Summary

1. A study has been made of the action of diazomethane on the cyclic ureides, uracil, thymine, cytosine and 4-methyluracil.

2. Uracil, thymine and 4-methyluracil were readily converted into their 1,3-dimethyl derivatives by the action of diazomethane.

3. Cytosine methylated very slowly; the unmethylated portion was a new crystalline variety of this compound; the methylated portion contained among other products a small quantity of 2-oxy-6-methylaminopyrimidine, which was isolated in the form of its picrate.

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[CONTRIBUTION NUMBER 404 FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY]

ACETOLYSIS OF CELLULOSE AND THE ISOLATION OF TWO CRYSTALLINE FORMS OF GLUCOSE PENTA-ACETATE[1]

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RECEIVED SEPTEMBER 5, 1929 PUBLISHED APRIL 7, 1930

Introduction

Glucose penta-acetate as an end-product of the acetolysis of cellulose is frequently mentioned: Weltzien and Singer,[2] Harold Hibbert,[3] Irvine and Soutar,[4] Freudenberg,[5] H. Ost.[6] In 1912 Klein[7] stated he believed the water-soluble products of acetolysis to be aceto-sulfates of dextrose or cellobiose. In the same year Ost[8] and Ost and Katayama[9] published two papers concerning the production of glucose penta-acetate in the acetolysis of cellulose.

The first note stated that acetolysis was carried to maximum water solubility. Ether extraction of the aqueous solution and reacetylation of the gum obtained with cold acetic anhydride and sulfuric acid yielded needles of glucose penta-acetate from alcohol. The second was concerned with the acetolysis of cellulose, hydrocellulose and alkali cellulose and in all cases after reacetylation penta-acetylglucose was obtained.

Ost in a more complete account of his work suggested that dextrose acetates are not to be looked for in the precipitate but in the ether ex-

[1] Presented before the Division of Cellulose Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] Weltzien and Singer, *Ann.*, **443**, 71 (1925).

[3] Hibbert, *J. Ind. Eng. Chem.*, **13**, 256 (1921).

[4] Irvine and Soutar, *J. Chem. Soc.*, **117**, 1489 (1920).

[5] Freudenberg, *Ber.*, **54**, 771 (1921).

[6] Ost, *Ann.*, **398**, 313 (1913).

[7] Klein, *Z. angew. Chem.*, **25**, 1409–1415 (1912).

[8] Ost, *Chem.-Ztg.*, **36**, 1099–1100 (1912).

[9] Ost and Katayama, *Z. angew. Chem.*, **25**, 1467 (1912).

tract of the mother liquor. The gum obtained, which he claims is uncrystallizable, upon reacetylation yields glucose penta-acetate. The necessity for reacetylation Ost states is due to the partial saponification of the penta-acetylglucose by the sulfuric acid to uncrystallizable lower acetates. He found that higher concentrations of sulfuric acid gave rise to sulfo-acetates, 10% sulfuric acid yielding principally glucose tetra-acetate.

Freudenberg improved the acetolysis procedure by using no acetic acid. He showed that cellobiose octa-acetate is very resistant to acetolysis.

No statement has been found in the literature concerning the partition of the glucose penta-acetate between the precipitate and the mother liquor.

Mention is made[6] that glucose penta-acetate is very difficultly soluble in water but fairly soluble in the acidic mother liquor.

The authors have found that glucose penta-acetate may be isolated from the mother liquors from the recrystallization of cellobiose octa-acetate and from the chloroform extract of the aqueous mother liquor. Also glucose penta-acetate in the form of plates can be obtained in both cases, though in isolating the compound from the mother liquors of the cellobiose octa-acetate recrystallization, the plates changed to needles during their isolation. So far as is known, glucose penta-acetate has not been previously reported as crystallizing in any other form than as needles. A crystallographic study of these two forms of glucose penta-acetate is contemplated.

It appears significant that the formation of crystals of glucose penta-acetate in the gum took place only when, instead of water, the acetolysis mixture was poured into dilute sodium carbonate or hydroxide solution sufficient to neutralize the sulfuric acid present. This appears to confirm Klein's[7] statement concerning sulfo-acetates and Ost's[6] relative to the saponification of glucose penta-acetate by the sulfuric acid.

