The above crystalline material was dissolved in 300 ml. of chloroform, 1300 ml. of 95% ethanol added, the solution cooled to the temperature of a solid carbon dioxide–acetone-bath and then warmed slowly to room temperature by placing it in an ice-bath and allowing this to melt at room temperature. This procedure induced crystallization; yield 11.2 g. The crystalline material was fractionally crystallized from chloroform–ethanol (95%) (1:3 by volume) into two compounds (A and B) whose constants remained unchanged on further crystallizations from the same solvent or from pyridine–ethanol; yield, 1.1 g. of compound A crystallizing in long, silky, white needles of m. p. 187–187.5° and $[\alpha]^{20}D$ −34° (*c* 1.2, pyridine); 0.9 g. of compound B of m. p. 154–156° and $[\alpha]^{20}D$ −10° (*c* 2.6, pyridine).

Anal. Calcd. for $C_{33}H_{38}O_{14}$: C, 60.17; H, 5.82. Found for compound A: C, 60.16; H, 5.87. Found for compound B: C, 60.14; H, 6.01.

Both of the above substances were non-reducing toward Fehling solution and liberated benzaldehyde (detected by odor) on heating with acids. Attempts to remove the substituent benzylidene or acetate groups resulted only in sirupy products.

Acknowledgment.—Preliminary experiments in this work were carried out by Messrs. S. W. Waisbrot, T. S. Gardner and R. L. Brown.

Summary

1. Dibenzylidene-L-fucitol is described.

2. The *p*-toluenesulfonate and triphenylmethyl ether of dibenzylidene-xylitol are reported. The former substance reacts with sodium iodide.

3. Two diastereoisomeric forms of tetraacetyl-D-glucopyranosido-dibenzylidene-xylitol are described.

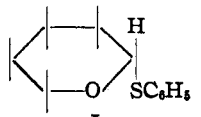
COLUMBUS, OHIO RECEIVED MARCH 17, 1947

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

Relations between Rotatory Power and Structure in the Sugar Group. XXXV.[1] Some 2′-Naphthyl 1-Thioglycopyranosides and their Acetates

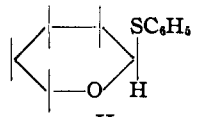
BY W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

Purves'[2] application of isorotation calculations to the rotations of the phenyl 1-thioglycopyranoside[3] acetates of various aldoses showed that the value of A_{SPh}, the portion of the molecular rotation in chloroform that is related to the presence of the phenylthio group on carbon atom 1, is nearly constant in the series and is thus approximately independent of the other portion B_x, the values of which are characteristic of the various sugars and are obtainable from the rotations of the α- and β-anomers of the fully acetylated sugars themselves. Purves' conclusions are illustrated by the values of B_x and A_{SPh} that are shown in columns six, eight and nine of Table I; A_{SPh} is approximately constant and thus independent of the corresponding B_x. His conclusions have led to the classification of these five phenyl 1-thioglycopyranoside acetates and the phenyl 1-thioglycopyranosides that result from their deacetylation, as β-D-anomers having in common the configurational element I.[4] It is to be noted for reference later that no arabinoside occurs in the list of Purves' derivatives. The corresponding α-D-anomers are not known but it is reasonable to assume that their molecular rotations will be found to approximate the values $B_x + A_{SPh}$ that can be calculated from the data of Table I. Consider an example from the D-glucose series. The



I

β-D-Anomers



II

α-D-Anomers

molecular rotation of the known phenyl 1-thio-β-D-glucopyranoside tetraacetate ($[\alpha]_D$ −18°, mol. wt. 428) is formulated as $B_{gl} - A_{SPh} = (-18)(428) = -7{,}700$. The value of B_{gl} is obtained as half the sum of the molecular rotations of the α- and β-D-glucopyranose pentaacetates (mol. wt. 390), which is $[(B_{gl} + A_{ac}) + (B_{gl} - A_{ac})] \div 2 = B_x = [(101.6 + 3.8)(390)] \div 2 = +20{,}600$[5]; the value of A_{SPh} from the D-glucose series thus becomes $(7{,}700 + 20{,}600) = +28{,}300$. The molecular rotation of the unknown phenyl 1-thio-α-D-glucopyranoside tetraacetate is assumed therefore to be approximately $B_{gl} + A_{SPh} = 20{,}600 + 28{,}300 = +48{,}900$, which corresponds to an $[\alpha]_D$ value of +114°. The difference that is to be expected between the values for the α- and β-anomers, which is 114 + 18 = 132°, is so large in comparison with reasonable limits of approximation in the isorotation calculations that it becomes possible to classify the anomers confidently.

