to give the preference to the highest figure. As the matter is not cleared up in the recently issued supplement to "Beilstein" (Vol. II), and as we have not been able to discover anything in the literature which would further enlighten us. it seemed of interest to investigate the subject, and to determine if possible which of these widely divergent melting-points (if any, indeed, were correct) represented the real melting-point of *p*-aminobenzonitrile, especially as a further study of this nitrile and its derivatives was contemplated.

The results obtained show quite clearly that the melting-point of 86°, as given by Griess,[5] is substantially correct. We have repeated the work of Engler, Fricke and Griess, and have also prepared the nitrile by a fourth method. The products obtained

[1] Read before the New York Section at its meeting May 20, 1902.

[2] *Ztschr. Chem.* (1868), p. 613; *Ann. Chem.* (Liebig), **149**, 297 (1869).

[3] *Ber. d. chem Ges.*, **7**, 1321 (1874).

[4] *Ibid.*, **8**, 861 (1875).

[5] *Loc. cit.*