Experimental

Part I. The Isolation of Glucose Penta-acetate from the Acetolysis Precipitation Liquid without Reacetylation.—Five acetolyses were carried out. In each case 11 cc. of concentrated sulfuric acid (sp. gr. 1.84) was added to 80 cc. of acetic anhydride (Eastman Kodak Company, white label). The temperature was 5° during mixing. Twenty grams of cotton linters was added and the mass stirred continuously until a sirup was formed, which required approximately two hours. During this stage the temperature was kept below 60°. The sirup was then held at 41° (±0.5°) for twenty-two hours. The material from each preparation, a dark red thin liquid, was poured into water containing in each case 155 cc. of 2.5 *N* sodium hydroxide. In three preparations 1500 cc. was the total volume of the precipitation liquid and in two 3500 cc. each was used. The precipitates of crude cellobiose octa-acetate were filtered off and the weight before and after crystallization, as well as the melting points of the once crystallized products, were obtained. The data are given in Table I.

In later work it was found that the cellobiose octa-acetate precipitated in dilute alkali gave a higher melting point, after crystallizing once from ethyl alcohol, than did materials precipitated in water.

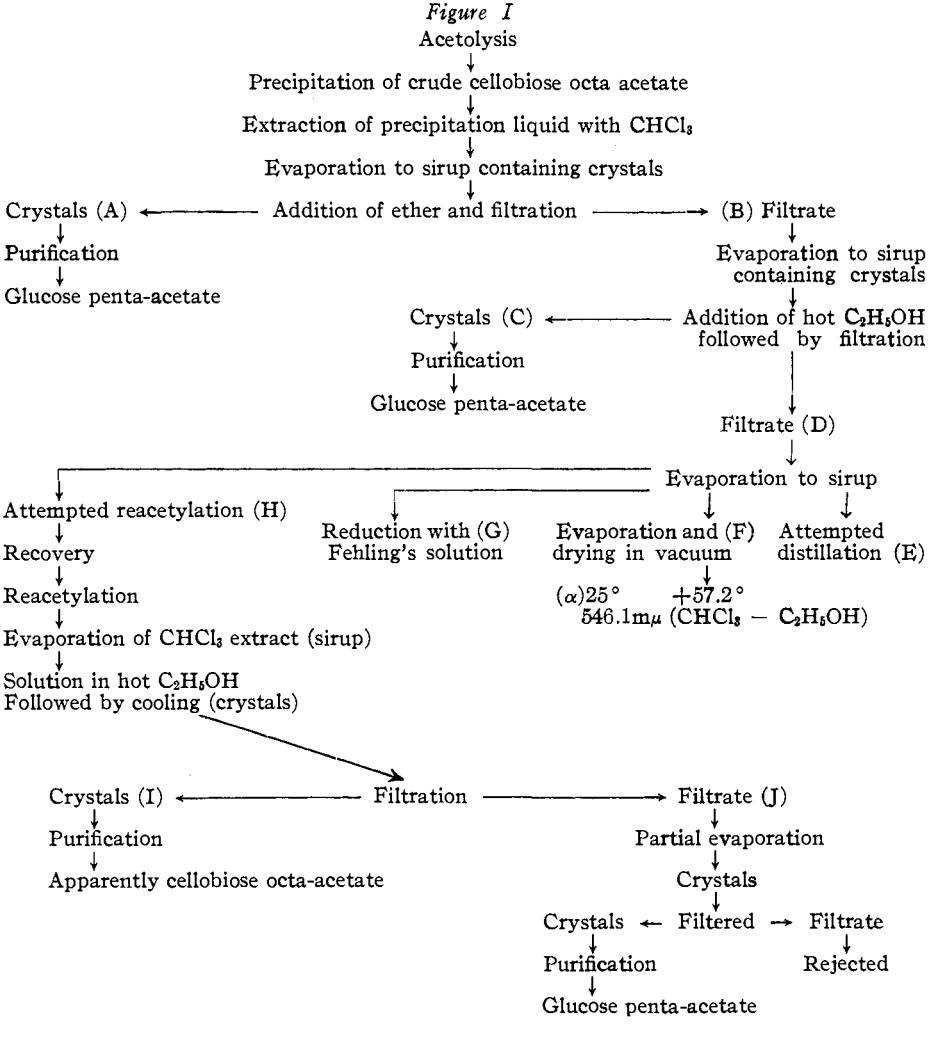
TABLE I

EXPERIMENTAL DATA

Preparation number	I	II	III	IV	V
Precipitate (crude), g.	20.2	20.3	17.2	17.0	16.0
Ppt. after cryst. from EtOH, g.	5.0	5.0	4.8	4.7	3.5
M. p. of crystals, uncorr., °C.	218–219	218–219	218–219	..	..

