change of rotation in a polariscope. It was found that the lactone was almost completely hydrolyzed to the acid within four hours. A change from the initial rotation of $[\alpha]_D$ +60° to +24° occurred within that time. After twenty-four hours the rotation had reached $[\alpha]_D$ +17°, which remained constant thereafter (Fig. 1). Since the rate of change in the rotation of this lactone due to hydrolysis is high, it is concluded that this methylated lactone, and therefore also the original pentose unit, possesses the pyranose configuration.

Oxidation of the Dimethyl-D-arabonic Acid.—A 0.017-g. sample of the lactone was oxidized by allowing it to remain at room temperature with 0.5 *M* sodium periodate[11] for thirty hours. In aqueous solution the lactone is converted to the straight chain acid in a few hours. Analysis of the solution showed that no periodate was used up, indicating that the substance was not oxidized, apparently, due to the fact that it did not contain any adjacent free hydroxyl groups. When a similar sample of 2,3,6-trimethylgluconic acid was oxidized with periodate under the same conditions, one mole of periodate was consumed in the reaction.

Acknowledgment.—The work reported in this paper was supported in part by a grant from the Corn Industries Research Foundation.

Summary

A reducing crystalline disaccharide consisting of D-glucose and L-arabinose has been synthesized from glucose-1-phosphate and L-arabinose by the agency of a phosphorylase from the organism *Pseudomonas saccharophila*.

On oxidation of the phenylosotriazole derivative of this disaccharide with sodium periodate, three moles of periodate are consumed with the formation of one mole each of formic acid and formaldehyde per mole of phenylosotriazole derivative. These data indicate that in the disaccharide D-glucose is linked through carbon atom 1 to carbon atom 3 of L-arabinose.

Methylation of the disaccharide produced a hexamethylmethyl derivative, which on hydrolysis with acid gave rise to 2,3,4,6-tetramethyl-D-glucose and 2,4-dimethyl-L-arabinose.

Evidence that the dimethyl-L-arabinose possesses the pyranose configuration was obtained from the rate of hydrolysis of the dimethyl-L-arabonolactone derivative to its acid and also from periodate oxidation of this lactone.

On the basis of these data, the new reducing disaccharide may be designated as 3-[α-D-glucopyranosido]-L-arabopyranose.

BERKELEY, CALIFORNIA RECEIVED AUGUST 25, 1947

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol,[1] 1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol and 1,5-Anhydro-D-galactitol[2]

BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

The palladium-catalyzed addition of hydrogen to the double bond of an acetylated 2-hydroxyglycal may, because of the new asymmetry introduced at carbon two, give rise to either or both of the predicted diastereomeric sugar alcohol anhydrides. Thus Zervas[3] reduced 2,3,4,6-tetraacetyl-2-hydroxy-D-glucal in a 61% yield to an anhydrohexitol which later was demonstrated[4] to be 1,5-anhydro-D-mannitol (styracitol), while Richtmyer, Carr and Hudson[4c] have more recently succeeded in obtaining a 4% yield of 1,5-anhydro-D-glucitol (polygalitol) by the same process.

The catalytic reduction of 2,3,4-triacetyl-2-hydroxy-D-xylal, which might lead to either 1,5-anhydro-xylitol or 1,5-anhydro-D-arabitol or to both, has recently been investigated[5]; only 1,5-anhydro-xylitol, isolated as its triacetate in a yield of 83%, was obtained.

In addition to the two cases above, the reduction of three other acetylated 2-hydroxy-glycals has been reported in the literature. Maurer and Plötner[6] reduced both heptaacetyl-2-hydroxy-cellobial (I) and heptaacetyl-2-hydroxy-gentiobial (V) in the presence of palladium to corresponding heptaacetyl-1,5-anhydro-(β-D-glucopyranosyl)-hexitols in yields, respectively, of 62 and 53%. The free anhydrides were termed "1.4-glucosido-styracitol" and "1.6-glucosido-styracitol," that is, as derivatives of an anhydride (styracitol) which is now known to have the mannitol configuration. Apparently these names were chosen solely on the assumption that the course of the reduction of the acetates of the two substituted 2-hydroxy-glycals had been similar to that of 2,3,4,6-tetraacetyl-2-hydroxy-D-glucal, which, as mentioned above, appears to give predominantly 1,5-anhydro-D-mannitol. Definitive proof, such as might have been obtained by the hydrolysis of the 1,5-anhydro-(β-D-glucopyranosyl)-hexitols, was apparently not adduced.

