sure at 40–45° to a volume of *ca.* 50 cc. This solution was passed slowly over a 1.6 cm. diam. column containing 50 g. of cation exchange resin (Amberlite IR-100[8]) and the effluent was passed in like manner over a similar column of anion acceptor resin (Amberlite IR-4[8]). The resultant solution was concentrated under reduced pressure to a crystalline residue which was generally contaminated with a small amount of silica. The latter was removed by treatment with a small amount of water followed by filtration. The filtrate, after solvent removal, yielded the crystalline sugar in the amount and purity listed in Table II.

Separation of D-Glucitol (Sorbitol) Hexaacetate and D-Mannitol Hexaacetate.—These compounds were not separable under the conditions listed in Table I (group II, class 2). Their separation was effected under the conditions given in Table II. Elution of each zone was effected with 100 cc. of acetone followed by filtration and washing with a further 300 cc. of acetone. Solvent removal yielded the crystalline acetates. The material from the D-glucitol hexaacetate zone was rechromatographed on a 4.4 × 22.5 cm. column of the same adsorbent and developed with 1250 cc. of benzene–ethanol (1000:1). The material in the main zone was recovered as described above. The small second zone was discarded.

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Summary

The suitability of a synthetic hydrated calcium acid silicate (Silene EF) for the chromatography of sugars and their derivatives (alcohols, glycosides, acetates and methyl ethers) is demonstrated. The streak (toward the alkaline permanganate indicator employed) and extrusive properties of this adsorbent are especially favorable.

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[8] A product of the Resinous Products and Chemical Co., Philadelphia, Pennsylvania.

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

Isosucrose Synthesis

BY W. W. BINKLEY[1] AND M. L. WOLFROM

The development of a chromatographic method for the separation of the sugar acetates[2] and an improved procedure for the preparation of 1,3,4,6-D-fructofuranose tetraacetate led us to an investigation of the condensation products formed between 1,3,4,6-D-fructofuranose tetraacetate and 2,3,4,6-D-glucopyranose tetraacetate with phosphoric anhydride.[3] Employing laborious and difficult crystallization techniques, Irvine and Stiller had found no sucrose in the products from this reaction. It was considered desirable to search the condensates for sucrose by employing these new chromatographic techniques.

Isosucrose octaacetate was crystallized from the products of this condensation. Adsorption of the residual material on "Magnesol"[2] led to the detection and isolation of a zone which yielded more isosucrose octaacetate. Adsorption of the material from this zone on Silene EF[4] under conditions established for the separation of sucrose and isosucrose octaacetates gave only one zone, that of isosucrose octaacetate. The material from the isosucrose octaacetate zone of the Magnesol chromatogram was deacetylated and allowed to react with freshly prepared diazo-uracil[5] (specific for sucrose); the results were negative.

1,3,4,6-D-Fructofuranose tetraacetate was prepared by the acetolysis of inulin triacetate following the procedure recommended by Irvine and Stiller[3] except that it was found that pure acetyl bromide produced only a negligible degree of hydrolysis. The addition of hydrogen bromide to the reaction mixture caused nearly complete acetolysis in less than three hours at 25° and a 54–58% yield of 1,3,4,6-D-fructofuranose tetraacetate resulted. It is thus apparent that hydrobromic acid accidentally introduced by moisture contamination is the active agent in this frequently used hydrolytic reagent.

Experimental

Ten grams of inulin triacetate (dried for two days under reduced pressure at 45°) was dissolved in a mixture of 100 cc. of glacial acetic acid (dried over anhydrous calcium sulfate) and 12 cc. of acetyl bromide (freshly prepared). The specific rotation (sodium D-line, 23°) of the reaction solution changed from −40 to −1° in three and one-half to four hours at 30°. Irvine and Stiller[3] stated that a final value of +80° was attained in about three hours.