The liquors from which the crude cellobiose octa-acetate was removed were combined and extracted three times with chloroform, with the addition of a minute quantity of acetone to decrease the tendency to form emulsions. The chloroform solution was evaporated and a sirup containing crystals was obtained on standing. A small amount of ether was added and the crystals filtered off. These are designated as "A" in the diagram (see Fig. 1). They were recrystallized from hot ethyl alcohol; yield, 4 g. of

Figure I



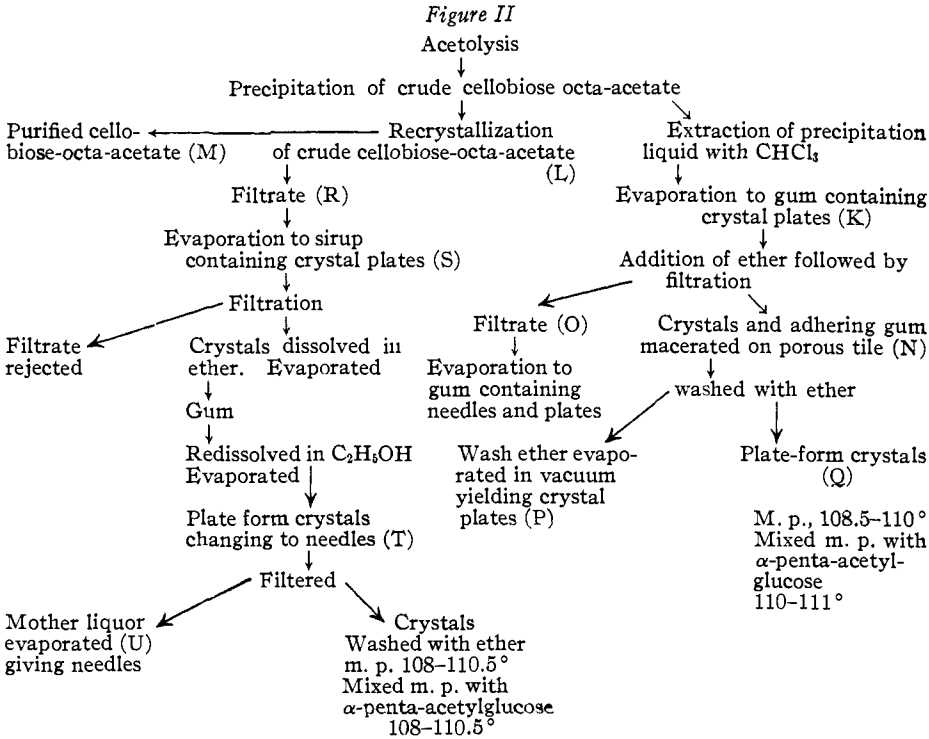
fine needles, m. p. 111–112°, specific rotation +122.5° at 25°, $c = 1$, $l = 1$, 546.1mμ line. These crystals correspond in melting point and optical rotation to glucose penta-acetate.

The filtrate in the diagram was evaporated to a gum containing crystals. The gum was dissolved in a minimum of hot ethyl alcohol and upon cooling crystals separated. These were filtered, washed with cold ethyl alcohol and dried on a porous tile; yield, 8 g. of fine needles, m. p. 110–111°, "C" in Fig. I. The acetyl content was 58.0% and the molecular weight in acetic acid 367, both of which appear to be in substantial agreement with the theoretical values of 57.8% and 390 for glucose penta-acetate.

To the filtrate from "C," "D" in Fig. I, was added an equal volume of water. Upon evaporation an emulsion resulted. Chloroform extraction yielded a sirup. A portion distilled at 6 mm. pressure (E in diagram) decomposed; a second portion was dried in a vacuum desiccator (F), dissolved in chloroform–alcohol (85:15) by volume) and a specific rotation of +57.2° obtained (25°, 546.1mμ $c = 1$, and $l = 1$). A third part (G) with Fehling's solution showed strong reducing properties.

The remainder (H) was reacetylated, using acetic anhydride and sodium acetate, but the product after precipitation in water, extraction with chloroform and evaporation was a sirup. This was reacetylated with acetic anhydride and sulfuric acid. Crystals were observed in the solution, water was added and the sulfuric acid neutralized with sodium bicarbonate. The solution was extracted with chloroform and evaporated. The resulting light brown gum was dissolved in hot ethyl alcohol, cooled and a crystalline precipitate obtained. The crystals (I) were filtered, washed with cold ethyl alcohol and dried, giving needles of m. p. 220–221°, and a specific rotation of +42.0°.

Figure II



The melting point of cellobiose octa-acetate is 226–227° and its specific rotation under similar conditions is +46.0°. The filtrate (J) was partially evaporated and the crystals were isolated. They were fine needles, m. p. 110–111°, indicating glucose penta-acetate.

Part II. Isolation and Identification of Two Crystalline Forms of α-Glucose Penta-acetate.—In earlier work on acetolysis (unpublished results) plate-form crystals were observed in the gum, "K," Figure II. Similar crystals had also been observed by Sir J. C. Irvine (informal discussion). Crystallization, if any, requires long standing at room temperature. Attempts to isolate these had previously met with failure.