A third acetylated 2-hydroxy-glycal, 2,3,4,6-tetraacetyl-2-hydroxy-D-galactal (IX), was reduced in the presence of palladium by Freuden-

(1) By D-glucitol we denote the hexitol corresponding in configuration to D-glucose and commonly termed sorbitol.

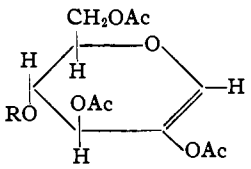
(2) This communication represents a portion of a paper presented before the Division of Sugar Chemistry and Technology at the Atlantic City meeting of the American Chemical Society, April 15, 1947.

(3) L. Zervas, *Ber.*, **63**, 1689 (1930).

(4) (a) L. Zervas and I. Papadimitriou, *Ber.*, **73**, 174 (1940); (b) N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **65**, 64 (1943); (c) N. K. Richtmyer, C. J. Carr and C. S. Hudson, *ibid.*, **65**, 1477 (1943); (d) R. C. Hockett and Maryalice Conley, *ibid.*, **66**, 464 (1944).

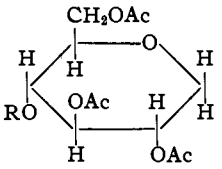
(5) H. G. Fletcher and C. S. Hudson, *ibid.*, **69**, 921 (1947).

(6) K. Maurer and K. Plötner, *Ber.*, **64**, 281 (1931).



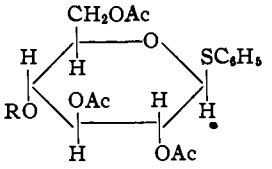
I

Heptaacetyl-2-hydroxy-cellobial
R = tetraacetyl-β-D-glucopyranosyl



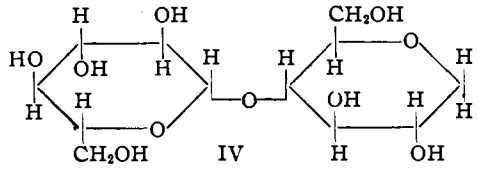
II

Heptaacetyl-1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol



III

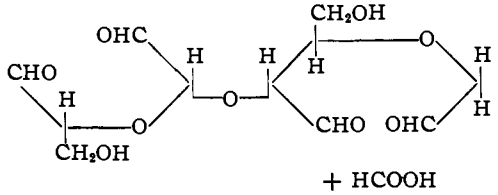
Phenyl 1-thio-β-cellobioside heptaacetate



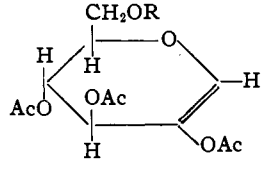
IV

1,5-Anhydro-4-(β-D-glycopyranosyl)-D-glucitol

$3NaIO_4$

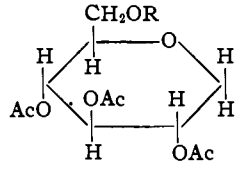


+ HCOOH



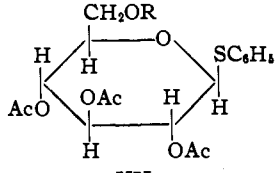
V

Heptaacetyl-2-hydroxy-gentiobial



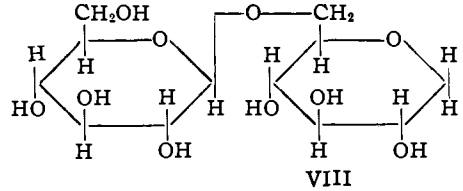
VI

Heptaacetyl-1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol



VII

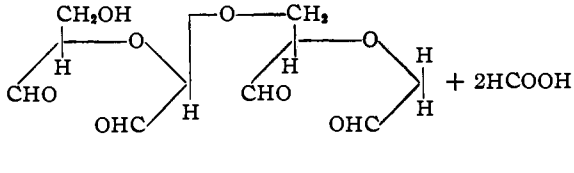
Phenyl 1-thio-β-gentiobioside heptaacetate