Ten grams of inulin triacetate (dried in air at room temperature) was dissolved in a mixture of 100 cc. of glacial acetic acid and 20 cc. of acetyl bromide. Then 20 cc. of 30–32% hydrogen bromide in glacial acetic acid solution was added and the mixture was allowed to stand for two to two and one-half hours at 25°. The specific rotation of the reaction solution changed from −40 to +83° during this reaction period. The reactants were then poured into a 3-liter beaker surrounded with ice and 100 g. of finely crushed ice was added to the beaker followed by 10 g. of sodium acetate. A total of 1.5 liters of distilled water was then added and the *p*H of the solution adjusted to 5.5 with sodium bicarbonate (*ca.* 170 g.). The neutralized solution was extracted 10 times with 100-ml. portions (total 1 liter) of chloroform. The extracts were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure at 40–45°. The average yield of

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[1] Research Associate of the Sugar Research Foundation, Inc. (Project 190 of The Ohio State University Research Foundation.) The laboratory assistance of Miss Eloise Carpenter is gratefully acknowledged. Preliminary work on this problem had been carried out in this Laboratory by Mrs. Ruth Haverstock Ness.

[2] W. H. McNeely, W. W. Binkley and M. L. Wolfrom, THIS JOURNAL, **67**, 527 (1945).

[3] J. C. Irvine and E. T. Stiller, *ibid.*, **54**, 1079 (1932).

[4] L. W. Georges, R. S. Bower and M. L. Wolfrom, *ibid.*, **68**, 2169 (1946).

[5] H. W. Raybin, *ibid.*, **55**, 2603 (1933); **59**, 1402 (1937).

red-orange sirup was 9.5 to 10 g. This sirup was dissolved in 100 ml. of benzene and the resultant solution was extracted 20 times with 100-ml. portions (total 2 liters) of distilled water. The water extracts were then extracted with 10 portions of 100 ml. each of chloroform (total 1 liter) and these extracts dried over anhydrous sodium sulfate. The average yield of 1,3,4,6-D-fructofuranose tetraacetate as a light-colored sirup was 6.5 to 7.0 g. after removal of solvent.

An amount of 6.94 g. of 1,3,4,6-D-fructofuranose tetraacetate and 6.94 g. of 2,3,4,6-D-glucopyranose tetraacetate was dissolved in 200 ml. of dry benzene. About 0.5 g. of phosphoric anhydride was added and the reactants were shaken vigorously for forty-eight hours. The benzene solution was decanted carefully and extracted with ten 200-ml. portions (total 2 liters) of water. A yield of 2.0 g. of amber-colored sirup was obtained after solvent removal at 40° under reduced pressure. An ether solution of this sirup yielded 0.2 g. of crystals; m. p. 131–132°, mixed melting point with an authentic specimen of isosucrose octaacetate[6] was 131–132°; $[\alpha]^{27}\mathrm{D} + 20.4°$ (*c* 4.9, chloroform). Irvine, Oldham and Skinner[7] cite for isosucrose octaacetate the constants: m. p. 131–132°, $[\alpha]\,\mathrm{D} + 20°$ (*c* 3.8, chloroform).

An amount of 1.0 g. of the above sirup was dissolved in 15 ml. of benzene. This solution was added at the top of a column (43 mm. in diameter by 200 mm. in length) of a mixture of 5 parts (by wt.) of Magnesol[8] and 1 part of Celite[9] previously wetted with 35 ml. of benzene. The chromatogram was developed with 750 ml. of 100–1: benzene–ethanol[10] (volume ratio). The column was extruded and streaked with the alkaline permanganate indicator.[2] The third zone, 42–65 mm. from the top of the column, was eluted from the adsorbent with acetone (yield, 209 mg.), and 26 mg. of crystal isosucrose octaacetate separated from ethanolic solution; m. p. 131–132°, mixed melting point with isosucrose octaacetate, 131–132°. An amount of 100 mg. of material from this zone was deacetylated with 10 ml. of 0.2 *N* sodium hydroxide and on the addition of freshly prepared diazo-uracil gave a negative color test[5] for sucrose.

