

on a filter, washed with cold water and dried over potassium hydroxide in a vacuum desiccator; m. p. 230–231°; yield 1.40 g. (72.5%). Removal of the solvent left a solid which weighed 0.3 g. and melted at 209–210°. Recrystallization of these solids from water raised their melting points to 233–234° and 210–211°, respectively.

The benzoate of the higher melting material, prepared in the usual manner, melted at 228–230° after recrystallization from acetone. A mixture melting point with the benzoate of 6-hydroxy-1,4-dithiacycloheptane tetroxide (V) showed no depression. Attempts to prepare the benzoate of the lower melting material failed.

1,4-Dithia-6-cycloheptanone Tetroxide (VII).—One gram of the hydroxy sulfone (VI) was suspended in 10 ml. of water to which had been added 0.92 g. of potassium dichromate. Concentrated sulfuric acid (10 ml.) was added dropwise over a period of one-half hour at 20–25°. Stirring was continued for one hour after which 50 ml. of water was added to the green reaction mixture. The ketone was collected on a filter and recrystallized from dioxane or water; yield 0.72 g. (72.7%); m. p. 252–253° (dec.).

Anal. Calcd. for $C_7H_8O_4S_2$: C, 28.29; H, 3.79; S, 30.21. Found: C, 28.68, 28.71; H, 3.66, 3.42; S, 30.07.

The phenylhydrazone was prepared by dissolving 0.2 g. of the ketone in 10 ml. of hot dioxane, cooling the solution and adding 1 ml. of phenylhydrazine and two drops of glacial acetic acid. The mixture was then heated on the steam-bath for ten minutes and cooled in ice. The addition of 20 ml. of water caused the immediate precipitation of the phenylhydrazone; m. p. 235–236° (dec.); yield 0.2 g. (70%). Recrystallization of the derivative from a dioxane-water mixture did not change its melting point.

Anal. Calcd. for $C_{11}H_{14}N_2O_4S_2$: C, 43.69; H, 4.66; N, 9.26; S, 21.21. Found: C, 43.95; H, 4.93; N, 9.24; S, 21.09.

1,4-Dithia-5-cycloheptene Tetroxide (VIII).—Five grams of 6-hydroxy-1,4-dithiacycloheptane tetroxide was dissolved in 75 ml. of hot anhydrous pyridine. The mixture was cooled in an ice-bath, and 4.6 ml. of phosphorus oxychloride was added dropwise with stirring. The reaction mixture was allowed to come to room temperature and then stirred at 60–70° for three hours. The slightly colored cycloheptene tetroxide was collected on a filter and washed well with ice-water; m. p. 279–280° (dec.); yield 3.4 g. (74%). Repeated recrystallization of the unsaturated sulfone from water raised its melting point to 280–280.5° (dec.). An aqueous solution of potassium permanganate was instantly decolorized when added to a dioxane solution of this compound.

Anal. Calcd. for $C_7H_8O_4S_2$: C, 30.60; H, 4.11. Found: C, 30.80, 30.75; H, 3.78, 3.71.

1,4-Dithiacycloheptane Tetroxide (IX).—Five grams of 10% palladium chloride on carbon¹⁰ was reduced in 25 ml. of anhydrous dioxane at three atmospheres pressure. To the reduced catalyst a solution of 0.6 g. of the cycloheptene tetroxide (VIII) in 75 ml. of dioxane was added. The hydrogenation was completed after seven hours at three atmospheres pressure. The contents were transferred to a flask, boiled and filtered. Two additional extractions of the catalyst were carried out with 100-ml. portions of dioxane. The 1,4-dithiacycloheptane tetroxide, which separated when the combined extracts were allowed to stand in the cold, was recrystallized from water; m. p. 279–280° (dec.); yield 0.4 g. (66%).

Anal. Calcd. for $C_7H_{10}O_4S_2$: C, 30.29; H, 5.08. Found: C, 30.41; H, 5.38.