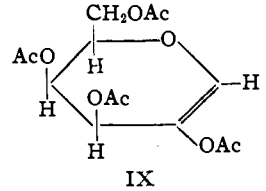
VIII

1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol

$4NaIO_4$

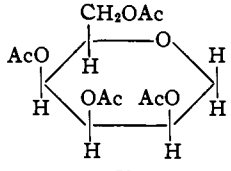


+ 2HCOOH



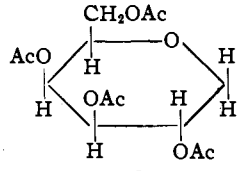
IX

2,3,4,6-Tetraacetyl-2-hydroxy-D-galactal



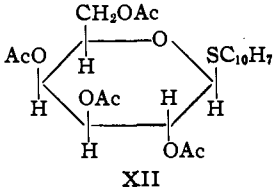
X

Tetraacetyl-1,5-anhydro-D-talitol



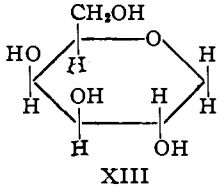
XI

Tetraacetyl-1,5-anhydro-D-galactitol



XII

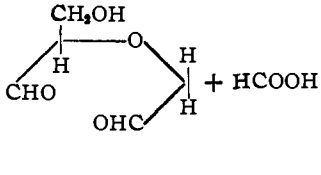
2'-Naphthyl 1-thio-β-D-galactopyranoside tetraacetate



XIII

1,5-Anhydro-D-galactitol

$2NaIO_4$



+ HCOOH

berg and Rogers[7] to give, in 70% yield, the tetraacetate of an anhydro-hexitol whose structure as either 1,5-anhydro-D-galactitol (XI) or 1,5-anhydro-D-talitol (X) remained uncertain.

The reductive desulfurization of acetylated 1-thio-aldose derivatives with Raney nickel which has recently been applied to the synthesis of 1,5-anhydro-D-glucitol,[4c,8a] 1,5-anhydro-xylitol[5] and 1,5-anhydro-D-arabitol,[8b] furnishes an easy method for preparing sugar-alcohol 1,5-anhydrides of unequivocal configuration. The present research was designed to afford such authentic anhydrides for comparison with the three reduction products of uncertain configuration mentioned above.

Phenyl 1-thio-β-cellobioside heptaacetate (III), prepared originally by Purves[9] through the condensation of heptaacetyl-α-cellobiosyl bromide with potassium thiophenolate, was subjected in warm ethanolic solution to the action of freshly prepared Raney nickel. The resulting crystalline heptaacetyl-1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol (II), as well as its parent polyalcohol (IV), obtained by catalytic deacetylation, was produced in satisfactory yield and they possessed melting points and rotations (Table I) which were at little variance from the corresponding values reported by Maurer and Plötner for the reduction product of heptaacetyl-2-hydroxy-cellobial. It appears, therefore, that the "1,4-glucosido-styracitol" of these authors is not a mannitol derivative as this name now implies but is 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol, a substituted polygalitol (4-(β-D-glucopyranosyl)-polygalitol).

