negative. The modified Kerr and Sorber[13] method for detecting phytosterol was applied but again the results were negative.

Thus the results given above show the presence of three fatty acids, that is, palmitic, oleic and linolic, and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of rice starch.

Determination of Iodine Numbers and Amounts of the Fatty Acids.—Having the qualitative data, the amounts of the fatty acids were estimated[3] from the determinations of the iodine numbers[3] of the mixed and unsaturated fatty acids portions.

TABLE I

RESULTS OF DETERMINATIONS

Fatty acid sample	Mixed	Mixed	Unsaturated	Unsaturated
Weight, g.	0.1277	0.2558	0.1979	0.1664
Iodine number	85.68	83.73	133.2	130.5

TABLE II

RESULTS OF DETERMINATIONS

Fatty acid	Palmitic	Oleic	Linolic
Percentage	36	35	29

Summary

The fatty acids (saturated and unsaturated) liberated by the hydrolysis of rice starch free from extraneous material have been identified and their amounts determined.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE ACETATE OF THE FREE ALDEHYDE FORM OF GLUCOSE

BY M. L. WOLFROM[1]

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The formula of glucose is at present considered to be best represented by the closed chain or lactal type of structure. In the study of the reactivity of the sugars, there has frequently arisen a need for characterizing these compounds as open-chain hydroxy-aldehydes or ketones, capable of showing keto–enol tautomerism. This is particularly true in the study of their behavior in alkaline media, as exemplified by the work of Nef and his students, and by the work being conducted in this Laboratory by Evans and co-workers. Accordingly, we have attempted to isolate a crystalline derivative of the open-chain, free aldehyde form of glucose. We have succeeded in obtaining this as the acetate. This compound may be char-

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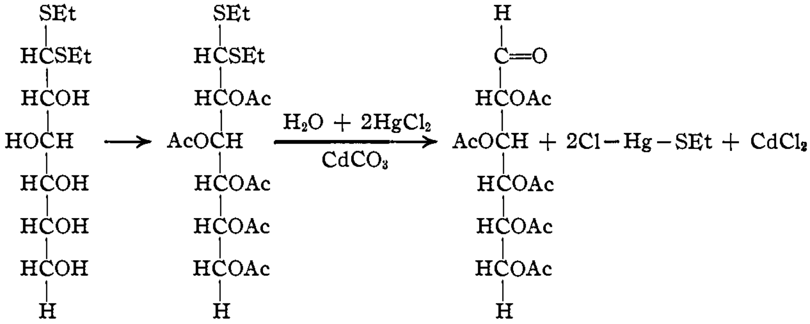
[13] Hertwig, Jamieson, Baughman and Bailey, *J. Assocn. Off. Agr. Chem.*, **8**, 439 (1925).

[1] National Research Fellow in Chemistry.

acterized as 2,3,4,5,6-penta-acetyl-*d*-glucose or, using the nomenclature proposed by T. M. Lowry[2] in considering the free aldehyde form as the intermediary in mutarotation, *μ*-*d*-glucose penta-acetate.

Emil Fischer[3] prepared the thio-acetal of glucose and of other aldoses. He showed that the thio-acetal groups could be removed with mercuric chloride and that the composition of the precipitate formed was Cl-Hg-S-Et. W. Schneider and J. Sepp[4] showed that under proper conditions one thio-acetal group could thus be removed, leaving the *α*-thio-glucoside. This procedure was improved by E. Pacsu.[5] Schneider and Sepp prepared the acetate of glucose-ethylmercaptal and unsuccessfully attempted to remove the thio-groups. We were unaware of this attempt at the time our experimental work was performed. P. A. Levene and G. M. Meyer[6] methylated glucose-diethylmercaptal and removed the thio-acetal groups with mercuric chloride, obtaining the 2,3,4,5,6-pentamethylglucose. They prepared its dimethyl acetal and extended the work to mannose and galactose.[7] Owing to the great difficulty of obtaining crystalline products in the methylated sugar series, all these compounds were obtained as distilled sirups.

By the employment of definite experimental conditions, we have succeeded in removing the thio-acetal groups from *d*-glucose-diethylmercaptal penta-acetate without de-acetylation. The steps involved are as follows



The resulting crystalline glucose penta-acetate differs in its characterizing constants from the two *α*-[8] and *β*-forms[9] known. It possesses a low optical rotation, as would be expected from its open-chain structure, and gives a definite Schiff aldehyde test. It dissolves in water on slight heating and

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[2] T. M. Lowry, *Z. physik. Chem.*, **130**, 125 (1928).

[3] E. Fischer, *Ber.*, **27**, 673 (1894).