The present research extends the scope of these correlations to seven members of a related series of aromatic 1-thioglycopyranoside acetates which carry the 2-thionaphthyl ("β-thionaphthyl") radical in their aglycon. These substances, which in general crystallize very satisfactorily, were prepared according to Purves' directions, with the substitution of 2-thionaphthol for thiophenol. When a chloroform solution of the appropriate

(1) Number XXXIV was published in THIS JOURNAL, **61**, 2972 (1939).

(2) Purves, *ibid.*, **51**, 3619, 3627, 3631 (1929). Through a typographical error the negative sign was given to the rotation of 49.0° on p. 3632; the substance is dextrorotatory, as was stated later in that article.

(3) In naming such thio-carbohydrate derivatives we follow the suggestions of A. L. Raymond in "Advances in Carbohydrate Chemistry," Vol. 1, Academic Press, New York, N. Y., 1945, p. 135.

(4) Hudson, THIS JOURNAL, **60**, 1537 (1938).

(5) Hudson and Dale, *ibid.*, **37**, 1264 (1915).

TABLE I

ANOMERIC CLASSIFICATION OF 2′-NAPHTHYL 1-THIOGLYCOPYRANOSIDE ACETATES THROUGH ISOROTATION RELATIONS

No. from Table II	Acetate of 2′-naphthyl 1-thioglycopyranoside from	Mol. wt.	$[\alpha]^{20}D$ (Chloroform)	$[M]^{20}D$ $B_x \pm A_{S2\text{-}Naph}$	$[M]^{20}D$ B_x	$[M]^{20}D$ $A_{S2\text{-}Naph}$	$[M]^{20}D$ (Purves' data) $B_x - A_{SPh}$[c]	$[M]^{20}D$ (Purves' data) A_{SPh}
2	D-Xylose	418	−40.8°	−17,000[a]	+10,200	+27,200	−21,700	+31,900
4	D-Arabinose	418	− 8.2°	− 3,400[b]	−30,200	+26,800	.....	.....
6	D-Glucose	490	−17.1°	− 8,400[a]	+20,600	+29,000	− 7,700	+28,300
8	D-Galactose	490	+ 6.4°	+ 3,100[a]	+25,300	+22,200	.....	.....
10	Lactose	778	−16.0°	−12,400[a]	+16,800	+29,200	−14,300	+31,100
12	Cellobiose	778	−25.7°	−20,000[a]	+ 9,000	+29,000	−20,700	+29,700
13	Maltose	778	+46.1°	+35,900[a]	+62,800	+26,900	+35,700	+27,100

[a] Since this molecular rotation of a member of the D-series is toward the *negative direction* from the corresponding B_x, it is to be formulated as $B_x - A_{S2\text{-}Naph}$. [b] Since this molecular rotation of a member of the D-series is toward the *positive direction* from the corresponding B_x, it is to be formulated as $B_x + A_{S2\text{-}Naph}$, as explained in the text. [c] All the molecular rotations in this column are to be formulated as $B_x - A_{SPh}$, as shown by Purves, because the rotations of these substances of the D-series are toward the *negative direction* from the corresponding B_x.