TABLE I

HEXITOL 1,5-ANHYDRIDES AND DERIVATIVES

	Fletcher and Hudson		Maurer and Plötner[6]	
	M. p., °C.	$[\alpha]_D$	M. p., °C.	$[\alpha]_D$
1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol heptaacetate	194–195	+ 4.0°[a]	187	+ 7.0°[a]
1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol	172	+29.3°[b]	173	+29.01°[b]
1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol heptaacetate	153	+13.0°[a]	152	+17.2°[a]
1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol	239–240	+ 3.6°[b]	223	+ 2.44°[b]
			Freudenberg and Rogers[7]	
1,5-Anhydro-D-galactitol tetraacetate	75–76	+49.1°[a]	108	−15.31°[a]
1,5-Anhydro-D-galactitol	114–115	+76.6°[b]	(sirup)	− 7.34°[b]

[a] In chloroform solution. [b] In aqueous solution.

In accord with its structure, 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol (IV) was found on a molar basis to consume three moles of periodate with the simultaneous formation of one mole of formic acid.

Phenyl 1-thio-β-gentiobioside heptaacetate was obtained from β-gentiobiose octaacetate in a manner similar to its cellobiose analog; the substance is classed as a β-pyranose derivative by comparison of its rotation with that of methyl β-gentiobioside heptaacetate and on the strength of the analogy with the similar pair of substances in the cellobiose series (Table II).

TABLE II

COMPARISON OF SOME MOLECULAR ROTATIONS IN THE CELLOBIOSE AND GENTIOBIOSE SERIES

	Mol. wt.	$[\alpha]_D$ ($CHCl_3$)	$[M]_D$	Difference
Methyl β-cellobioside heptaacetate	651	−25.1°	−16300	4600
Phenyl 1-thio-β-cellobioside tetraacetate	729	−28.7°	−20900	
Methyl β-gentiobioside heptaacetate	651	−18.9°	−12300	4200
Phenyl 1-thio-β-gentiobioside heptaacetate	729	−22.7°	−16500	

Phenyl 1-thio-β-gentiobioside heptaacetate was also treated with Raney nickel to yield heptaacetyl-1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol (VI). The physical constants of this crystalline compound, together with those of its unacetylated parent (Table I), approached quite closely the constants for the corresponding compounds which Maurer and Plötner obtained through the reduction of heptaacetyl-2-hydroxy-gentiobial (V). It therefore appears that the "1,6-glucosido-styracitol" which these authors recorded is actually 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol, a substituted polygalitol (6-(β-D-glucopyranosyl)-polygalitol).

In conformity with its structure, 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol (VIII) reduces on a molar basis four moles of periodate with the simultaneous liberation of two moles of formic acid.

Reductive desulfurization with Raney nickel of 2′-naphthyl 1-thio-β-D-galactopyranoside tetraacetate (XII), prepared as recently reported by Haskins and Hudson,[10] gave tetraacetyl-1,5-anhydro-D-galactitol (XI). The physical constants of this latter compound as well as of the free crystalline 1,5-anhydro-D-galactitol (Table I) were found to differ markedly from those reported by Freudenberg and Rogers[7] for the comparable substances which they obtained by the reduction of 2,3,4,6-tetraacetyl-2-hydroxy-D-galactal (IX). The optical rotations of the two substances, for instance, were opposite in sign as well as numerically different from those reported by Freudenberg and Rogers. It would therefore appear that the anhydride of these authors is probably 1,5-anhydro-D-talitol (corresponding to X). A study directed to the synthesis of authentic 1,5-anhydro-D-talitol is at present being pursued in this Laboratory.

One of us (H. G. F.) held the Chemical Foundation Research Associateship while carrying out this research. We are indebted to Mr. Charles A.

(7) W. Freudenberg and E. F. Rogers, THIS JOURNAL, 59, 1602 (1937).

(8) (a) H. G. Fletcher, *ibid.*, 69, 706 (1947); (b) H. G. Fletcher and C. S. Hudson, *ibid.*, 69, 1672 (1947).

(9) C. B. Purves, *ibid.*, 51, 3619 (1929).

(10) W. T. Haskins and C. S. Hudson, *ibid.*, 69, 1668 (1947).

Kinser and Mrs. Betty Mount for combustion analyses.