[4] (a) W. Schneider and J. Sepp, *Ber.*, **49**, 2054 (1916); (b) *ibid.*, **51**, 220 (1918).

[5] E. Pacsu, *Ber.*, **58**, 511 (1925).

[6] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **69**, 175 (1926).

[7] P. A. Levene and G. M. Meyer, *ibid.*, **74**, 695 (1927).

[8] Erwig and Koenigs, *Ber.*, **22**, 1464, 2207 (1889).

[9] Tanret, *Bull. soc. chim.*, [3] **13**, 261 (1895).

reacts with semicarbazide to form a crystalline glucose-semicarbazone penta-acetate.

The free aldehyde form of glucose may be considered one of the important tautomeric phases of this compound. It is perhaps the intermediary in mutarotation phenomena.[2] Certainly it is the form first involved in enolic transformations. H. Kiliani[10] has recently called attention to the unimportance of the position of the oxygen bridge in many of the most important reactions of glucose, the end result being the same regardless of the type of ring assumed. The lactal structure may be considered as a passive tautomeric phase, opening, when required, to form the more reactive free aldehyde phase. Thus, the lactal form may be a device of nature for more nicely regulating the reactivity of the aldose or ketose molecule. The so-called γ-ring forms, which are best characterized in the sugar acetate series, are known to possess the property of ease of lactal rupture. Their sensitivity to reagents may then be due to the ease of formation of the open-chain forms, the latter being the true reactive phases.

Further work on this compound and the extension of the reactions to other sugars is in progress.

Experimental

Preparation of Glucose-ethylmercaptal Penta-acetate.—A procedure different from that of W. Schneider and J. Sepp[4b] was employed. Five g. of glucose-ethylmercaptal (m. p. 127°) was dissolved at room temperature in 18 cc. of dry pyridine. The solution was cooled in ice and 36 cc. of acetic anhydride added gradually. A considerable amount of solid was thrown out of solution in a fine state of subdivision. It was kept at 0° with occasional shaking until the solid had redissolved, about ten minutes being required. The solution was allowed to stand overnight and was then gradually poured into a liter of ice water, with stirring. A sirup was formed which crystallized after standing in the ice box for about ten days. This was filtered and washed with cold water, 8.1 g. of product being obtained. This was recrystallized by dissolving in methyl alcohol, adding water to opalescence, nucleating and allowing to stand in the ice box. A sirupy phase was first formed which gradually crystallized in very good condition. Further portions of cold water were then added, a 97% recrystallization yield of pure product being possible.

After one recrystallization, the substance melted at 45–47° and showed $[\alpha]_D^{30} = +11.4°$ (0.4050 g. subs., 10.07 cc. of chloroform soln., $\alpha_D = +0.46°$, 1-dm. tube) in chloroform solution. After four recrystallizations, the m. p. was 45–47° and the rotation in chloroform solution was $[\alpha]_D^{29} = +11.2°$ (1.255 g. subs., 24.88 cc. of chloroform soln., $\alpha = +1.13°$, 2-dm. tube). A rotation in acetylene tetrachloride gave the value $[\alpha]_D^{28} = +17.4°$ (1.250 g. subs., 24.88 cc. of acetylene tetrachloride soln., $\alpha = +1.75°$, 2-dm. tube). W. Schneider and J. Sepp[4b] give the melting point as 42–45° and $[\alpha]_D^{20} = +17.7°$ in acetylene tetrachloride.

2,3,4,5,6-Penta-acetyl-*d*-glucose.—An amount of glucose-ethylmercaptal penta-acetate (m. p. 45–47°) equal to 25.2 g. (1 mol.) was dissolved in 90 cc. of acetone and 45 cc. of water added. The clear solution was held in a 3-necked, round-bottomed flask provided with a reflux condenser and a mercury-sealed mechanical stirrer. An

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[10] H. Kiliani, *Z. angew. Chem.*, **42**, 16 (1929).

