A similar mercuration of phenol using mercuric chloride instead of the acetate gave the same product.

Unsuccessful Attempts at Mercuration in Alkaline Solution. **α-Naphthol** was oxidized immediately by this procedure. Similar results were obtained with aniline.

o-**Nitrophenol.**—On adding mercuric acetate solution to a boiling alkaline solution of *o*-nitrophenol a permanent precipitate of mercuric oxide formed. The experiment was discontinued. Similar results were obtained with anthranilic acid, sulfanilic acid, benzenesulfonic acid, 1-naphthoic acid and phthalic acid.

Summary

It has been found that certain organic compounds can be mercurated in alkaline solution while other compounds of very similar structure cannot.

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THE MOLECULAR STRUCTURE OF INULIN. ISOLATION OF A NEW ANHYDROFRUCTOSE

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The first researches designed to investigate the molecular structure of inulin with the precision rendered possible by the methylation method were carried out by Irvine and Steele.[1] These authors showed that the polysaccharide although converted by hydrolysis into the normal levorotatory form of fructose is actually based on the unstable dextrorotatory variety of the hexose known as γ-fructose. The research was subsequently extended[2] to include a more detailed examination of dimethyl- and trimethylinulin, together with the dimethyl- and trimethylfructoses obtained, respectively, from these derivatives by hydrolysis.

The collective evidence, although complicated by a number of minor irregularities such as the tendency of trimethylinulin to undergo depolymerization from a levorotatory powder to a dextrorotatory sirup, pointed to the idea that the molecule of inulin is symmetrical in the sense that all of the fructose residues belong to the γ-type and that in each fructose residue three hydroxyl groups occupy the same positions. This view was based on the fact that on hydrolysis trimethylinulin gave a homogeneous trimethyl-γ-fructose, and all subsequent speculations on the structure of inulin have been founded on this observation. In the course of the past five years we have, however, accumulated much incidental evidence that the inulin problem is not so simple as at one time appeared, and we have accordingly continued our investigations; in the meantime Haworth has published what is, in effect, a repetition of our earlier work,

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[1] Irvine and Steele, *J. Chem. Soc.*, **117**, 1474 (1920).

[2] Irvine, Steele and Shannon, *ibid.*, **121**, 1060 (1922).

contributing, however, the new observation that our trimethyl-γ-fructose is capable of yielding a phenylosazone.[3] Lest the idea should prevail that the molecular structure of inulin is now fully solved, it is advisable to contribute some results which show that such is not the case.

The first indication that the molecular unit of inulin is not homogeneous is found in the results of Irvine and Steele. The sequence of reactions

$$\text{Inulin} \longrightarrow \text{Trimethylinulin} \longrightarrow \text{Trimethyl-}\gamma\text{-fructose}$$

proceeded smoothly, giving good yields at each stage, but the yield of sugar, relative to the weight of trimethylinulin from which it is formed, was invariably of the order of 80%. The loss of 20% is accounted for by the fact that in the purification of the sugar by distillation a small first fraction, consisting of a mobile sirup, was collected. This constituent is now being examined in detail and we have traced its origin to the existence in inulin of at least one component yielding an anhydro-fructose of an unknown type. The new anhydro-sugar can be prepared from inulin in various ways, all of which emphasize its stability. For example, when triacetylinulin is dissolved in chloroform containing fuming nitric acid, the anhydro-ring of most of the fructose residues is opened and from its properties the essential product appears to be a triacetylfructose dinitrate. The reaction is therefore analogous with that studied by Oldham,[4] who converted triacetylglucosan into triacetylglucose-1,6-dinitrate by similar processes. On treating the crude triacetylfructose dinitrate with methyl alcohol, conversion into triacetylmethylfructoside mononitrate took place and a crop of crystals separated which amounted to approximately 20% by weight of the triacetylinulin initially taken. The product, which crystallized in needles melting at 123° and showed $[\alpha]_D + 1.5°$ in chloroform, was a triacetylanhydrofructose. As was to be expected, this acetate of anhydrofructose is devoid of action upon Fehling's solution but, unexpectedly, the anhydro-ring proved to be unusually stable, being opened only by prolonged heating with acids.

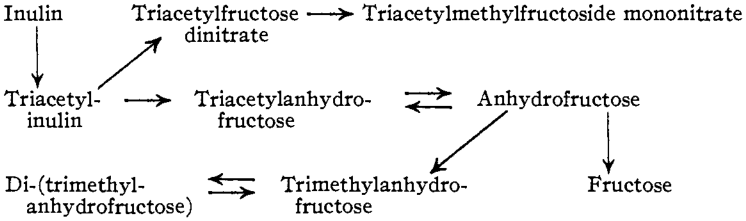
On removing the acetyl groups by the action of dimethylamine, the parent anhydrofructose separated in spheroidal crystals melting at 143–145° and showing $[\alpha]_D + 30.17°$ in water. It is significant that although the new anhydro-sugar can be hydrolyzed to give normal fructose in almost quantitative amount, it is much more stable than the known derivatives of γ-fructose. For example, although heating with $N/100$ hydrochloric acid effects the rapid hydrolysis of sucrose and likewise converts about 80% of inulin into fructose, the same reagent has little effect in opening the anhydro-ring of the particular form of anhydrofructose now under consideration. The importance of this observation will be referred to later.