Experimental[11]

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol Heptaacetate (II).—Ten grams of phenyl 1-thio-β-cellobioside heptaacetate prepared according to the method of Purves,[9] melting at 225–226°[12] and rotating −28.7° in chloroform (*c*, 1.36), was suspended in 100 ml. of absolute alcohol, treated with approximately 100 g. of freshly prepared Raney nickel in absolute alcohol and then boiled gently for one hour. After cooling, the supernatant solution was decanted and the nickel washed by decantation with three successive 100-ml. portions of boiling absolute alcohol. The combined decantates, after filtration through a fine sintered glass plate, were concentrated at 80° (bath) under a slight vacuum to a volume of 125 ml.; crystallization of the product as a mass of very fine needles was spontaneous. Concentration of the mother liquor afforded a very small quantity of additional material: yield 5.9 g. or 69%. Two recrystallizations from warm 95% ethanol furnished with little loss material melting at 194–195° and rotating +4.0° in chloroform (*c*, 1.39).

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol heptaacetate is readily soluble in acetone, chloroform and hot alcohol, and relatively insoluble in cold alcohol, water and pentane.

Anal. Calcd. for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.85. Found: C, 50.51; H, 5.73.

1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol (IV).—Three grams of 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol heptaacetate was deacetylated catalytically with barium methylate to give 1.4 g. (89%) of 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol as minute prismatic needles. Recrystallized from aqueous alcohol, the pure substance melted at 172° and appeared to decompose very slowly at this temperature. In water the compound showed a rotation of +29.3° (*c*, 4.64). It is readily soluble in water, somewhat soluble in alcohol and insoluble in ethyl acetate and pentane.

Anal. Calcd. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.79. Found: C, 44.44; H, 6.72.

Sodium Metaperiodate Oxidation of 1,5-Anhydro-4-(β-D-glucopyranosyl)-D-glucitol.—The technique of Jackson and Hudson[13] was employed. The 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol (0.1013 g.) was dissolved in a little water, treated with 5.0 ml. of 0.480 *M* sodium metaperiodate solution and the solution diluted to 25.0 ml. with water. After twenty-four hours at room temperature a 5.0-ml. sample was titrated for formic acid and residual oxidant. On a molar basis the compound consumed 2.99 moles of oxidant while 1.22 moles of formic acid was liberated.

Phenyl 1-Thio-β-gentiobioside Heptaacetate (VII).—The procedure which Purves[9] devised for the preparation of phenyl 1-thio-β-cellobioside heptaacetate gave phenyl 1-thio-β-gentiobioside heptaacetate in a yield of 33% from β-gentiobiose octaacetate. The very fine needle-like crystals obtained by repeated recrystallization from 8 parts of alcohol melted at 172° and rotated in chloroform −22.7° (*c*, 1.64). Comparison of this rotation with that of methyl β-gentiobioside heptaacetate (Table II) indicates that the glycoside is of the β-configuration.

Phenyl 1-thio-β-gentiobioside heptaacetate is readily soluble in acetone, chloroform and boiling alcohol, very sparingly soluble in cold alcohol, and relatively insoluble in water and pentane.

Anal. Calcd. for $C_{32}H_{40}O_{17}S$: C, 52.74; H, 5.53; S, 4.40. Found: C, 52.54; H, 5.35; S, 4.15.

1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol Heptaacetate (VI).—Six grams of phenyl 1-thio-β-gentiobioside heptaacetate was desulfurized with Raney nickel in a manner similar to that described above for its cellobiose analog. Three recrystallizations of the crude product (3.7 g.; 72%), first from 7 parts of warm alcohol, then from a mixture of 1 part acetone and 3 parts of ether, and finally from seven parts of warm alcohol, gave with little loss pure 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol heptaacetate melting at 153° and rotating in chloroform +13.0° (*c*, 1.27).

The compound is soluble in methyl cellosolve, dioxane and ethyl acetate. At elevated temperature it dissolves in *n*-butanol, benzene and alcohol.

Anal. Calcd. for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.85. Found: C, 50.49; H, 5.80.