excess, 45–50 g., of washed cadmium carbonate was added and under rapid stirring a solution of 49.5 g. (3.6 mols.) of mercuric chloride dissolved in 72 cc. of acetone was gradually added. Stirring was maintained at room temperature for twenty-four hours, with occasional additions of small amounts of fresh cadmium carbonate. At the end of this period the reaction flask was encased in a water-bath, and this rapidly heated to 50° and held at this temperature fifteen minutes, very vigorous mechanical stirring being maintained. The bath was then rapidly heated until refluxing began and the solution was refluxed gently for fifteen minutes. The solution was then filtered from the excess cadmium carbonate and Cl-Hg-S-Et precipitate, an excess of fresh cadmium carbonate being placed in the suction flask, and the precipitate washed with acetone. The filtrate was then concentrated to dryness at 30–35° under reduced pressure and in the presence of excess cadmium carbonate. The residue was dried by repeatedly adding acetone and distilling under reduced pressure. The residue was extracted with warm chloroform, filtered, and the chloroform evaporated at room temperature in a vacuum desiccator. The crude product crystallized during the course of this evaporation. This was dissolved in 50 cc. of hot acetone, 25 cc. of alcohol-free ether added and then petroleum ether (40–60°) to opalescence. The substance crystallized out in plates. After standing for several hours in the ice box, the material was filtered, washed with a cold mixture of the same composition as the mother liquor and finally with petroleum ether. The amount of the product was 10.1 g., m. p. 116.5°. A further crop of 1.9 g. was obtained from the filtrate by the addition of more petroleum ether.

After one recrystallization the product melted at 116.5° and gave the value $[\alpha]_D^{25} = +3.3°$ (1.244 g. subs., 24.88 cc. of acetylene tetrachloride soln., $\alpha = +0.33°$, 2-dm. tube) in acetylene tetrachloride. After three recrystallizations performed in the same general way, the melting point was 119.5–120.5° and the polarization value in the same solvent was $[\alpha]_D^{26} = +2.6°$ (0.4985 g. subs., 10.08 cc. of acetylene tetrachloride soln., $\alpha = +0.14°$, 1.1-dm. tube). After five recrystallizations the melting point was 116–118° and the polarization value in the same solvent was $[\alpha]_D^{25} = +2.7°$ (0.5028 g. subs., 10.05 cc. of acetylene tetrachloride soln., $\alpha = +0.15°$, 1.1-dm. tube). A mixed melting point with pure β-glucose penta-acetate (m. p. 131°, $[\alpha]_D^{25} = +4.2°$, $CHCl_3$) gave the value 106–109°. In chloroform (U.S.P.) solution the values $[\alpha]_D^{24} = -4.6°$ ($c = 4.997$) and $[\alpha]_D^{24} = -4.8°$ ($c = 4.725$) were obtained. This value changed slowly to dextro, due probably to acetal formation with the ethyl alcohol present in the U.S.P. chloroform. In methyl alcohol the initial rotation was $[\alpha]_D^{25} = +10°$ ($c = 4.980$; $c = 2.013$), changing slowly in the dextro direction. α-Glucose penta-acetate shows the melting point 113° and $[\alpha]_D^{20} = +101.6°$ ($CHCl_3$), while β-glucose penta-acetate possesses the melting point 132° and $[\alpha]_D^{20} = +3.8°$ ($CHCl_3$).[11]

Anal. Subs., 0.2183: CO_2, 0.3947; H_2O, 0.1124. Subs., 0.2039: CO_2, 0.3697; H_2O, 0.1092. Subs., 0.0993: 12.7 cc. of 0.1 *N* KOH. Calcd. for $C_6H_7O_6(CH_3CO)_5$: C, 49.20; H, 5.69; cc. 0.1 *N* KOH, 12.7. Found: C, 49.31; H, 5.76; C, 49.45; H, 5.99; S, absent.

I am indebted to Professor W. J. McCaughey of the Department of Mineralogy of this University for the following crystallographic description of the compound.

"Crystal, monoclinic, tabular in direction parallel to side (clino) pinacoid. On the flat tabular face emerges an acute bisectrix; the optic angle is small, probably around 40°. On the clinopinacoid, the index of refraction of beta (β) and gamma (γ) can be measured. Sometimes when crystalliza-

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[11] C. S. Hudson, *Scientific Papers of the Bureau of Standards*, No. 533, 379 (1926).

tion takes place from dilute solution, the crystals separate in elongated forms showing parallel extinction and negative elongation (elongation || to (α) alpha). With this orientation alpha (α) can be measured. The optical sign of the crystal is negative; the indices are $\alpha = 1.460$, $\beta = 1.500-$, $\gamma = 1.515$.

"The vibration direction of beta (β) is inclined to what is taken to be crystallographic axis c by 1–2°. The vibration direction alpha is parallel to crystallographic axis $\bar{b}$. The crystal faces present are basal pinacoid, clinopinacoid, orthopinacoid and an orthodome. When the crystal habit shows growth in the direction of crystallographic axis $\bar{b}$ it appears as square prisms. When the crystal is tabular in the direction of $\bar{b}$ it shows hexagonal outline but the adjacent angles are not 120° as in a truly hexagonal crystal.

