(*Reprinted from Nature, Vol. 225, No. 5233, pp. 626–628, February 14, 1970*)

Crystalline Structures of Alginic Acids

WE have recently obtained X-ray diffraction photographs from orientated samples of alginic acid preparations in which the ratio of mannuronic acid to guluronic acid was known. The purified unorientated material was supplied by Dr A. Haug, and our results form the basis for structure determinations of polymannuronic acid and polyguluronic acid respectively.

The discovery that alginic acid preparations, of different composition, could give rise to different X-ray powder photographs was made originally by Frei and Preston[1]. Although they recognized that the analyses of their alginic acids had to be interpreted with caution, they nevertheless concluded then that there were two types of X-ray powder photographs and they correlated these with polymannuronic acid and polyguluronic acid.

Fig. 1*a* shows the X-ray fibre diffraction photograph obtained from a sample of alginic acid consisting of 96 per cent mannuronic acid. To our knowledge this is the first authentic standard for polymannuronic acid. Fig. 1*b* is the X-ray fibre diffraction photograph of a specimen of alginic acid isolated by us from the brown alga, *Fucus serratus*. This is clearly the same X-ray fibre diagram as Fig. 1*a* and therefore must refer to polymannuronic acid. Fig. 1*c* shows the "usual" alginic acid X-ray fibre diagram as obtained by Astbury[2] in the 1940s from samples of commercial alginic acid and supposed, by him, to refer to polymannuronic acid. Fig. 1*d* shows the X-ray fibre diffraction photograph we have obtained from a sample of alginic acid containing 73 per cent guluronic acid and 27 per cent mannuronic acid. (This sample was the richest in guluronic acid from which orientated specimens could be prepared.) This latter substance gave the same X-ray powder diagram (see Fig. 2) as a degraded[3] sample of alginic acid containing 92 per cent guluronic acid. It therefore appears that the mannuronic acid units in the 73 per cent guluronic acid sample do not contribute to the X-ray diffraction pattern (as suggested previously[1]). We therefore conclude that the X-ray fibre diagram shown in Figs. 1*c* and 1*d* is indeed that of polyguluronic acid.

We are able to give the following preliminary details of the structures of these two substances.

Polymannuronic acid: The X-ray fibre diffraction photograph (Fig. 1*b*) has been indexed to an orthorhombic unit cell in which $a = 7{\cdot}58$ Å, $b = 10{\cdot}35$ Å (fibre axis) and $c = 8{\cdot}58$ Å, the unit cell containing two disaccharide chain segments with probable space group $P2_12_12_1$. Chemical

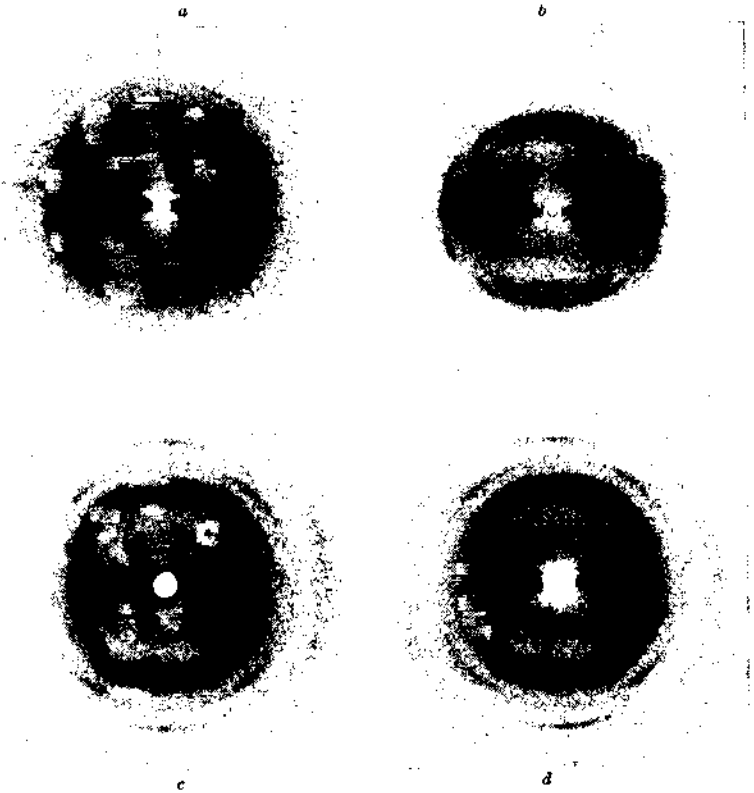

Fig. 1. X-ray fibre diffraction photographs of alginic acids. *a*, 96 per cent mannuronic acid; *b*, specimen isolated from *Fucus serratus*; *c*, commercial alginic acid; *d*, 73 per cent guluronic acid.