1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol (VIII).—Two grams of 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol heptaacetate was deacetylated in the customary manner with sodium methylate to give 0.6 g. (57%) of material as minute clusters of thin prisms. Recrystallized from a mixture of 1.7 parts of water and 2.5 parts of alcohol the 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol melted at 239–240° and rotated in water +3.6° (*c*, 4.43).

The compound is insoluble in benzene, acetone, ethyl acetate and alcohol. It may be recrystallized by solution in a limited quantity of warm water.

Anal. Calcd. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.79. Found: C, 43.86; H, 6.93.

Sodium Metaperiodate Oxidation of 1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol.—The oxidation was carried out in the same manner as that of its isomer described above. On a molar basis 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol was found to consume 4.04 moles of oxidant with the concomitant liberation of 1.96 moles of formic acid.

1,5-Anhydro-D-galactitol Tetraacetate (XI).—Ten grams of 2′-naphthyl 1-thio-β-D-galactopyranoside tetraacetate (m. p. 113–114°; $[\alpha]^{20}D$ +6.55° ($CHCl_3$, *c*, 1.37)), prepared as recently reported by Haskins and Hudson,[10] was desulfurized with Raney nickel in absolute alcoholic solution and yielded 4.91 g. (73%) of nearly pure product. Recrystallized first from a mixture of 1.2 parts of ether and 0.6 parts of pentane and then from a mixture of 1.3 parts of absolute alcohol and 0.94 parts of pentane, the material melted at 75–76° and rotated in chloroform +49.1° (*c*, 0.82). 1,5-Anhydro-D-galactitol tetraacetate is soluble in acetone, ether and hot alcohol, and relatively insoluble in cold alcohol, pentane and water.

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.67; H, 6.17.

1,5-Anhydro-D-galactitol (XIII).—Five grams of 1,5-anhydro-D-galactitol tetraacetate was deacetylated catalytically with barium methylate, the product (2.37 g., 96%) being precipitated from its concentrated solution in methanol by the addition of ethyl acetate. Recrystallized once from 7 parts of boiling absolute alcohol and once from aqueous alcohol, the small, clear prisms melted at 114–115° and rotated in water +76.6° (*c*, 1.08).

1,5-Anhydro-D-galactitol is readily soluble in water, sparingly soluble in alcohol, and relatively insoluble in ethyl acetate, benzene and pentane.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.18; H, 7.38.

Sodium Metaperiodate Oxidation of 1,5-Anhydro-D-galactitol.—The quantitative oxidation of 1,5-anhydro-D-galactitol with sodium metaperiodate was carried out in the same manner as described for the two anhydrides above. On a molar basis the substance consumed 2.00 moles of oxidant while 0.97 mole of formic acid was liberated.

(11) Melting points below 200° were taken with a calibrated Anschütz-type thermometer completely immersed in the bath liquid; those above 200° were measured in a Berl and Kullmann copper block, the thermometer readings being corrected for stem exposure. Rotations are specific rotations for sodium light at 20°; concentration is expressed in g. of substance per 100 ml. of solution.

(12) Purves (ref. 9) reported that this compound "decomposed in the neighborhood of 295°." A sample of his material was found to melt at 225–226° either alone or in admixture with that prepared in the course of the present research.

(13) E. L. Jackson and C. S. Hudson, THIS JOURNAL, **59**, 994 (1937).

Summary

Reductive desulfurization of phenyl 1-thio-β-cellobioside heptaacetate with Raney nickel has furnished 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol heptaacetate. The physical constants of this substance, as well as of the 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol obtained from it by deacetylation, conform quite closely with the constants which are recorded in the literature for the corresponding products obtained through the palladium catalyzed reduction of heptaacetyl-2-hydroxy-cellobial.

1,5-Anhydro-6-(β-D-glucopyranosyl)-D-glucitol and its heptaacetate have similarly been obtained through the reductive desulfurization of phenyl 1-thio-β-gentiobioside heptaacetate and found to possess physical constants in substantial agreement with those reported in the literature for the comparable substances arising through the palladium-catalyzed reduction of heptaacetyl-2-hydroxy-gentiobial.

