

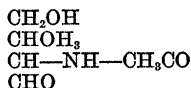
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SPECIAL ARTICLES

THE CHEMICAL CONSTITUTION OF CHITIN¹

THE prevalent ideas concerning the molecular structure of chitin have been based upon the fact that it gives off acetic acid when acted upon by strong reagents, such as concentrated acid or alkali, and that its elementary composition suggests the empirical formula $C_8H_{15}NO_6$.² Since it is also known that chitin yields on decomposition glucosamin it was a logical inference that the above formula represents an acetylated glucosamin



of which chitin is the polymere.

This hypothesis regarding the structure of chitin has been strengthened by other observations, viz., that if chitin is dissolved in strong sulphuric acid, allowed to stand several days and then diluted with a large quantity of water, a white precipitate is formed which on analysis proves to be a monoacetylglucosamin. Occasionally, however, a substance is isolated which represents a monoacetyldiglucoamin.

An investigation upon chitin of lobsters which I conducted recently at the Woods Hole Fisheries Biological Laboratory brought out certain facts which indicate that, while the observations and analyses mentioned previously are doubtless correct, the hypothesis to which they gave origin is based largely upon misconception. I shall present here a brief outline of the principal results of the investigation, reserving a more detailed statement for publication in the near future.

It will not be necessary in this preliminary

¹ Published with the permission of the Commissioner of Fisheries.

² The formula actually computed from the analytical data is $C_8H_{14}NO_6$, but $C_8H_{15}NO_6$ is the one usually given because it corresponds to the hypothesis.

note to discuss the experimental procedure beyond the mere statement that pure chitin was hydrolyzed with varying strengths of sulphuric acid, and for varying lengths of time, the cleavage products as well as the volatile substances formed during hydrolysis having been quantitatively determined.

The results of fundamental significance yielded by this investigation are the following:

First. Very little volatile acid is formed in the early period of hydrolysis of chitin, though all its glucose molecules may already be split off. A very large production of volatile acid is invariably found when the sugar molecule itself is attacked by the acid medium.

Second. The volatile acid produced is not acetic only. At least in one experiment it was possible to show that two per cent. of the acid was formic. There is good reason for believing that other volatile acids, too, may be formed, but the attempt at isolating and identifying those has not yet succeeded.

Third. The maximum yield of sugar is about 81 per cent.

Fourth. The amino group is readily split off from the glucosamine. The hydrolyzed material contains the ammonium sulphate which can be distilled off directly by making it alkaline, and the ammonia can be collected in standard acid.

Fifth. The nitrogen of the amino group does not represent the total nitrogen in the chitin molecule. There is another nitrogenous part in the molecule which is characterized by great resistance, so that the nitrogen of that small fraction can be obtained only by digesting with concentrated sulphuric acid. There is a remarkably constant relation between this easily detachable nitrogen group and the stable nitrogen fraction. In my experiments, the latter formed 12.04 to 12.45 per cent. of the total nitrogen.

The interpretation of these results is very obvious. The chitin molecule is certainly more complex than previously assumed. It may be regarded as consisting of two parts: one containing all the glucose and all the amino groups, the other being a stable nitrogenous compound which yields no glucose. It would be venturesome at this time to express an

opinion as to the nature of the latter fraction. The efforts to isolate it for detailed study have not been successful thus far, but the work in this direction is continued.

The volatile acid given off, of which acetic is the more predominant constituent, does not represent a component part of the molecule. It is a decomposition by-product of the glucose. It is possible to lower greatly the yield of sugar by hydrolyzing chitin with strong acid or by raising the temperature or increasing the duration of the hydrolysis. A great evolution of volatile acid from the chitin will occur simultaneously. The very small quantity of acid formed even in the cold must be likewise attributed to the slow oxidative action of the strong sulphuric acid which must be used in order to dissolve the chitin.

Assuming that the empirical formula for chitin is correct (elementary analyses are in progress now to verify this) we may interpret the above facts in its light, without recourse to the hypothesis that the chitin molecule contains an acetyl group. If we assume that the chitin is a polymere of eight $C_6H_{13}NO_6$ molecules, this should yield on hydrolysis seven molecules of glucosamin, $C_6H_{13}NO_6$, one molecule of glucose, $C_6H_{12}O_6$, and one molecule of the yet unidentified nitrogenous fraction. As the amino groups are cleaved off in the hydrolysis, we get altogether eight glucose molecules to seven ammonia nitrogens and one residual nitrogen. Theoretically, then, the chitin molecule should yield 81.1 per cent. of glucose, and 87.5 per cent. of amino nitrogen and 12.5 per cent. of nitrogen in a stable combination. The facts obtained by hydrolysis agree remarkably with these theoretical expectations.

I could hardly enter here upon a discussion of the bearing of these results further than to say that monoacetylglucosamine, or for that matter monoacetyldiglucoamine, have no relation to chitin. They are secondary products, and are formed after the chitin molecule has been broken down by the action upon it of the sulphuric acid.

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OUTLIERS OF THE MAXVILLE LIMESTONE IN OHIO NORTH OF THE LICKING RIVER¹

It is well known to those familiar with Ohio geology that the Maxville limestone is the uppermost formation of the Mississippian System found in the Ohio scale, that its outcrop is limited in extent, patchy in character, and that the overlying Pennsylvanian beds rest upon it unconformably. Up to the present, all the known outcrops of this formation occur south of the Licking River in central Ohio and they lie in a belt ten or twelve miles wide, which extends from the above river on the north to the Ohio River on the south.

It has long been supposed that the formation once extended northward to northern Ohio and was removed by late Mississippian erosion. The supposition was based upon the presence of lime cobblestones more or less silicified which are found in places in the bottom of the Coal Measure basal conglomerate, and which were said to carry Mississippian fossils. Since no other Mississippian limestone was known to occur in the state, it was concluded the cobble stones must have been derived from the Maxville.

It is the purpose of the writer to (1) point out the northward extension of this limestone, to (2) throw further light on the origin of the cobble stones, and to (3) emphasize a reason for the absence of the limestone in northern Ohio.

Beginning at the Licking River various outcrops of this limestone were found as far as forty miles north of the city of Zanesville in a belt ten to twelve miles wide. They invariably occur in isolated patches, are unconformable with superjacent beds, vary in thickness from two to nine feet, and are clearly erosion remnants of a former continuous stratum. Where it is not weathered it presents the same blue-gray, fine-grained, compact character found far to the southward. In places it is fairly fossiliferous, and when fully weathered there remains a residual ochreous earth of deep yellow to chocolate color, mingled with silicious concretions. The latter weather

¹ Read before Section E, A. A. A. S., Columbus meeting, 1915.