SOME NOTES ON XYLAN CRYSTALS

by

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Several years ago YUNDT[2] succeeded in obtaining a pure partly depolymerized barley straw xylan in crystalline form. Photomicrographs and electron micrographs showed hexagonal platelets, dumbbell shaped in cross-section, and it was reported that these crystals were birefringent and showed X-ray diffraction.

With the intention of obtaining some additional information about these crystals, we also prepared them, but unlike YUNDT, we did not start from barley straw holocellulose, but from commercial bleached rye straw sulphate pulp. Xylan was isolated with a yield of 25% according to HEUSER as described by DORÉE[1]. YUNDT's methods were used to prepare three samples of crystals from this xylan.

Two samples were obtained after prehydrolysing 10 g xylan in 150 ml 0.2% oxalic acid at 100° C for 5 hours. One of these was prepared from the undissolved, presumably insufficiently hydrolyzed residue, by autoclaving three times at 120° C for 5 hours after adjusting the pH at 5–6. After the first and the second autoclavation, the crystalline material was dissolved and reprecipitated in amorphous form.

The other sample was prepared by the same method from the part dissolved during the prehydrolysis and obtained by ethanol precipitation. The third sample was prepared according to YUNDT's simplified method.

In the light microscope and in the electron microscope the size and the form of the crystals of the three samples were similar, although those of the third one apparently were the best crystallized ones.

In spite of the identical method of prehydrolysis and crystallization, however, they were quite different from the crystals obtained by YUNDT. Fig. 1 shows that each crystal is constituted of many elongated platelets and looks like a pair of whiskers, about 4.5 μ long. In addition to these, some xylan spherocrystals were found. They were irregularly lobed and had a diameter of 5–10 μ. With YUNDT's crystals as a third crystal form it is clear that xylan is not characterized by the shape of its crystals.

These compound crystals are negatively birefringent with reference to the long axis, *i.e.* the higher refractive index is transversely oriented. This would suggest that the chain molecules are either transversely oriented or have the form of axially oriented spirals with a pitch of less than 45 degrees.

TABLE I

X-ray interferences of		
xylan	*cellohexaose*	*cellulose II*
8.36 vf	7.19 s	7.44 s
6.71 vf	4.44 s	4.45 s
5.68 n	4.01 s	4.05 s
5.25 vf		
4.84 vf		
4.36 s		
4.01 f		
3.62 f		
3.36 f		
2.68 vf		

vf = very faint
f = faint
n = normal
s = strong

In Table I the spacings, as deduced from the X-ray ring diagram depicted in Fig. 2, are tabulated together with those of cellulose II and of cellohexaose crystals prepared according to the method

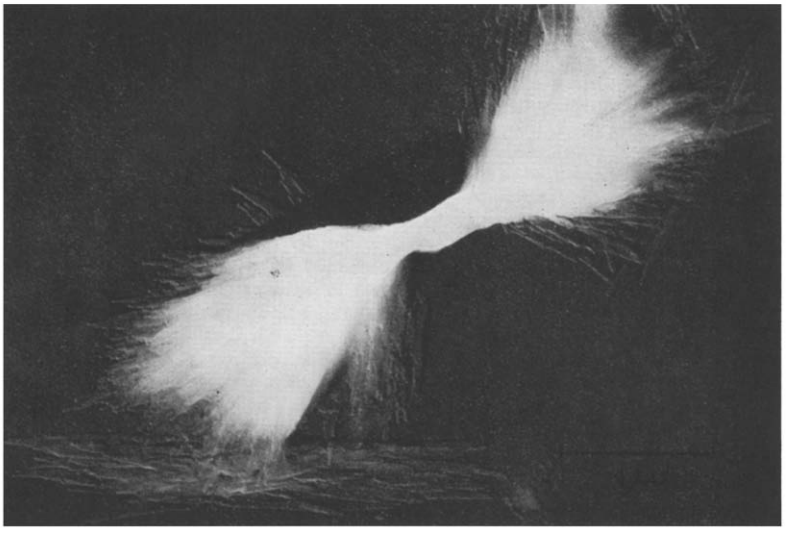

Fig. 1. Electron micrograph of rye straw xylan crystal.

of ZECHMEISTER AND TOTH[3]. Apparently, the crystal structure of xylan is different from those of cellohexaose and cellulose II, which are similar; (the sphero-crystals of cellohexaose are negatively birefringent, which suggests tangential molecular orientation, since a flat helical molecule form is excluded here).

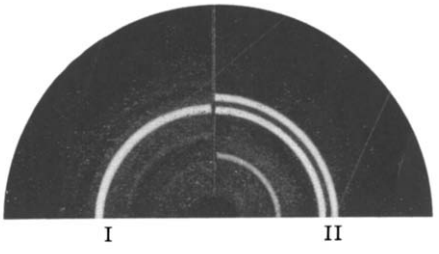

Fig. 2. Quadrants of X-ray powder diagrams of xylan (I) and cellohexaose (II). Specimen-film distance 40 mm.

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ON THE NATURE OF FLORIDEAN STARCH AND *ULVA* STARCH

by

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Floridean starch, the reserve substance of some of the red algae, has been studied by several investigators. It is still an open question, however, to what extent this material may be regarded as a true starch, comparable to that of the higher plants. KYLIN's observation[1] that floridean starch