TABLE II

PROPERTIES OF SOME 2′-NAPHTHYL 1-THIOGLYCOPYRANOSIDES AND THEIR ACETATES

No.	Substance	M. p., °C.	Specific rotation $[\alpha]^{20}D$	Formula	Analyses, % Carbon	Hydrogen
1	2′-Naphthyl 1-thio-β-D-xylopyranoside	193	−52.4° (*c*, 0.4) (95% alcohol)	$C_{15}H_{16}O_4S$	Calcd. 61.60 Obs. 61.77	5.52 5.40
2	Triacetate of 1	141	−40.8° (*c*, 0.9) (chloroform)	$C_{21}H_{22}O_7S$	Calcd. 60.25 Obs. 60.17	5.30 5.14
3	2′-Naphthyl 1-thio-α-D-arabinopyranoside	141	+86.9° (*c*, 0.9) (95% alcohol)	$C_{15}H_{16}O_4S$	Calcd. 61.60 Obs. 61.69	5.52 5.49
4	Triacetate of 3	110	− 8.2° (*c*, 2.1) (chloroform)	$C_{21}H_{22}O_7S$	Calcd. 60.25 Obs. 60.42	5.30 5.32
5	2′-Naphthyl 1-thio-β-D-glucopyranoside[a]	147	−44.2° (*c*, 0.8) (95% alcohol)	$C_{16}H_{18}O_5S$	Calcd. 59.59 Obs. 59.65	5.63 5.62
6	Tetraacetate of 5	111	−17.1° (*c*, 0.9) (chloroform)	$C_{24}H_{26}O_9S$	Calcd. 58.74 Obs. 58.90	5.34 5.35
7	2′-Naphthyl 1-thio-β-D-galactopyranoside	145	−50.2° (*c*, 0.9) (95% alcohol)	$C_{16}H_{18}O_5S$	Calcd. 59.59 Obs. 59.44	5.63 5.55
8	Tetraacetate of 7	113	+ 6.4° (*c*, 1.0) (chloroform)	$C_{24}H_{26}O_9S$	Calcd. 58.74 Obs. 58.89	5.34 5.37
9	2′-Naphthyl 1-thio-β-D-lactopyranoside	217	−38.2° (*c*, 0.9) (pyridine)[b]	$C_{22}H_{28}O_{10}S$	Calcd. 54.51 Obs. 54.38	5.83 5.89
10	Heptaacetate of 9	142	−16.0° (*c*, 1.0) (chloroform)	$C_{36}H_{42}O_{17}S$	Calcd. 55.50 Obs. 55.35	5.44 5.40
11	2′-Naphthyl 1-thio-β-D-cellobiopyranoside	185	−58.3° (*c*, 0.8) (95% alcohol)	$C_{22}H_{28}O_{10}S$	Calcd. 54.51 Obs. 54.43	5.83 5.73
12	Heptaacetate of 11	203	−25.7° (*c*, 0.8) (chloroform)	$C_{36}H_{42}O_{17}S$	Calcd. 55.50 Obs. 55.45	5.44 5.31
13	Heptaacetate of 2′-naphthyl 1-thio-β-D-maltopyranoside	136	+46.1° (*c*, 0.8) (chloroform)	$C_{36}H_{42}O_{17}S$	Calcd. 55.50 Obs. 55.43	5.44 5.58

[a] The glycoside crystallizes as a hemihydrate; the data were obtained from an anhydrous sample which had been dried at 138°. [b] Measured in pyridine because of low solubility in alcohol.

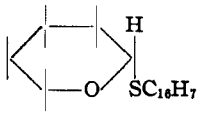
acetylated glycopyranosyl bromide reacts with an alcohol solution of the potassium salt of 2-thionaphthol, potassium bromide separates and the resulting 2′-naphthyl 1-thioglycopyranoside acetate may be isolated from the washed chloroform solution. The pyranose ring is assigned to these derivatives, as was the case with the phenyl 1-thioglycosides, because of their origin from the normal acetylated glycopyranosyl bromides. This ring structure has been confirmed for several of them. Thus, the action of strong alkali on phenyl 1-thio-β-D-glucopyranoside converts it to levoglucosan[6] (D-glucosan <1,5> β <1,6>), the reductive desulfurization of phenyl 1-thio-β-D-xylopyranoside triacetate by Raney nickel yields 1,5-anhydroxylitol triacetate[7] and the same reductive reaction produces 1,5-anhydro-D-arabitol triacetate from

(6) Montgomery, Richtmyer and Hudson, *J. Org. Chem.*, **10**, 196 (1945).

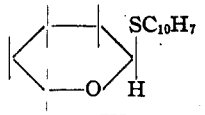
(7) Fletcher and Hudson, THIS JOURNAL, **69**, 922 (1947).

