1599

 $C_6H_{11}O_6NH_2.HCl, 6.49\%); [\alpha]_D^{20} + 64.8^\circ$  (pure  $C_6H_{11}O_6-NH_2Cl [\alpha]_D^{20} + 72.5^\circ$ ). The filtrate from the crude glucosamine hydrochloride was diluted with water and the acetone removed by repeated dilution with water and distillation. The residual solution was then analyzed for nitrogen and reducing compounds: found, 33.0 mg. N; copper reducing value equivalent to 73.0 mg. of glucosamine hydrochloride.

Comparative Stability of Glucose and Glucosamine Hydrochloride toward Boiling Hydrochloric Acid.—0.6941g. of glucose monohydrate (0.6316 g. anhydrous glucose) was refluxed with 50 cc. of concentrated hydrochloric acid (initially 37%). After a few minutes of boiling, the solution turned dark brown, and insoluble material began to separate out. After refluxing for ten hours, the solution was filtered, and the humus was washed with a small quantity of water and dried at  $100^\circ$ : weight, 0.0961 g., equivalent to 15.2% yield by weight. The copper reducing value of the filtrate was equivalent to 24.9 mg. glucose, equal to 3.9% of the sample, indicating that 96.1% was destroyed.

0.6241 g. of pure glucosamine hydrochloride was subjected to the same treatment as the glucose sample; weight of humus material, 0.0027 g., equivalent to 0.4% yield by weight. The copper reducing value of the filtrate was equivalent to 0.4710 g. of glucosamine hydrochloride, equal to 75.4% of the sample, indicating that 24.6% was destroyed.

## Summary

A chitinous complex was isolated from the mycelium of Penicillium javanicum in quantity equivalent to 17.4% of the fat-free tissue, which contained 45.04% carbon, 6.38% hydrogen and 4.34% nitrogen. Hydrolysis of this material with hydrochloric acid of an initial concentration of 37% resulted in considerable destruction of the primary products of hydrolysis. The nitrogen of the hydrolyzed chitinous complex was distributed as follows: 7.0% in insoluble humus-like material; 45.5% in glucosamine hydrochloride; and 36.9% in non-reducing nitrogen compounds remaining in solution after recovery of the glucosamine. Insoluble nitrogen-containing humuslike material was formed to the extent of 13.0%by weight, probably chiefly from glucose anhydride units in the chitinous complex. Glucosamine hydrochloride was decomposed to the extent of 25% by prolonged boiling with concentrated hydrochloric acid, with the formation of 0.4% by weight of humus-like material.

WASHINGTON, D. C.

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#### [CONTRIBUTION FROM BOTANICAL LABORATORY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Rate of Carbohydrate Condensation on a Cell Wall

## BY O. L. SPONSLER

It is possible to determine the rate at which cell-wall material is deposited during the growth of a new cross wall in certain green algae. Observations of that process were made on dividing cells of a species of *Rhizoclonium*, a genus in the family Cladophoraceae, in which the cross wall grows from the side walls toward the center of the cell. The alga is a filament consisting of a single row of cylindrical cells placed end to The cells are about 100 microns long and end. 20 microns in diameter. The new cross wall starts as a ring-like projection on the inside of the wall and grows by addition of material on its inner edge, gradually building the ring into a solid disk, somewhat as an iris diaphragm shutter of a camera may be slowly closed to form a solid disk. When the disk is completed, the cell is divided into two new cells, equal in size.

The growth of the new wall was observed under the microscope and measurements were made of the progress of growth. An eyepiece micrometer was used for making the measurements. Its smallest unit was equivalent to 4 microns (0.004 mm.) when the magnification was 440 diameters. Estimations to 1 micron were therefore fairly accurate.

The green cylindrical threads when seen under the microscope appeared as two-dimensional flat threads consisting of rectangular cells, end to end; and the growing cross walls were seen as minute projections extending inward from the side walls as indicated in the figure. The growth of the cross walls, as seen on this edge view, was indicated by the slow increase made in the length of these lateral projections. The growth continued until the lines met, closing the wall completely across the cell. The new cross wall thus formed was a disk 20 microns in diameter and 1 micron in thickness. There was no change in thickness from the time it started as a minute projection on the side wall of the cell until it had grown into the completed solid disk.

At the time it was initiated as a ring-like projection the inner edge of the ring was a surface 1 micron wide, with a length equal to the circumference. At that time the radius was 10 microns and the surface therefore was 63.2 square microns. As the growth continued by deposition of cell-wall material on this surface, the radius became smaller and smaller and the surface upon which the deposition was taking place therefore decreased still more rapidly until the central hole of the disk was completely closed.

Measurements were taken of the length of the new wall projections and of the distance between their ends at intervals usually of fifteen minutes. Thus the amount of growth, on a radius, could be checked against the diameter of the opening in the disk. By good fortune four adjoining cells of a single filament were found in the process of cell division. They were under the microscope all at the same time when the measurements given below were made. Observations were difficult to make at the beginning of growth of a new wall and also at the closing of the hole in the disk. In fact, none of the new walls were found until about 2 microns of growth, on the radius, had been made. However, over the greater part of the growth the measurements offered but little difficulty and seemed to be in fair enough agreement to allow a few interesting deductions to be drawn.

The measurements which were taken of the four growing walls are shown here in the graph Fig. 1 where the radius in microns is plotted against time in five-minute intervals. The points fall nearly enough on a line to allow the use of averages for discussion.

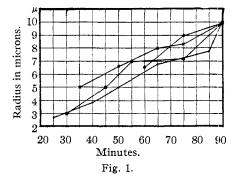


Figure 2 represents uniform consecutive stages of growth drawn from the averages. Here, for example, the growth from stage 2 to stage 3 was produced in fifteen minutes and the amount of

growth was 1.6 microns on a radius. The whole disk was completed in about eighty-five minutes.