1,5-Anhydro-D-galactitol and its tetraacetate have been prepared through the reductive desulfurization of 2′-naphthyl 1-thio-β-D-galactopyranoside tetraacetate. The physical constants of these two compounds depart markedly from those reported for the corresponding substances, derived through the palladium-catalyzed reduction of 2,3,4,6-tetraacetyl-2-hydroxy-D-galactal.

The behavior of 1,5-anhydro-4-(β-D-glucopyranosyl)-D-glucitol, 1,5-anhydro-6-(β-D-glucopyranosyl)-D-glucitol and 1,5-anhydro-D-galactitol toward sodium metaperiodate has been examined and found in each case to conform to the assigned structure.

BETHESDA, MARYLAND RECEIVED JUNE 14, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Deacetylation of Acetylated Carbohydrate Derivatives with Potassium Alkoxides

BY WILLIAM A. BONNER AND WAYNE L. KOEHLER

Fischer and Bergmann[1] were apparently the first to extend the catalytic deacylation of esters with sodium ethylate to the sugar acetates. In succeeding years Zemplén and his co-workers[2] gave a mechanistic interpretation to this reaction and extended it widely in the field of carbohydrates. Today the Zemplén–Pacsu deacylation, using a catalytic amount of sodium in methanol, is one of the standard tools employed by workers in this field.

One disadvantage inherent in deacylations with sodium methylate is the retention in solution of sodium ions. This is not serious where the deacylated product crystallizes directly from the methanol solvent and the sodium ion remains in the mother liquor. However it constitutes a source of non-removable impurity in cases where the deacylated product does not crystallize and must be isolated by distillation of the solvent and volatile constituents of the reaction mixture.

A procedure capable of obviating this difficulty is found in the use of barium methylate, a modification introduced by Weltzien and Singer[3] and subsequently extended by others.[4] In this technique the barium ion is quantitatively precipitated by addition of an equivalent amount of sulfuric acid. While excellent in principle, this method suffers from the colloidal nature of the precipitated barium sulfate and consequent added difficulties in its removal, as well as from the extra trouble involved in the preparation and standardizations of the solutions employed.

It became desirable to develop a simple and rapid procedure which would permit the isolation of sirupy deacetylation products in a substantially ash-free state. The procedure developed employs a potassium methylate or ethylate in place of the sodium or barium methylates used previously, followed by a quantitative precipitation of potassium ion as perchlorate on potentiometric titration with concentrated perchloric acid.

This procedure was tested by application to several known acetylated sugar derivatives. After deacetylation was complete and potassium was removed as perchlorate, the free sugar derivative was isolated from the filtrate by evaporation *in vacuo* of the volatile constituents. Physical constants and ash analyses were determined on the crude residues to determine their purity. The data obtained, tabulated in the Experimental Part, indicate that the method can be applied to instances where sirupy deacetylation products result with assurance that reasonably pure sirups will be obtained in substantially quantitative yield.

Although methanol has been the solvent commonly employed by previous workers, we have studied the efficacy of higher alcohols as solvents in deacetylations employing both sodium and potassium alkoxides as catalysts. Primary alcohols, whether straight-chained or branched, gave yields of deacetylated products very close to theoretical, but secondary and tertiary alcohols gave yields up to 55% high. This is apparently due to a decrease in the rate of deacetylation in these cases and, on grounds of steric hindrance, is in

(1) Fischer and Bergmann, *Ber.*, **52**, 852 (1919).

(2) Zemplén and Kunz, *ibid.*, **56**, 1705 (1923); Zemplén, *ibid.*, **59**, 1258 (1926); **60**, 1555 (1927); Zemplén and Pacsu, *ibid.*, **62**, 1613 (1929).

(3) Weltzien and Singer, *Ann.*, **443**, 104 (1925).

(4) Brauns, THIS JOURNAL, **48**, 2784 (1926); Mitchell, *ibid.*, **63**, 3534 (1941); Isbell, *Natl. Bur. Standards J. Res.*, **5**, 1185 (1930).