[3] Drew and Haworth, *J. Chem. Soc.*, **133**, 2690 (1928).

[4] Oldham, *ibid.*, **127**, 2840 (1925).

In order to gain an insight into the structure of the anhydrofructose, the compound was subjected to the methylation process, it being found necessary to supplement the methyl sulfate reaction by treatment with silver oxide and methyl iodide. The product proved to be a di-(trimethylanhydrofructose) showing that either the methylation, or more probably the vacuum distillation necessary to isolate the compound, had occasioned polymerization. This is not an abnormal experience in the case of methylated fructoses and, as is usual with polymers of low molecular weight in the inulin series, the rotation was dextrorotatory ($[\alpha]_D + 23.8°$). By employing the general method of diminishing polymerization by heating with methyl alcohol containing hydrogen chloride, the above dimeride was converted into the monomeric form of trimethylanhydrofructose, the structural study of which is now in progress.

The scheme of reactions involved in the research is represented below.



Discussion

In the particular method of preparing the anhydro-fructose now described, the possibility must not be overlooked that the use of a powerful reagent such as nitric acid may cause intramolecular changes in triacetylinulin, thereby forming triacetyl-anhydrofructose as an adventitious product. This possibility is ruled out as, when triacetylinulin is hydrolyzed by acetic acid containing 0.03% of sulfuric acid, the same triacetyl-anhydrofructose can be isolated from the products. Moreover, when inulin is subjected to graded acetolysis by Barnett's method,[5] 18% of the polysaccharide fails to pass into solution and triacetyl-anhydrofructose is obtained from this stable fraction. The accumulated evidence[6] is thus in favor of the idea that inulin is not homogeneous but consists of at least two main components one of which is easily hydrolyzed while the other is relatively resistant to hydrolytic agents. These components fall into two classes present in the approximate ratio of 4:1 and for the time being, it is not safe to claim that more than 80% of the inulin aggregate is based on γ-fructose. It is possible that the remainder may also be derived from γ-fructose but in such an event the anhydro-ring must occupy a more stable position than in the major component of the polysaccharide; alternatively,

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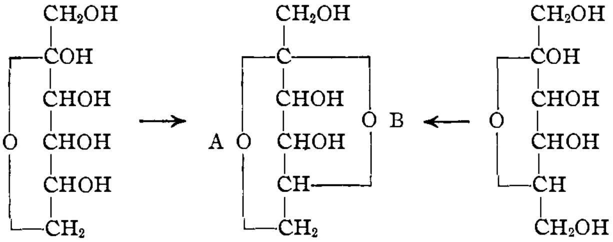
[5] Barnett, *J. Soc. Chem. Ind.*, **40**, 8T (1921).

[6] See also Irvine, Oldham and Skinner, This Journal, **51**, 1279 (1929).

this constituent may be related to normal fructose or to an isomeric form of the ketose hitherto unknown.

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. For example, inulin may be a polymeride of individual anhydrofructoses differing from each other, or it may be a polymeride of condensed fructose residues in which the structure of some of the C_6 units differs from that of others. This does not exhaust the possibilities, but until our structural examination of triacetyl-anhydrofructose is complete it is premature to develop the situation further or to utilize constitutional formulas in illustration. Obviously the solution of the inulin problem now demands a critical study of the relative stability of oxygen rings in the fructose series and also of methods whereby anhydrosugars can be referred to their parent type. Thus, the anhydrofructose now under discussion might originate in either normal fructose or in γ-fructose and, in turn, the anhydro-ring may occupy the butylene-oxide or the amylene-oxide position. This is shown below.



Two oxygen-rings (A and B) are present in the anhydride and it is impossible to designate one as the anhydro-ring and the other as the oxygen-ring characteristic of the sugar. Nor is it always possible to identify which ring is opened during hydrolysis and which one is unaffected. Research on this problem is well advanced and the results will be applied in a further discussion on the structure of inulin to be communicated later.

Experimental

Action of Nitric Acid on Triacetylinulin.—The inulin employed was obtained from four different sources but no variation was found either in the composition or in the yields of the various products. Pringsheim's method was used for the preparation of inulin triacetate, the crude product being purified by dissolving in hot alcohol and pouring the solution into a large excess of water; all the specimens employed in the subsequent experiments were analyzed and conformed to the following standard: m. p. 97°; $[\alpha]_D = -33.9°$ in chloroform and $-37.1°$ in glacial acetic acid ($c = 2.5$ in each case).