2′-naphthyl 1-thio-α-D-arabinopyranoside triacetate.[8]

Various properties of the acetates of the new 2′-naphthyl 1-thioglycopyranosides are recorded in Table II and the anomeric classification of them that results from the consideration of rotatory relations is shown in Table I. Inspection of columns seven and nine of Table I shows that the value of $A_{S2\text{-}Naph}$, which is formulated as the contribution that carbon atom one makes in the total molecular rotation, is approximately constant in the series and is nearly the same in magnitude as the contribution A_{SPh} which Purves found in the series of phenyl 1-thioglycopyranoside acetates. However, in selecting the signs of these $A_{S2\text{-}Naph}$ values, a notable anomaly in the case of the arabinose derivative is apparent; if this derivative is formulated $B_x - A_{S2\text{-}Naph}$ the value of $A_{S2\text{-}Naph}$ is of the expected magnitude but of opposite sign from all the others, which is a fundamental contradiction of theory. We interpret this striking contradiction as decisive evidence that the synthetic method which yields 1-thioglycopyranoside acetates of the β-D-anomeric configuration (III) in the cases of D-xylose, D-glucose, D-galactose and the three bioses (which are 4-hexopyranosyl-D-glucoses), produces in the D-arabinose series the derivative which contains the α-D-anomeric element of configuration (IV) and that therefore this derivative should be formulated $B_x + A_{S2\text{-}Naph}$, an arrangement which conforms with theory.



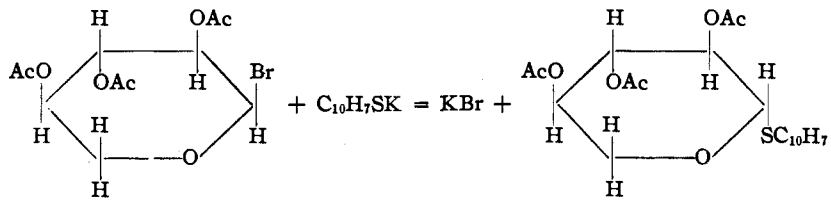
III
β-D-Anomers



IV
α-D-Anomers

This derivative is named accordingly 2′-naphthyl 1-thio-α-D-arabinopyranoside triacetate. The five crystalline derivatives which Purves obtained were all phenyl 1-thio-β-D-glycopyranoside acetates; there is good reason to believe that if the corresponding substance in the D-arabinose series could be obtained in pure crystalline form its rotation would show it to be an α-D-anomer. Similar contrasts between D-arabinose and D-xylose have been observed previously in the course of other syntheses. The triacetyl-α-D-xylopyranosyl halides represent the stable forms but in the D-arabinose series the stable anomers are the triacetyl-β-D-arabinopyranosyl halides.[9] When equilibrium is established between the α- and β-anomers of D-xylopyranose tetraacetate in acetic anhydride solution with an acid catalyst such as zinc chloride, the predominating anomer is the α-D-xylopyranose tetraacetate[10] but in the D-arabinose series it is the β-D-arabinopyranose tetraacetate.[11]

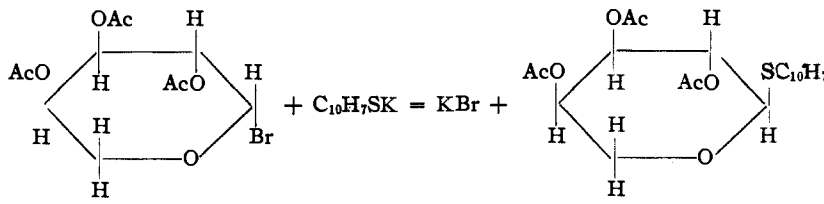
The contrast between the courses of synthesis in the D-xylose and D-arabinose series that have produced the 2′-naphthyl 1-thio derivative is shown in the accompanying reaction equations.



V
Triacetyl-α-D-xylopyranosyl bromide
($[\alpha]_D$ + 212°)

Potassium 2-thionaphtholate

VI
2′-Naphthyl 1-thio-β-D-xylopyranoside triacetate
($[\alpha]_D$ −40.8°)



VII
Triacetyl-β-D-arabinopyranosyl bromide
($[\alpha]_D$ −288°)

VIII
2′-Naphthyl 1-thio-α-D-arabinopyranoside triacetate
($[\alpha]_D$ −8.2°)

In both series the usual Walden inversion occurs when the bromine atom of V or VII is replaced by the 2-thionaphthyl grouping. Explanation for the fact that V, an α-D-anomer, is the stable form in one series while VII, a β-D-anomer, is the stable form in the other series, can be correlated with the arrangements of the attachments to carbon atom 3; the more stable form of the halide anomer carries in both series its bromine atom of carbon one and its acetoxy group of carbon atom 3 in *trans* position with respect to the pyranose ring. A more extended discussion of such steric influence in the pentose, hexose and higher-carbon sugar series will be published in a later article.