1,4-Dithiacycloheptane was synthesized in 7.9% yield (m. p. 47°) according to the procedure of Reid,^{5,8} who reported the same melting point and a yield of 8.2%. The sulfone was prepared with 30% hydrogen peroxide in glacial acetic acid in a yield of 59%; m. p. 277.5–278.5° (dec.). A mixture of this sulfone with that prepared in the preceding experiment decomposed at 278–279°. The melting point of the sulfone has been given as 282°⁷ and 287–288°^{6,8}.

Anal. Calcd. for $C_7H_{10}O_4S_2$: C, 30.29; H, 5.08. Found: C, 30.41; H, 5.00.

2-Methyl-1,4-dithiane Tetroxide.—2-Methyl-1,4-dithiane, prepared according to the method of Tucker and Reid,⁶ melted at 20–22°. The reported melting point is 20°. After two sublimations at low pressure, the clear, colorless sulfide was converted to the sulfone by the usual method. It was recrystallized from water; m. p. 304–306° (dec.).

Anal. Calcd. for $C_8H_{10}O_4S_2$: C, 30.29; H, 5.08. Found: C, 30.09; H, 5.11.

Summary

Ethanedithiol has been found to react with 2,3-dibromo-1-propanol or 1,3-dibromo-2-propanol to give 6-hydroxy-1,4-dithiacycloheptane. The structure of the product has been established by unequivocal methods.

(10) Mozingo, "Org. Syntheses," **26**, 77 (1946).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A Polymer-homologous Series of Sugar Acetates from the Acetolysis of Cellulose¹

By E. E. DICKEY² AND M. L. WOLFROM

The chain scission of cellulose by hydrolysis in mineral acids and by acetolysis has yielded, in addition to D-glucose and cellobiose, specific sugars composed of three, four and six D-glucopyranose units as fragments of the original cellulose chains.³ We wish to report herein the isolation of such a

(1) Presented before the combined meeting of the Division of Cellulose Chemistry and the Division of Sugar Chemistry and Technology at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13–17, 1948.

(2) Research Foundation Associate, The Ohio State University, Project 212.

(3) A survey of the products obtained from the acid degradation of cellulose may be found in E. Heuser, "The Chemistry of Cellulose," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 512–515.

polymer-homologous series of sugars (as the α -D form of the acetates) complete from α -D-glucopyranose pentaacetate through a α -cellohexaose eicosacetate (Table I). This has been accomplished through the application of the general method for the chromatography of sugar acetates as developed in this Laboratory.^{4,5}

α -D-Glucopyranose pentaacetate, *aldehydo*-D-glucose heptaacetate⁶ and α -cellobiose octaacetate

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

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

(6) K. Freudenberg and K. Soff, *Ber.*, **70**, 264 (1937).