Stage 2	3	4	5	6	78
20 μ	14,44	10.4,4	72,0		
Minutes $15 \rightarrow   \leftarrow 15 \rightarrow   \leftarrow 15 \rightarrow   \leftarrow 15 \rightarrow   \leftarrow 15 \rightarrow   10$					
Fig. 2.					

Although the data shown in Fig. 1 are not of an especially high order of accuracy they are about what may be expected from living organisms and are sufficiently in agreement to throw some light upon the process of cell-wall growth. As indicated, the growth on a radius is approximately 0.1 micron per minute; that is, concentric layers 0.1 micron thick are deposited on the inner edge of the ring at the rate of one layer per minute. This rate of deposition, as will be seen from the curve, is practically the same at all stages of growth. In other words, a layer of cell wall material about 0.1 micron thick was deposited during each minute of growth no matter how great or how small the total surface was upon which the deposition was made.

The material which was deposited was without doubt of carbohydrate origin and since the change was from soluble carbohydrates dissolved in the surrounding protoplasmic matrix to the insoluble wall, it seems quite probable that the monosaccharides were condensed into polysaccharide chains. In the latter form they appeared somewhat like cellulose and remained as such rather than later undergoing lignification. Most of the polysaccharide structures in plants, whether amorphous or having a more or less regular molecular structure, have approximately the same density. Their anhydrous unit of structure then is of about the same size, spatially, as that of cellulose; that is, about  $5 \times 6 \times 6$  Å. The 0.1 micron layer deposited each minute may be thought of as consisting of smaller layers of monomolecular thickness, where the monosaccharide unit is considered as the unit of molecular measurement, although the wall is actually amorphous. During the fifteen-minute interval of growth from one stage to the next of Fig. 2, there were deposited then about.3200 layers, each of the thickness of a monosaccharide unit, or between 3 and 4 per second. Since so little is known about the condition of the monosaccharides as they occur in the protoplasmic matrix and about the matrix itself, it is scarcely worth while to speculate fur-

There are, however, two or three additional points of interest which came out of these observations. The fact that during the whole growth of the disk the thickness remains the same makes it seem quite obvious that the deposition occurs only on the inner edge of the slowly closing ring. That being the case, it may be assumed then that the chain molecules have their active ends sticking out toward the center of the hollow disk where deposition takes place, and that growth occurs by addition of new residues on these ends. That conception of growth may be reinforced slightly by the commonly known fact that cell-wall formation is always associated with the presence of living protoplasm in contact with the growing wall. It is still further strengthened by the fact that only local activity may be seen in these growing walls. The protoplasm seems to be in contact

with the side surfaces of the disk as well as with the inner edge yet it is only on the inner edge that deposition takes place. That the protoplasm takes an active part in the deposition seems evident, for the rate of deposition may be slowed down very materially or even stopped completely by very slight changes in the environment of the algal cells.

From what has been said above there appears to be a marked difference in the process of deposition between the animate and inanimate. In the former, for example, the surface may decrease rapidly as deposition occurs, while in the inorganic process such as crystallization the active surface usually becomes greater.

May we say in conclusion that in this report we have tried to make the conception of cellwall growth, in at least one phase of its construction, somewhat less vague by introducing a molecular picture into the process.

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[Contribution from the School of Chemistry and Physics of the Pennsylvania State College]

Los Angeles, Calif.

# The Reaction of Diethylzinc on Acetoxime

# By David F. Menard and John G. Aston

This paper describes a study of the reactions of diethylzine on acetoxime in which it is shown that the products are analogous to those obtained by the action of dimethylzine on methanol.<sup>1</sup>

When one mole of diethylzinc was added to an ether solution containing two moles of acetoxime, two moles of ethane was evolved and an insoluble zinc compound was formed, by the consecutive reactions A and B

$$Zn(C_{2}H_{\delta})_{2} + (CH_{3})_{2}CNOH \longrightarrow$$

$$(CH_{3})_{2}CNOZnC_{2}H_{\delta} + C_{2}H_{\epsilon} \quad (A)$$

$$ethyl zinc acetoximate$$

$$(CH_{3})_{2}CNOZnC_{2}H_{5} + (CH_{3})_{2}CNOH \longrightarrow$$

$$[(CH_{3})_{2}CNO]_{2}Zn + C_{2}H_{\epsilon} \quad (B)$$

$$zinc diacetoximate$$

The reaction of one mole of diethylzinc with one mole of acetoxime formed a soluble zinc compound and one mole of ethane was evolved according to reaction (A). In each of these reactions the pure zinc compound was isolated and identified.

Upon hydrolysis of zinc diacetoximate acetoxime was formed, while hydrolysis of ethyl zinc acetoximate formed ethane and acetoxime.

(1) Tolkátschew, Chem. Zentr., 11, 1200 (1901).

### Experimental

Apparatus and Manipulation.—The apparatus (Fig. 1) was tested for leaks and swept completely with dry carbon dioxide before each experiment. The acetoxime solution was introduced into the 250-cc. reaction flask, A, through tube, E, taking care to exclude air. The calculated amount of diethylzinc was added dropwise from the calibrated pipet, B. This pipet had been connected to the addition side arm by a ground glass joint covered with paraffined heavy rubber tubing.

Fig. 1 — Apparatus for reactions with zinc alkyls.

The gas evolved passed through the condenser and the sulfuric acid traps, D, to remove ether vapor. It was collected in a gas holder over saturated salt solution.