Deacetylation of the 2′-naphthyl 1-thioglycopyranoside acetates yielded crystalline glycosides except in the case of the maltoside. The steric formulas and anomeric names of these 2′-naphthyl 1-thioglycopyranosides follow directly from those shown for their acetates since Walden inversions are not encountered in the deacetylation of such types of substances. The rotations of the 1-thio-

(8) Fletcher and Hudson, THIS JOURNAL, **69**, 1672 (1947).

(9) Hudson, *ibid.*, **46**, 462 (1924); Hudson and Phelps, *ibid.*, **46**, 2501 (1924).

(10) Hudson and Johnson, *ibid.*, **37**, 274 (1915).

(11) Hudson and Dale, *ibid.*, **40**, 992 (1918).

glycosides were measured in alcohol, or in one case in pyridine, because the substances are nearly insoluble in cold water and the 1-thiolactoside is nearly insoluble also in cold alcohol. The rotations in alcohol of these 1-thioglycosides are not readily interpretable through isorotation calculations; Purves reached the same conclusion with respect to the rotations in water of the phenyl 1-thioglycosides and attributed the anomaly to the possible influence of hydroxyl groups on the unsaturated sulfur atom, a hypothesis which can apply equally to the present 2′-naphthyl 1-thioglycosides. However, this anomaly is not of present importance because the normal character of the rotations in chloroform of the acetates of such phenyl and 2′-naphthyl 1-thioglycosides permits their allocation as α- or β-anomers.

The sulfur–carbon bond in these 2′-naphthyl 1-thioglycopyranosides is such a strong one that the 1-thiobiosides can be hydrolyzed by acids to the corresponding hexose and 2′-naphthyl 1-thio-β-D-glucopyranoside without serious attack upon the latter. In this way the 2′-naphthyl 1-thio-β-D-cellobiopyranoside hydrolyzes to yield D-glucose and the 1-thioglucoside just mentioned, whereas this 1-thioglucoside and D-galactose result from the limited acid hydrolysis of the 2′-naphthyl 1-thio-β-D-lactopyranoside. This behavior is like that which Fischer and Delbrück[12] first noticed in the case of phenyl 1-thio-β-D-lactopyranoside.

Experimental

Fully Acetylated Derivatives of 2′-Naphthyl 1-Thioglycopyranosides.—A solution of one-tenth mole of the appropriate crystalline pyranose acetate in 100 ml. of glacial acetic acid was saturated at 0° with hydrobromic acid gas and allowed to stand two hours at 5°. Chloroform (200 ml.) was then added and the solution was washed well with water followed by sodium bicarbonate solution. The washed and dried clear chloroform solution containing the acetylated glycopyranosyl bromide was then added to an ethanol solution of potassium 2-thionaphtholate which was prepared by dissolving 0.11 mole (10% excess) of 2-thionaphthol in 100 ml. of *N* ethanolic potassium hydroxide. The condensation was effected in the case of the monose derivatives by refluxing the solution one hour, but with the biose derivatives the reaction was carried out at room temperature overnight. The reaction mixture was then washed well with water, the chloroform was removed by distillation under reduced pressure and the residual solid material was crystallized from aqueous ethanol to constant melting point and rotation. The maltoside and arabinoside acetates were recrystallized from three or four parts of 95% ethanol, the xyloside, galactoside and glucoside acetates from eight or ten parts and the cellobioside acetate from fifty parts of this solvent. Six parts of 65% ethanol were used for the lactoside acetate. The colorless crystals of all seven substances were of acicular appearance; the analyses, melting points and rotations are recorded in Table II. The yields were 70–80% except for the 1-thiomaltoside where it was about 40%. (The experiments were performed in 1937 and it seems likely that a better yield of the 2′-naphthyl 1-thiomaltoside heptaacetate may be possible by following more recent directions[13] for preparing the heptaacetylmaltosyl bromide.)