TABLE I
CONSTANTS OF SUGAR ACETATES ISOLATED FROM CELLULOSE ACETOLYZATE BY CHROMATOGRAPHIC PROCEDURES

| | D. P. (degree of poly- meriza- tion) | [α] _D ²⁰ - ₂₅ ^D chloroform (<i>c</i> > 5) | Melting point, ^d °C. | Molecular weight | | Analyses, % | | | |
|--|--|---|---------------------------------------|---------------------|------------------------------|-------------|--------|-------|------|
| | | | | Calcd. | Found (Rast) ^b | C | Calcd. | H | C |
| α -D-Glucopyranose pentaacetate | 1 | + 97.3° | 105-109 | 383 | 382 | ... | ... | ... | ... |
| | | | | 390 | 355 | ... | ... | ... | ... |
| α -Cellobiose octaacetate | 2 | + 39.6 | 225-226 | 750 | 668 | ... | ... | ... | ... |
| | | | | 678 | 640 | ... | ... | ... | ... |
| α -Cellotriose hendecaacetate | 3 | + 22.6 | 223-224 | 1000 | 967 | 49.69 | 5.630 | 49.78 | 5.65 |
| | | | | 990 | 930 | 49.73 | 5.68 | 49.73 | 5.68 |
| α -Cellotetraose tetradecaacetate | 4 | + 13.4 | 230-234 | 1340 | 1255 | 49.76 | 5.622 | 49.82 | 5.65 |
| | | | | 1180 | 1150 | 49.73 | 5.60 | 49.73 | 5.60 |
| α -Cellopentaose heptadecaacetate | 5 | + 4.17 | 240-241 | 1480 | 1543 | 49.80 | 5.617 | 49.67 | 5.54 |
| | | | | 1470 | 1360 | 49.73 | 5.51 | 49.73 | 5.51 |
| | | | | 1360 | 1340 | | | | |
| | | | | 1340 | 1300 | | | | |
| α -Cellohexaose eicosaacetate | 6 | - 0.23 | 252-255 | 2030 | 1831 | 49.83 | 5.613 | 49.62 | 5.54 |
| | | | | 1840 | 1700 | 49.63 | 5.57 | 49.63 | 5.57 |
| | | | | 1700 | 1670 | | | | |
| | | | | 1670 | 1600 | | | | |

^a All melting points were taken on a Fisher-Johns melting point block, Fisher Scientific Co., Pittsburgh, Pa., and are uncorrected. ^b The precautions cited by J. H. C. Smith and W. G. Young, *J. Biol. Chem.*, **75**, 289 (1927), and W. B. Meldrum, L. P. Saxer and T. O. Jones, *THIS JOURNAL*, **65**, 2023 (1943), were followed in the determination of molecular weights by the method of Rast. ^c Accepted values as reported by Hudson and Johnson, ref. 15. ^d Specific rotation and melting point reported by Hess and Dziengel, ref. 10. ^e Accepted values.

are known products of the acetolysis of cellulose.⁷ The trisaccharide, "procellulose," was first obtained by Bertrand and Mlle. Benoist,⁸ as an amorphous solid after saponification and fractionation of a cellulose acetolyzate. By a similar procedure, Ost⁹ succeeded in isolating the crystalline, trisaccharide and named it cellotriose. By the acetolysis of cotton linters followed by saponification and fractionation, Hess and Dziengel¹⁰ prepared a carefully purified sample of cellotriose which evidently crystallized as the α -form, [α]_D +32.0°, initial \rightarrow +23.2°, final (in water). α -Cellotriose hendecaacetate was then prepared by acetylating the free sugar in pyridine and acetic anhydride, and repeatedly crystallizing the acetate to maximum purity (Table I). Crystalline cellotetraose was obtained by Willstätter and Zechmeister¹¹ from wood cellulose by hydrolysis in fuming hydrochloric acid (*d*₄¹⁵ 1.21), and later, crystalline cellohexaose was isolated from the hydrolyzate by Zechmeister and Tóth.¹² Crystalline cellotriose hendecaacetate and cellotetraose

tetradecaacetate were prepared by Zechmeister and Tóth¹² by acetylating the free sugars in acetic anhydride and pyridine, but cellohexaose failed to yield a crystalline acetate. As indicated by the specific rotation, the acetates prepared by Zechmeister and Tóth were undoubtedly mixtures of both the α - and β -forms. The viscosity and molecular weight (Rast) of the cellohexaose acetate,¹³ along with the lower members of the series, were determined by Staudinger and Leupold¹⁴ who believed that the hexaose was actually a cellopentaose heptadecaacetate. Until all the free sugars of this series have been prepared and characterized, the identity of Zechmeister and Tóth's hexaose will remain somewhat in question. The triose and the tetraose have been obtained, also, in the form of their crystalline methyl ethers and phenylosazones.³

As shown by Hudson and Johnson,¹⁵ mainly the α -form of a sugar acetate exists in an acetylating mixture of acetic anhydride and sulfuric acid. Since, in the present investigations, a cellulose acetolyzate was resolved directly into the polymer-homologous series, the preponderance of the α -form of each sugar acetate is to be expected (Table I).

