

is proved by the fact that, in solutions just below the strength required for micelle formation, contact between mineral and a newly formed bubble may be possible when contact with an aged bubble is impossible.

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<sup>1</sup> Wark, I. W., *J. Phys. Chem.*, **40**, 661 (1936).

<sup>2</sup> Adam, N. K., and Shute, H. L., *Trans. Farad. Soc.*, **31**, 759 (1933).

### Structure of Alginic Acid

ALGINIC acid, the industrial importance of which is increasing, constitutes a large proportion of the dry weight of certain seaweeds. It is noteworthy among polysaccharides in that it appears to be built up entirely of *d*-mannuronic acid residues, although its resistance to hydrolysis is so great that no quantitative transformation to *d*-mannuronic acid has been achieved<sup>1</sup>. The results we have recently obtained from a study of the action of methyl alcoholic hydrogen chloride on the polysaccharide show that high yields of *d*-mannuronic acid are obtainable from alginic acid.

Furthermore, we succeeded in isolating, by the use of the same reagent, a partially degraded form of alginic acid of comparatively low molecular weight. Except for the lower viscosity of its solutions, this material differed little from the original alginic acid, but it was more amenable to chemical transformation. From it, by use of thallium ethoxide and methyl iodide, we obtained the corresponding fully methylated derivative. This methyl derivative was exceptionally stable towards hydrolytic agents, but two methods were developed which gave insight into its chemical structure. When boiled with strong nitric acid it underwent hydrolysis, followed by degradative oxidation, with formation of *meso*-dimethoxy succinic acid (v). This indicated that in each of the manuronic acid residues the methyl groups were attached at C<sub>2</sub> and C<sub>3</sub>.

Conclusive proof of this was provided as follows. Methylated alginic acid on drastic treatment under pressure with methyl alcoholic hydrogen chloride

gave the methyl ester of 2:3-dimethylmannuronide (ii). The latter, after hydrolysis followed by oxidation (bromine water), yielded 2:3-dimethyl mannosaccharic acid (iii), and this in turn was oxidized by periodic acid (reagent for oxidative degradation of  $\alpha$   $\beta$  glycols<sup>2</sup>). The products were glyoxylic acid (iv), and the half aldehyde of *meso*-dimethoxy succinic acid from which the crystalline methyl *meso*-dimethoxy succinate (v) was then obtained quantitatively. It follows that in the methylated alginic acid the methyl groups were situated at C<sub>2</sub> and C<sub>3</sub> respectively, and it appears that alginic acid is composed of *d*-mannuronic anhydride residues linked glycosidically. In addition, it is clear that in alginic acid there occurs a chain of *d*-mannuronic acid residues in each of which the hydroxyl groups at C<sub>2</sub> and C<sub>3</sub> are free. The glycosidic linkage must therefore be either 1:4 (pyranose ring structure) or 1:5 (furanose ring structure).

In view of the extreme stability of alginic acid and its large negative rotation, it is highly probable that the ring structure is pyranose and that the linkage between the residues is 1:4. We conclude therefore that at least the major portion of the alginic acid molecule is composed of  $\beta$ -*d*-mannuronic acid residues linked as shown in (i). At present, owing to the experimental difficulties connected with the hydrolysis of such intractable material, it is not possible to say whether the whole of the alginic acid molecule is so constituted, and further work on this subject is in progress.

The structural resemblance between (i) and the formula for cellulose (chains of  $\beta$ -*d*-glucopyranose units with 1:4 linkage) is apparent, and a further point of interest is that in pectic acid<sup>3</sup>, as shown recently in this laboratory and by Dr. F. Smith of the University of Birmingham, a similar structure is encountered, the residues in this case being  $\alpha$ -*d*-galacturonic acid (pyranose form) linked glycosidically through positions 1 and 4.

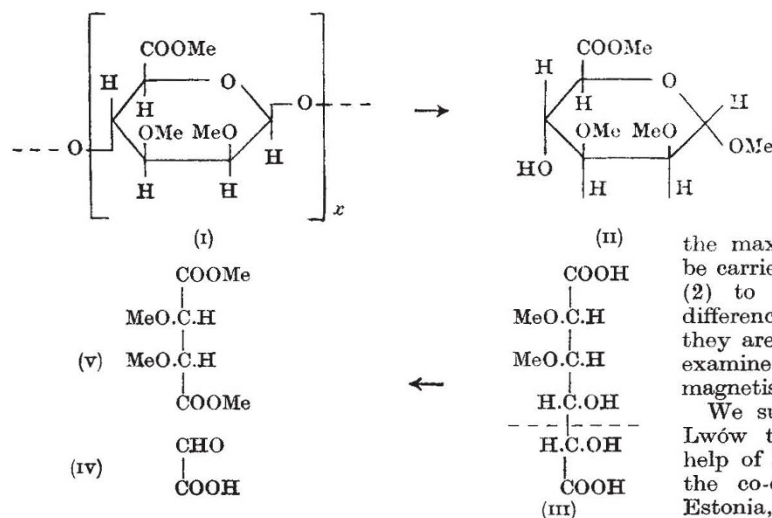
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<sup>1</sup> Nelson and Cretcher, *J. Amer. Chem. Soc.*, **51**, 1914 (1929); **54**, 3409 (1932). Bird and Haas, *Biochem. J.*, **25**, 403 (1931). Schoeffel and Link, *J. Biol. Chem.*, **100**, 397 (1933).

<sup>2</sup> Hudson and Maclay, *J. Amer. Chem. Soc.*, **60**, 2059 (1938).

<sup>3</sup> *Chemistry and Industry*, **58**, 363 (1939).



### Further Experiments on Homing in Storks

As previously stated<sup>1</sup>, white storks have a prominent instinct of direction. In order to obtain further information on this problem we carried out the following experiments in 1938: (1) to ascertain the maximal distance from which birds may be carried and still remain capable of homing; (2) to ascertain whether the birds show differences in their homing abilities, when they are taken in different directions; (3) to examine the possible influence of terrestrial magnetism on homing.

We succeeded in catching in Butyny near Lwów twelve adult birds. Thanks to the help of Polish Airways "LOT", as well as to the co-operation of naturalists in Finland, Estonia, Germany and Portugal, the storks