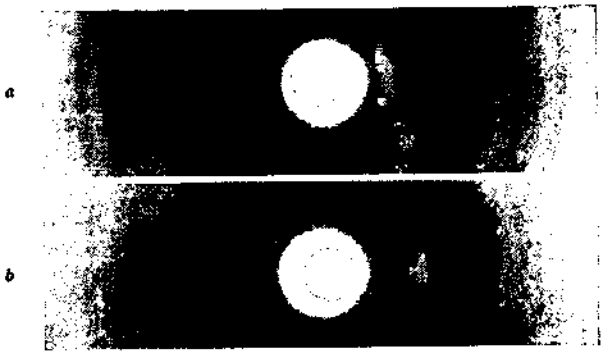

Fig. 2. X-ray powder photographs of (*a*) 92 per cent guluronic acid and (*b*) 73 per cent guluronic acid.

evidence indicates that the D-mannuronic acid units are β-1→4 linked, and it is therefore satisfying that the fibre repeating distance of 10·35 Å is the same as that observed in the three other β-1→4 linked hexosans, cellulose chitin and mannan[4,5]. In models of these substances, the required repeating distance can be obtained by constructing chains in which the monosaccharide units are in the energetically favourable Cl chair conformation, while simultaneously maintaining an *intra* residue hydrogen bond between the $-O_3H$ and the ring oxygen atom (O_5) of the next sugar unit in the chain (that is, $O_3 \ldots O_5$ distance of 2·7–2·8 Å). A chain built in this way automatically contains di-equatorially (1e, 4e) (ref. 6) linked sugar units (without regard to the nature of the sugar units itself). This is the basic structural form which we have adopted in model building studies of polymannuronic acid.

Polyguluronic acid. The X-ray fibre diffraction photograph of this substance (Fig. 1*d*) has been indexed to an orthorhombic unit cell also containing two disaccharide chain segments and in which $a = 8{\cdot}6$ Å, $b = 8{\cdot}72$ Å (fibre axis) and $c = 10{\cdot}74$ Å with probable space group $P2_12_12_1$ (see also ref. 2). The most significant difference from the polymannuronic acid structure is the fibre repeat of 8·72 Å. This value can be obtained in molecular models by maintaining the 1→4 linked L-guluronic acid units in the 1*C* conformation[7], the glycosidic linkages having the α-configuration. Thus the building units are di-axially (1*a*,4*a*) linked. When the sugar units are arranged in this way, it is found that several possibilities exist for the formation of *intra* residue hydrogen bonds between the equatorial hydroxyl group of the C_2 atom ($-O_2H$) and either oxygen atom in the carboxyl group of the adjacent sugar unit in the chain. It is likely that other examples of 1*a*,4*a* linked structures exist. For example, poorly orientated fibre diffraction photographs of pectic acid (α-1→4 linked poly D-galacturonic acid) show the same fibre repeating distance of 8·7 Å (see also refs. 2 and 8), and this can be understood if the D-galacturonic acid units are in the *C*1 conformation.

Attention is currently being directed to the arrangement of the chains of polymannuronic and polyguluronic acid in the unit cells and the nature and extent of inter-chain bondings. Trial structure factors have been calculated and refinement of the models is in progress.

It is expected that the structural determinations of these substances will provide information which will be helpful in reaching an understanding of the physical and biological properties of these molecules.

We thank Professor R. D. Preston and Dr Eva Frei for useful discussions and Dr K. M. Rudall for providing

the photograph in Fig. 1c. One of us (E. E. S.) acknowledges an award from the International Atomic Energy Agency.

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Received October 2; revised December 11, 1969.

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Printed in Great Britain by Fisher, Knight & Co., Ltd., St. Albans.