(7) A. P. N. Franchimont, *Ber.*, **12**, 1938 (1879); Z. H. Skraup and J. König, *ibid.*, **34**, 1115 (1901); *Monatsh.*, **22**, 1011 (1901).

(8) G. Bertrand and Mlle. S. Benoist, *Bull. soc. chim.*, [4] **33**, 1451 (1923).

(9) H. Ost, *Z. angew. Chem.*, **39**, 1117 (1926).

(10) K. Hess and K. Dziengel, *Ber.*, **68**, 1594 (1935).

(11) R. Willstätter and L. Zechmeister, *ibid.*, **62**, 722 (1929).

(12) L. Zechmeister and G. Tóth, *ibid.*, **64**, 854 (1931).

(13) The sample was prepared by Zechmeister and Tóth, ref. 12.

(14) H. Staudinger and E. O. Leupold, *Ber.*, **67**, 479 (1934).

(15) C. S. Hudson and J. M. Johnson, *THIS JOURNAL*, **37**, 1276 (1915).

TABLE II
YIELDS OF SUGAR ACETATES ISOLATED FROM CELLULOSE ACETOLYZATE (10 g.) BY CHROMATOGRAPHIC PROCEDURES

| | 1st chromatographic separation on "Silene EF" (cf. Fig. 1), g. | Effluent fraction on "Magnesol" (cf. Fig. 2), g. | After rechromatographing to maximum purity, mg. | Recrystallized material | |
|--|--|--|---|-------------------------|--------------------------------------|
| | | | | Mg. | Crystallization medium |
| α -D-Glucopyranose pentaacetate | 3.07 | 0.305 | ... | 50 | Ether-petroleum ether (b. p. 65-69°) |
| α -Cellobiose octaacetate | | 1.16 | ... | 915 | Ethanol (95%) |
| α -Cellotriose hendecaacetate | | 0.99 | 470 | 384 | Chloroform-ether |
| α -Cellotetraose tetradecaacetate | 1.68 | .. | 323 | 220 | Dioxane-ether |
| α -Cellopentaose heptadecaacetate | 1.33 | .. | 305 | 218 | Dioxane-ether |
| α -Cellohexaose eicosaacetate | 1.09 | .. | 246 | 178 | Dioxane-ether |
| Remainder (highly adsorbed material) | 2.50 | .. | ... | .. | |
| Total recovered | 9.47 | .. | ... | 1965 | |

In the work herein described, cellulose in the form of filter paper was subjected to the procedure of Hess and Dziengel¹⁰ for mild acetolysis. The cellulose acetolyzate was chromatographed on "Silene EF"⁵ to effect a preliminary fractionation of the mixture. Three zones, as shown in Table II and Fig. 1, subsequently yielded the tetraose, pentaose and hexaose acetates, respectively. The

solvent (Table II). The data for the purified samples of specific sugars obtained from the cellulose acetolyzate are summarized in Table I and Fig. 3.

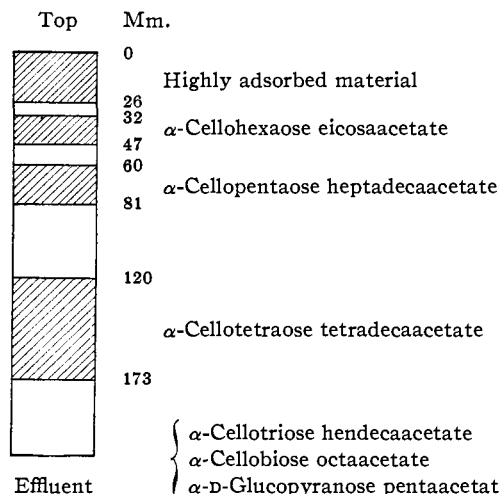


Fig. 1.—Cross section of a typical chromatogram of 1.5 g. of cellulose acetolyzate in 30 ml. of chloroform adsorbed on a column of adsorbent (44 mm. in diameter and 215 mm. long) composed of 5 parts by wt. of "Silene EF"¹⁹ and 1 part of "Celite"²⁰ as developed with 1.4 liters of benzene-ethanol (100:1 by vol.).