Numerous preliminary trials were necessary in order to ascertain the best conditions under which triacetylinulin is acted on by nitric acid. Using chloroform as the solvent, the addition of nitric acid up to 20% caused an alteration in the rotation from levo to dextro, but the product nevertheless consisted chiefly of unchanged triacetylinulin.

When the acid concentration was raised in successive experiments to 70% the dextrorotation of the liquid increased to the maximum, +48.8°, but the yield of product was then seriously diminished. Ultimately, a 30% solution of nitric acid in chloroform was selected as the most suitable reagent and the course of the reaction was followed polarimetrically, the results showing that the action was complete in thirty minutes, when the rotation had attained the value $[\alpha]_D$ +34°.

Triacetyl-anhydrofructose.—The conditions established above were used as the basis of the preparation of triacetyl-anhydrofructose but it was found advisable to carry out the preparation in successive experiments with small quantities of material. Five grams of well-dried triacetylinulin was dissolved in 70 cc. of chloroform and 30 cc. of fuming nitric acid (sp. gr., 1.55) added. The flask was stoppered and cooled, as heat is developed in the course of the reaction, and, from time to time, phosphorus pentoxide was added to remove traces of water. After thirty minutes the clear solution was poured into a separating funnel containing 200 cc. of water mixed with ice and shaken until all coloring matter had passed into the aqueous layer, the chloroform being then run off and dried over anhydrous sodium sulfate. A small quantity of barium carbonate was added to the filtered liquid, after which the solvent was distilled, fresh chloroform added, the solution again filtered and taken to dryness, the process being completed at 100° under diminished pressure. In this way 4.5 g. of a mobile sirup was obtained showing $[\alpha]_D$ +22° in chloroform for $c = 2.28$. As explained in the introduction, analysis showed this material to be a mixture consisting essentially of triacetylfructose dinitrate and triacetyl-anhydrofructose, the former constituent being convertible into the corresponding triacetylmethylfructoside mononitrate by boiling a 10% solution in methyl alcohol in the presence of barium carbonate.

When the sirup was dissolved in hot absolute alcohol the solution slowly deposited crystals, the weight of which was remarkably uniform in different experiments and amounted to 20% of the sirup taken. After recrystallization from absolute alcohol and drying at 100°, a pure product was obtained, but, considering the origin of the material, it was desirable to carry out a careful analytical survey. Nitrogen and ethoxyl were absent, no double bond was present, and the action of Fehling's solution was negative until after drastic hydrolysis. Analysis showed that the crystals contained half a molecule of combined acetic acid.

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.05; H, 5.66; CH_3CO, 47.3. Found: C, 49.15, 48.99; H, 5.86, 5.90; CH_3CO, 46.1.

Difficulty was experienced in confirming the molecular weight. Using the cryoscopic method and employing benzene as a solvent, the mean of four experiments was 438, a value which indicates molecular association. In glacial acetic acid the freezing point depressions were irregular, but the molecular weight averaged 299, thus corresponding with a monomolecular form (calcd. for $C_{12}H_{16}O_8$, 288; for $C_{13}H_{18}O_9$, 318). Triacetylanhydrofructose crystallizes from alcohol in needles melting at 123°. The compound, which is readily soluble in organic solvents generally and in hot water, is practically inactive, $[\alpha]_D$ +1.5° in chloroform for $c = 2.272$.

Anhydrofructose.—This preparation was likewise carried out in a succession of small-scale experiments. Five grams of triacetyl-anhydrofructose was added to 25 cc. of dry methyl alcohol containing 5% of dimethylamine. On shaking in the cold for twenty minutes the material passed into solution and the solvent was thereafter removed under diminished pressure, the residue being dried by raising the temperature slowly to 100°. The product consisted of a clear deliquescent glass weighing 2.6 g. and on dissolving in absolute alcohol and adding a few drops of dry ether a crystalline precipitate separated which was washed with ether–alcohol and finally with ether.

The anhydrofructose thus obtained forms transparent spheroidal crystals melting at 143–145°, is highly hygroscopic and fails to reduce Fehling's solution. In water, for $c = 2.32$, $[\alpha]_D = +30.17°$, but it is difficult to guarantee these constants in view of the hygroscopic character of the compound and in consideration of the fact that analysis disclosed the presence of a trace of acetyl.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.17; CH_3CO, nil; mol. wt., 162. Found: C, 44.49; H, 6.28; CH_3CO, 1.0; mol. wt. by the freezing-point method in water, 162.