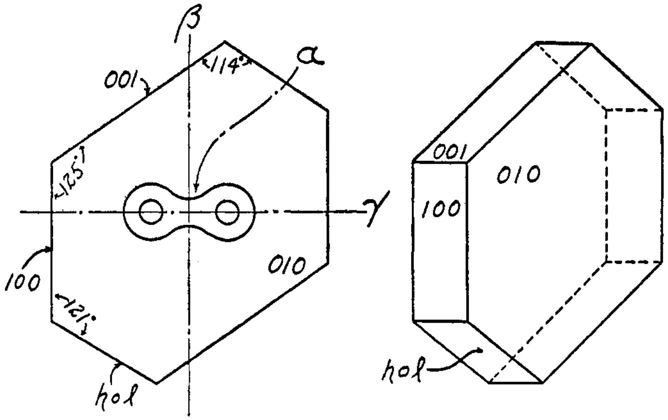

Fig. 1.—Crystalline form of *μ-d*-glucose penta-acetate, tabular habit.

The face having the hexagonal outline is the side or clinopinacoid. The size of the crystals was 0.2 mm.

"β-Glucose penta-acetate consists of needles showing parallel extinction and negative elongation. Indices: low = 1.47; high < 1.50."

The crystals of the new penta-acetate are very soluble in chloroform, soluble in acetone, alcohol and warm water, moderately so in ether and benzene and practically insoluble in petroleum ether (40–60°). The substance gave a positive fuchsin or Schiff aldehyde reaction. The fuchsin solution available gave a negative reaction with vanillin. With benzaldehyde a faint coloration was obtained at one minute and a distinct coloration at one and a half minutes. On dissolving 50–70 mg. of the acetate in about 0.5 cc. of warm acetone, cooling to room temperature, and adding 2.5 cc. of the reagent, a faint coloration was obtained at one and one-half to two minutes, becoming very distinct at five minutes. A blank on the acetone used gave negative results.

d-Glucose-semicarbazone Penta-acetate.—Four and one-half g. (1 mol.) of pure μ-glucose penta-acetate was dissolved in 45 cc. of warm water, cooled to room temperature, and a mixture of 1.1 g. of semicarbazide hydrochloride (0.9 mol.) and 1.8 g. of potassium acetate (1.6 mols.) was added in the solid form. In a few minutes the solution became cloudy and an oil was gradually deposited. On standing overnight at room temperature this solidified. This was filtered and washed with cold water, 3.6 g. being obtained. The material was dissolved in methyl alcohol, treated with decolorizing carbon, filtered and water added. On standing at ice-box temperature 1.4 g. of crystals (m. p. 148–150°) in the form of minute elongated prisms was deposited. These were removed by filtration, washed with water and a further crop of 1.3 g. (m. p. 148–150°) obtained from the filtrate by further addition of water. On two further recrystallizations the substance melted at 150–151° and on two more (5) melted at 150°.

Anal. Subs., 0.2055: N_2, 18.83 cc. (751.5 mm., 28°). Calcd. for $C_7H_{10}O_6N_3(CH_3CO)_5$: N, 9.40. Found: N, 9.87. Calcd. for 0.2019: 22.6 cc. 0.1 *N* KOH. Found: 22.7 cc. Calcd. for 0.2074: 23.2 cc. 0.1 *N* KOH: Found: 23.1 cc.

The writer wishes to acknowledge his indebtedness to Professor W. L. Evans for his inspirational counsel and advice.

Summary

1. A new form of d-glucose penta-acetate has been prepared in pure condition.

2. Evidence is given that this compound possesses the open-chain, free aldehyde structure and the suggestion is made that the name μ-d-glucose penta-acetate be applied to the substance.

3. The crystalline semicarbazone of this aldehyde has been prepared in pure form.

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[Contribution from the Chemistry Department, University of Illinois]

PREPARATION OF SOME METHYLATED GALLIC ACIDS

By R. L. Shriner and P. McCutchan

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During the course of a study of some anthocyan pigments it was desired to have samples of certain methylated gallic acids, since these are produced by degradation of the anthocyanidin. The compounds desired were: 3,5-dimethylgallic acid, 3,4-dimethylgallic acid and 3-methylgallic acid. The first of these, syringic acid, is easily prepared by the method of Bogert and Ehrlich,[1] and its properties and derivatives[2] have been thoroughly studied. However, the data available in the literature on the other two methylgallic acids are very meager. The 3,4-dimethylgallic acid has been previously prepared by Zincke and Francke[3] and Her-

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[1] Bogert and Ehrlich, This Journal, **41**, 798 (1919).

[2] Bogert and Coyne, *ibid.*, **51**, 569 (1929).

[3] Zincke and Francke, *Ann.*, **293**, 191 (1896).