highly adsorbed material at the top of the column is under further investigation. The solids recovered from the effluent were then chromatographed on "Magnesol"⁴ to yield the three lower sugar acetates (Table II and Fig. 2) as well as two unidentified, crystalline substances under further investigation. It is probable that these substances represent impurities originating in the wood which was the source of the cellulose used. Corresponding zones from several chromatograms were combined, rechromatographed on "Magnesol" or "Silene EF" and crystallized from a suitable

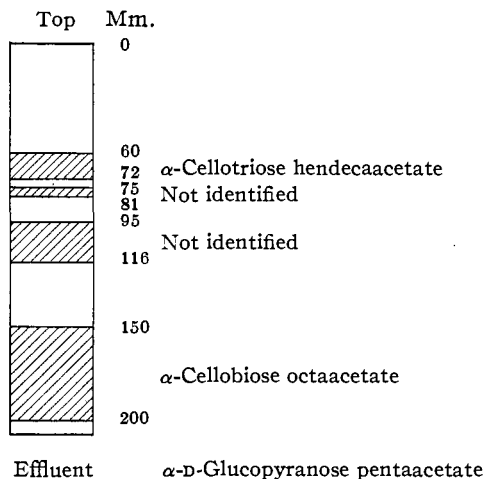


Fig. 2.—Cross section of a typical chromatogram of 1.8 g. of solids from the "Silene EF" effluent (cf. Fig. 1) in 30 ml. of chloroform adsorbed on a column of adsorbent (44 mm. in diameter and 220 mm. long) composed of 5 parts by wt. of "Magnesol"²² and 1 part of "Celite"²⁰ as developed with 1.5 liters of benzene-ethanol (100:1 by vol.).

The trend of melting points and specific rotations (Table I) is toward the constants for cellulose triacetate, $[\alpha]_D^{25}$ ca. -20° ¹⁶ and m. p. (softening point) ca. 295° .¹⁷ Such a trend was found by Zechmeister and Tóth¹² for the corresponding series of free sugars, excluding the cellopentaose.

Freudenberg and co-workers¹⁸ have shown that if the type of linkage in a polymer-homologous series is uniform, the expression $[M]_n/n$ plotted against $(n-1)/n$ (where $[M]$ is the molecular rotation and n is the degree of polymerization)

(16) K. Hess, G. Schultze and E. Messmer, *Ann.*, **444**, 266 (1925).
 (17) K. Hess, "Die Chemie der Zellulose und ihrer Begleiter," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, p. 512.
 (18) K. Freudenberg, "Tannin, Cellulose, Lignin," J. Springer, Berlin, 1933, p. 104.

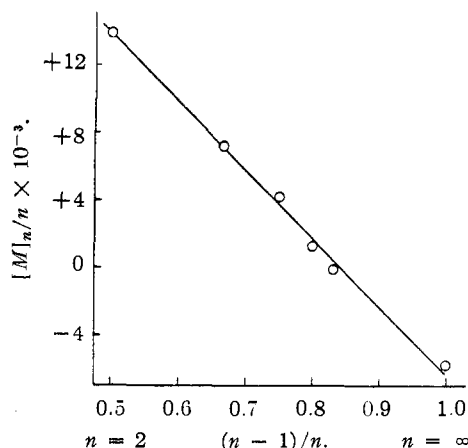


Fig. 3.—Relation between D. P. and molecular rotation.

should yield a straight line for $n \geq 2$. Figure 3 shows that this linear relation holds for the α -D acetates of this series.

The determination of molecular weight by the method of Rast, Table I, tends to decrease in reliability as the molecular weight is increased. However, when the experimental molecular weights were correlated with specific rotations, melting points and relative positions on the chromatographic columns (Figs. 1–3) agreement with the proposed series was evident. As more material of better quality becomes available, the physical properties herein reported may be somewhat revised.

