346. *Polysaccharides. Part XVI. The Molecular Structure of Inulin and of the Derived Difructofuranose Anhydride.*

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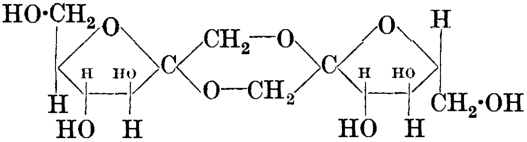
Three years ago, Irvine and Stevenson (*J. Amer. Chem. Soc.*, 1929, **51**, 2197) published an account of a substance which they had isolated by the action, on inulin acetate, of nitric acid dissolved in chloroform. The product was described as a crystalline substance, m. p. 123°, containing half a molecule of combined acetic acid, and having the molecular formula $C_{13}H_{18}O_9$. In glacial acetic acid the freezing point depressions were reported as irregular, but the molecular weight was said to average 299 in agreement with the above formula, which requires 318. We have prepared this substance in the way described by these authors, and find that it is an impure product which, when purified or alternatively when prepared under better experimental conditions and correctly analysed, has the molecular formula $C_{24}H_{32}O_{16}$ and M.W. 576 (as determined by two methods). Although the earlier authors comment : " It will at once be evident that a serious complication is introduced into the constitutional study of inulin, as the lack of homogeneity now revealed may be due to several causes," which they proceed to enumerate, yet it appears to us that no irregularity in the behaviour of inulin is revealed by the formation of this substance. It is a product of the depolymerisation of inulin and its formation was visualised by one of us in a report to the International Congress of Chemistry at Liège (Report to Liège Congress, 1930, p. 55). In advancing a molecular structure to represent inulin (see later) one of us then remarked: " The tendency of such a complex to suffer depolymerisation to looped chains of smaller dimensions would be very marked, since rupture may occur at several of the $-O-$ linkings, followed by reunion to smaller loops or finally to the difructose-anhydride :



This structural conception explains completely the ease with which inulin is known to suffer degradation with mild reagents to give less complex molecules."

The crystalline substance now under review is indeed a compound of the above constitution having six acetyl groups substituting six hydroxyl positions. The de-acetylated product is identical with that of Jackson and Goergen and its constitution was determined by Haworth and Streight (*Helv. Chim. Acta*, 1932, **15**, 693; compare also Schlubach and Elsner, *Ber.*, 1932, **65**, 519). It was there shown that this substance when methylated gives rise, by hydrolytic cleavage, to the same trimethyl fructofuranose as that which is derived by hydrolysis of methylated inulin itself. Its ready formation, either by the method of the direct hydrolysis of inulin followed by Jackson and Goergen, or by the action (already described) of acid reagents on inulin acetate, is understood from an inspection of the formula of the polysaccharide itself (II in the preceding paper). The formation of difructofuranose anhydride occurs by the rupture of the primary valency bonds of fructofuranose units and their reunion to the more stable difructofuranose anhydride, which may indeed be looked upon as a substituted dioxan. That the hexa-acetyl difructofuranose anhydride does not occur as such in inulin acetate is shown by the fact that the former dissolves in hot water, whilst inulin acetate is insoluble.

EXPERIMENTAL.

Preparation of Hexa-acetyl Difructofuranose 1 : 2-*Anhydride.*—The following reagents were mixed in a 2 l. flask with good stirring and maintained at 4°: inulin acetate (40 g., prepared as described by Haworth and Streight; *Helv. Chim. Acta*, 1932, **15**, 609); dry $CHCl_3$ (560 c.c.); fuming HNO_3 (240 c. c., freshly distilled). Over a period of 2 hrs., P_2O_5 (120 g.) was added and thereafter the $CHCl_3$ suspension was poured on ice, and the whole repeatedly extracted with $CHCl_3$. (Much of the product tends to remain in the aq. phosphoric acid unless this is sufficiently diluted.) The dried extracts yielded on evaporation a syrup, which crystallised in EtOH, yield 10·4 g. (25·8% of theo.). Recryst. alternately from H_2O and EtOH and finally from EtOH, it had m. p. 128°. After melting, the cooled substance congeals to a partly amorphous solid and thereafter melts at 137°, but on recrystn. from EtOH it again has m. p. 128°, $[\alpha]_D^{16^\circ} + 0{\cdot}65^\circ$ (*c*, 1·5 in $CHCl_3$). Both products give the same analytical data [Found: C, 50·0; H, 5·7; $CH_3{\cdot}CO_2H$, 45·0; *M*, 565 (Rast method), 570 (cryoscopic in C_6H_6). $C_{24}H_{32}O_{16}$ requires C, 50·0; H, 5·6; $CH_3{\cdot}CO_2H$, 44·8%; *M*, 576].

The product, m. p. 123°, $[\alpha]_D + 1{\cdot}5^\circ$, described by Irvine and Stevenson (*loc. cit.*) as $C_{13}H_{18}O_9$ was prepared. Crystallographic *X*-ray examination of the product, m. p. 123°, showed the presence of two substances, one of which was identical with the above substance, m. p. 128°. Various recryst. specimens showed a variation in C content of nearly 1% owing to the presence of impurity. When 10 g. were quickly distilled (8 mins.) from a metal-bath at 280—295°, the cryst. product had $[\alpha]_D + 0{\cdot}6^\circ$, m. p. 128°, and in all other respects, including analytical figures, was identical with the above hexa-acetyl fructofuranose anhydride, $C_{24}H_{36}O_{16}$ (yield, 9·1 g.). It gave on de-acetylation the same difructose anhydride as that described below.

Difructofuranose 1 : 2-*anhydride* was obtained by de-acetylation of the above hexa-acetate with a slight excess of dimethylamine, or alternatively by $Ba(OH)_2$, and gave a crude cryst. product, m. p. 158—160°; purified by recrystn. from EtOH, m. p. 163—164°, $[\alpha]_D$ + 27° (in H_2O); yield, 85% [Found: C, 44·3; H, 6·25; *M*, 319 (ebullioscopic in H_2O). Calc.: C, 44·4; H, 6·2%; *M*, 324].

This difructofuranose anhydride was re-acetylated to yield the above hexa-acetate, m. p. 128°.

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