Twenty-nine acetolyses were carried out, conditions were varied and three different types of cellulose material were used: cotton linters, rag paper without sizing and esparto pulp. The acetolysis was carried out as described in Part I, the temperature being varied from 136° for two and one-half minutes to 25° for fourteen days.

The yield of cellobiose octa-acetate obtained was higher when the reaction temperature was low, and the product could be more easily purified. Esparto pulp gave yields of cellobiose octa-acetate comparable with that from other sources.

The acetolysis mixture was poured into 1500 cc. of water alone and containing alkali as described in Part I.

The mother liquors were extracted with chloroform, the extract evaporated and a gum obtained in all cases. Upon standing for several days one of the gums contained plate-form crystals as shown in the photomicrograph Plate I. The usual crystals of α-glucose penta-acetate are given in Plate II.

Plate 1.

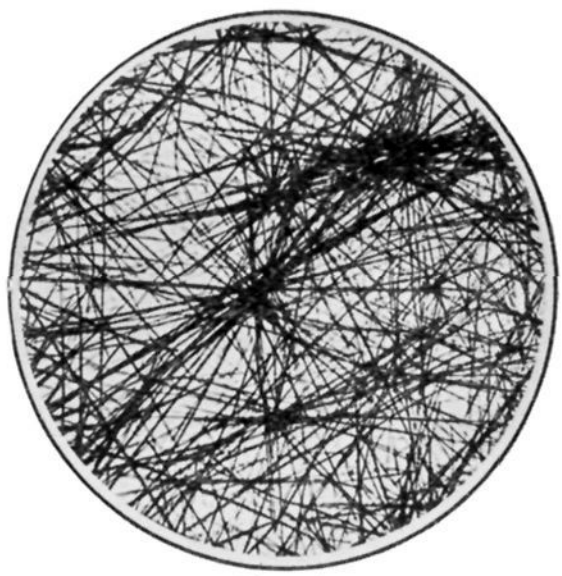


Plate 2.

The preparation which yielded plate-form crystals was made using unsized rag paper with acetolysis in an oil-bath at 113° until the internal temperature had risen to 109°. Precipitation was made in dilute alkali; yield, 35 g. (L); after crystallization from ethyl alcohol, five grams (M). The gum from extraction with chloroform and evaporation weighed 8.7 g. (K). To it a small amount of ether was added, with caution, since the crystals were fairly soluble in ether. The solution was filtered and the crystals with adhering gum (N) were worked on a porous tile with a spatula. The filtrate (O) was evaporated and a gum containing both plate and needle-form crystals obtained. The ether washings evaporated in vacuum yielded more crystal plates (P). The washed crystals (Q) melted at 108.5–110°; specific rotation in chloroform–alcohol (85:15 by volume) +112.5°, at 25° (546.1mμ line). This would indicate the plate-form crystals to be α-penta-acetylglucose.

Three melting points were made simultaneously. In one tube was placed a known sample of glucose penta-acetate, prepared as described in Part I; in the second tube, the plate-form crystals; and in the third, a mixture of the two. The melting points were 111.5, 110–111 and 108.5–110°, respectively.

The filtrate (R) was then examined. Evaporation at room temperature yielded plate-form crystals (S). These were removed by filtration, dissolved in ether and evaporated, giving a gum. This was taken up in alcohol and again evaporated at room temperature. Plate-form crystals (T) separated, changing in the course of two days mostly to the more usual needle-form of α-glucose penta-acetate. These were filtered off and washed with ether. Melting points of these crystals, of α-penta-acetyl glucose and a mixture of these two were taken simultaneously. The melting points were 108–110.5, 111.5 and 108–110.5°, respectively. The filtrate (U) was observed to give a further yield of needle-like crystals upon evaporation.

Summary

1. Two crystalline forms of α-glucose penta-acetate have been isolated from the chloroform extract of the precipitation liquid of the acetolysis of cellulose, without reacetylation.

2. Further yields of glucose penta-acetate and of cellobiose octa-acetate have been obtained by the reacetylation of the gum obtained after isolation of crystalline glucose acetate, mentioned in 1.

3. α-Glucose penta-acetate has been isolated from the mother liquors of the crystallization of crude cellobiose octa-acetate obtained in the acetolysis of cellulose.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF TWELVE AROMATIC HYDROCARBONS[1]

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RECEIVED SEPTEMBER 27, 1929 PUBLISHED APRIL 7, 1930

In the preceding paper[5] the results of a study of the heat capacities, entropies and free energies of some saturated, non-benzenoid hydrocarbons were reported. The present investigation is essentially similar but deals with aromatic hydrocarbons. We shall first present heat capacity data

[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a Research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930).