An amount of 5 mg. each of sucrose and isosucrose octaacetates in 1 ml. of benzene was added at the top of a column (19 mm. in diameter by 120 mm. in length) of a mixture of 5 parts (by wt.) of Silene EF[11] and 1 part of Celite (previously wetted with 10 ml. of benzene). The chromatogram was developed with 150 ml. of 250–1: benzene–ethanol (volume ratio). After extruding the column and streaking it with the alkaline permanganate indicator, two zones were detected and isolated by elution with acetone. Zone 1 was 59–79 mm. from the top; zone 2 was 85–97 mm. An ethanolic solution of the material from zone 1 gave crystals, m. p. 84–85°, mixed melting point with sucrose octaacetate 84–85°; a similar treatment of the material from zone 2 gave crystals, m. p. 131–132°, mixed melting point with isosucrose octaacetate 131–132°. An amount of 10 mg. of material from the previously described third zone of the Magnesol chromatogram was adsorbed on Silene EF exactly as described above. Only one zone, 91–101 mm. from the top of the column, was detected and isolated. An ethanolic solution of this zone material yielded crystals; m. p. 131–132°, mixed melting point with isosucrose octaacetate 131–132°.

Summary

1. New directions are cited for the preparation of 1,3,4,6-D-fructose tetraacetate from inulin.

2. An investigation, by chromatographic brush techniques, of the condensation products of 1,3,4,6-D-fructose tetraacetate and 2,3,4,6-D-glucose tetraacetate yielded only isosucrose octaacetate.

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(6) Kindly supplied by Dr. E. T. Stiller.

(7) J. C. Irvine, J. W. H. Oldham and A. F. Skinner, THIS JOURNAL, **51**, 1279 (1929).

(8) Westvaco Chlorine Products Co., South Charleston, West Virginia.

(9) No. 535, Johns–Manville Co., New York, N. Y.

(10) All ethanol used in the chromatographic work was absolute; all benzene was thiophene-free.

(11) Columbia Chemical Division, Pittsburgh Plate Glass Co., Barberton, Ohio.

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The Preparation of β-Tetralone by the Catalytic Reduction of β-Naphthol

BY GILBERT STORK AND E. LEON FOREMAN

In spite of its very interesting and sometimes unexpected properties, β-tetralone has been a comparatively unavailable compound. It is true that a number of methods have been devised for its preparation but they either give very low yields or involve a great number of steps.

Bamberger and Lodter,[1] who first prepared this compound, used the reaction of 2-hydroxy-3-chloro-1,2,3,4-tetrahydronaphthalene with quinoline and obtained a poor yield of β-tetralone. Almost simultaneously, Einhorn and Lumsden prepared the ketone by the dry distillation of the calcium salt of the dicarboxylic acid obtained by the reduction of either 2-hydroxy-1-naphthoic acid or of 2-hydroxy-3-naphthoic acid with sodium and alcohol.[2] The isomerization of the oxide of 3,4-dihydronaphthalene under the influence of anhydrous hydrogen chloride was used by Straus and Rohrbacher,[3] while more recently Tchoubar performed this isomerization with the help of magnesium bromide.[4]

Another approach to the problem was that of v. Braun and his collaborators who isolated good yields of β-tetralone from the pyrolysis of the methiodide of 1-dimethylamino-2-hydroxy-1,2,3,4-tetrahydronaphthalene. Unfortunately, the method of preparation of the last mentioned compound required numerous steps from *ac*-tetrahydro-β-naphthol.[5] Crowley and Robinson devised a method starting with γ-phenylbutyric acid which consisted essentially of the Curtius degradation of ethyl 3,4-dihydro-β-naphthoate.[6] In spite of the considerable theoretical interest which some of these methods present, they are ill-suited

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(1) Bamberger and Lodter, *Ber.*, **26**, 1833 (1893).

(2) Einhorn and Lumsden, *Ann.*, **286**, 257 (1895).

(3) Straus and Rohrbacher, *Ber.*, **54**, 40 (1921).

(4) Tchoubar, *Compt. rend.*, **214**, 117 (1942).

(5) v. Braun, Braunsdorf and Kirschbaum, *Ber.*, **55**, 3648 (1922).

(6) Crowley and Robinson, *J. Chem. Soc.*, 2001 (1938).