Experimental

Cellulose Acetolyzate.—Using the general procedure of Hess and Dziengel,¹⁰ 90 g. of filter paper (no. 1, prepared by W. & R. Balston, Ltd., England) was dissolved with mechanical stirring in a mixture of 340 ml. of glacial acetic acid, 340 ml. of acetic anhydride and 36 ml. of concentrated sulfuric acid. The temperature of the reaction mixture was held at ca. 40° by external cooling with ice-water during the addition of the filter paper. After standing at room temperature for sixty hours, the clear, yellow solution was filtered through a sintered glass funnel and the filtrate poured slowly and with efficient mechanical stirring into 3 liters of cold water. The mixture was neutralized with sodium bicarbonate until just acid to congo red paper and allowed to stand overnight. The white precipitate was removed by filtration, washed on the filter with water until the filtrate was neutral to litmus and dried to constant weight in a vacuum desiccator over anhydrous calcium chloride; yield ca. 140 g. The product was powdered in a mortar and stored in a desiccator over solid sodium hydroxide and anhydrous calcium chloride.

First Chromatographic Fractionation of Cellulose Acetolyzate.—Using the general procedure of Georges, Bower and Wolfrom⁵ for the chromatographic separation of sugar acetates on "Silene EF"¹⁹ and "Celite,"²⁰ the cellulose

acetolyzate was fractionated as shown in Fig. 1 and Table II. The extruded column was brushed with the streak reagent²¹ and showed three zones in addition to the strongly adsorbed material at the top of the column (Fig. 1). The zones were separated, eluted with acetone and the eluates evaporated to dryness. The effluent from the chromatogram was also evaporated to dryness; the yields obtained are shown in Table II.

Chromatographic Resolution of the Effluent Fraction on "Magnesol."—Following the general procedure of McNeely, Binkley and Wolfrom,⁴ the effluent fraction of solids was chromatographed on "Magnesol"²² as shown in Fig. 2 and Table II. The column was extruded and brushed with the streak reagent. The α -D-glucopyranose pentaacetate was washed from the column and was recovered from the effluent by evaporating the solvent. α -Cellobiose octaacetate and α -celotriose hendecaacetate along with the two unidentified substances were obtained by sectioning the column and eluting with acetone (Fig. 2 and Table II).

Final Purification of Fractions.—The α -D-glucopyranose pentaacetate and α -cellobiose octaacetate were not rechromatographed but were crystallized twice as shown in Table II. α -Celotriose hendecaacetate was rechromatographed twice in the above-described manner on "Magnesol" and was then chromatographically pure. The product was finally crystallized twice, α -Celloetraose tetradecaacetate was rechromatographed twice in the above-described manner on "Silene EF" and was finally crystallized as shown. α -Cellopentaose heptadecaacetate and α -cellohexaose eicosacetate were each rechromatographed once on "Silene EF" and were crystallized as shown (Table II). The constants and elementary analyses obtained on these finally purified fractions are shown in Table I and are plotted in Fig. 3.

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Summary

1. A product obtained by the acetolysis of cellulose has been resolved by a chromatographic technique into a polymer-homologous series of crystalline α -D acetates ranging in D. P. (degree of polymerization) from 1 to 6, inclusive.

2. A correlation of melting points and specific rotations with degrees of polymerization has been made.

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(19) A synthetic calcium acid silicate manufactured by the Pittsburgh Plate Glass Co., Columbia Chemical Division, Barberton, Ohio.

(20) No. 535, a siliceous filter-aid manufactured by Johns-Manville Co., New York, N. Y.

(21) 100 mg. of potassium permanganate dissolved in 10 ml. of 2.5 N sodium hydroxide.

(22) A synthetic, hydrated magnesium acid silicate manufactured by the Westvaco Chlorine Products Co., South Charleston, West Virginia.