The properties of anhydrofructose are simple. When acetylated under standard conditions it is reconverted almost quantitatively into the original triacetyl-anhydrofructose melting at 123° and showing $[\alpha]_D +1.5°$ in chloroform. The opening of the anhydro-ring of anhydrofructose was effected by heating at 100° a 2.5% solution of the substance in water containing 3% of oxalic acid, a polarimetric record of the reaction showing that the initial specific rotation of +25.7° altered regularly to the constant value −87.7°, so that the figures plotted on a smooth curve. This corresponds to a nearly quantitative conversion into normal fructose and, on working up the product in the usual manner, the sugar crystallized and was thereafter converted into glucose phenylosazone showing the correct constants.

Methylation of Anhydrofructose.—A preliminary methylation, carried out by means of methyl sulfate and sodium hydroxide, gave a partly alkylated product which was extracted with boiling alcohol and recovered. After three subsequent methylations with the same reagents, but using chloroform as the extracting agent, a quantitative yield of a transparent fairly mobile sirup was obtained which, when distilled at 206° (0.35 mm.) showed $n_D = 1.4731$ and gave a methoxyl content of 43.2%. The methylation was accordingly completed by dissolving the sirup in excess of methyl iodide and boiling with dry silver oxide, the extracting agent in this case being ether. The product, isolated in the customary manner, boiled at 166° (0.1 mm.); examination showed that the refractive index remained at 1.4730 but the methoxyl content had increased to the theoretical value.

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.84; OCH_3, 45.58. Found: C, 52.74; H, 8.14; OCH_3, 45.68.

When again distilled and collected in two equal fractions, the same constants and analytical composition were duplicated, so that the material was a homogeneous pure specimen of trimethylanhydrofructose. The specific rotation in chloroform for $c = 2.5$ was +23.8°. In view of the high boiling point, the value of the refractive index and the viscosity of the sirup, the compound had evidently undergone polymerization to some extent and, in an attempt to effect depolymerization, a solution was prepared in dry methyl alcohol containing 0.5% of dry hydrogen chloride and heated at the boiling point of the solvent. The specific rotation, initially +33.5°, increased steadily to the constant value +48.7°, which was attained in 150 minutes. After neutralizing with barium carbonate and isolating the product in the usual manner, a low-boiling mobile fraction was obtained which still retained the composition of a trimethyl-anhydrofructose, but the refractive index had altered to 1.4610, a value which corresponds to a monomeric form. Nevertheless, the depolymerization was incomplete, as higher-boiling fractions identical with the original material were also collected. These results show that the action of acid methyl alcohol had effected depolymerization but that, as is frequently the case in the methylated fructose series, molecular association was induced by distillation.

The authors desire to express acknowledgment to the Carnegie Trust for the Universities of Scotland for a Research Scholarship awarded to one of them.

Summary

1. When triacetylinulin is dissolved in chloroform and acted on by nitric acid the greater part of the material is converted into triacetylfructose dinitrate, the esterification being preceded by the opening of the anhydro-linkages.

2. One component of triacetylinulin present to the extent of 20% is resistant to the hydrolytic action and is isolated as triacetyl-anhydrofructose (m. p. 123°; $[\alpha]_D + 1.5°$ in chloroform). The same compound can be obtained in similar yield from other reactions in which triacetylinulin is used as the starting material.

3. Anhydrofructose (m. p. 143–145°; $[\alpha]_D + 30.17°$ in water) has been prepared from the triacetate by the action of dimethylamine. The compound is quantitatively convertible into fructose but is much more stable toward hydrolysts than the known derivatives of γ-fructose.

4. Anhydrofructose has been converted into trimethyl-anhydrofructose, which was isolated in a dimeric form.

5. The main conclusion drawn is that inulin is not related exclusively to a single form of γ-fructose but contains two classes of components in the approximate ratio of 4:1. Of these, one is relatively much more stable toward hydrolysis. The additional complication introduced into the constitutional study of inulin through these results is discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. II. OCTANES WITH BRANCHED CHAINS

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I. Introduction

In Part I of this paper[1] data were presented on the vapor phase oxidation of *n*-octane, which indicated that under the conditions in question the oxidation proceeds almost entirely according to certain simple reactions. These reactions are: (1) the formation of octaldehyde; (2) the oxidation of octaldehyde to carbon monoxide, water and aldehydes of successively smaller number of carbon atoms; and (3) a side reaction in which octaldehyde is oxidized to carbon dioxide, water and aldehydes of successively smaller number of carbon atoms.

In Part II data are presented on the vapor phase oxidation of five isomeric octanes, 3-methylheptane, 3-ethylhexane, 2-methyl-3-ethylpentane, 2,5-dimethylhexane and 2,2,4-trimethylpentane. These data were ob-

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[1] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875 (1929).