2′-Naphthyl 1-Thioglycopyranosides.—To an ice-cold solution of 0.05 mole of 1-thioglycoside acetate in 100 ml. of chloroform a solution of *N* sodium methylate in methanol was added in an amount equivalent to the acetyl content of the 1-thioglycoside acetate. After thirty minutes an equivalent quantity of *N* sulfuric acid was added, the precipitated sodium sulfate was removed and the 1-thioglycoside recovered by removal of the solvent. The yields of crystalline material were nearly quantitative except in the case of the maltoside, which failed to crystallize. Four of the others were recrystallized from 95% ethanol to constant melting point and rotation, the amounts of solvent used being as follows: xyloside, 16 parts; arabinoside and cellobioside, 4 to 5 parts; lactoside, 85 parts. Three parts of absolute ethanol were used for the galactoside. These five glycosides crystallized in anhydrous acicular form. The glucoside crystallized from eight parts of 95% ethanol or twenty-five parts of water as a hemihydrate of $[\alpha]^{20}D$ −42.8° (*c*, 1.0) in 95% ethanol; these crystals were lath-like and melted in the range 117–125° according to the rate of heating; their water of hydration was retained when they were heated *in vacuo* two hours at 78°, but it was slowly lost at 110° and removed quantitatively at 138°, and the melting point of the dried substance was 147°. It is well known that methyl β-D-glucopyranoside crystallizes as a hemihydrate which also holds its water of hydration rather tenaciously. Analyses, melting points and rotations of these 2′-naphthyl 1-thioglycopyranosides are recorded in Table II. A determination of the sulfur and water content of the hemihydrate of 2′-naphthyl 1-thio-β-D-glucopyranoside showed the following values. Calcd. for $C_{16}H_{18}O_5 \cdot 0.5H_2O$: S, 9.67; H_2O, 2.72. Found: S, 9.80; H_2O, 2.72.

Hydrolyses of 2′-Naphthyl 1-Thio-β-D-cellobiopyranoside and 2′-Naphthyl 1-Thio-β-D-lactopyranoside.—A solution of 2.0 g. of the 1-thiocellobioside in 35 ml. of *N* sulfuric acid was refluxed for two hours; as the solution cooled there crystallized 1.0 g. (75%) of 2′-naphthyl 1-thio-β-D-glucopyranoside hemihydrate (m. p. 122–125°) which was converted to its tetraacetate (m. p. 112°; $[\alpha]^{20}D$ −17.6°) to confirm identification. The mother liquor, from which the sulfuric acid had been removed as barium sulfate, was treated with phenylhydrazine and acetic acid and phenyl D-*arabo*-hexosazone[14] was obtained in a yield of 34% from the D-glucose produced as a result of the hydrolysis. A similar hydrolysis of 2′-naphthyl 1-thio-β-D-lactopyranoside also yielded 2′-naphthyl 1-thio-β-D-glucopyranoside hemihydrate and in this case phenyl-D-*lyxo*-hexosazone was obtained from the D-galactose that was present in the filtrate.

Summary

Several fully acetylated crystalline 2′-naphthyl 1-thioglycopyranosides have been prepared. It is shown through rotatory relations that the thioxyloside, thioglucoside, thiogalactoside, thiolactoside, thiocellobioside and thiomaltoside acetates are β-D-pyranoside anomers, but that the arabinoside acetate is an α-D-pyranoside anomer. Deacetylation of these acetates yielded the crystalline corresponding thioglycopyranosides except in the maltose series where the substance remained amorphous. The sulfur–carbon bond in these 1-thioglycopyranosides is rather resistant to hydrolysis by acids, as has been known previously for this bond in the case of the phenyl 1-thioglycopyranosides, and it is found that the 2′-naphthyl 1-thio-β-D-cellobiopyranoside can be hydrolyzed

(12) Fischer and Delbrück, *Ber.*, **42**, 1476 (1909).

(13) Hudson, *J. Org. Chem.*, **9**, 471 (1944).

(14) Sowden, THIS JOURNAL, **69**, 1047 (1947) This is the name which he has suggested for the phenylosazone long known as phenyl D-glucosazone, a substance which is the same as phenyl D-mannosazone or phenyl D-fructosazone. In like manner the designation phenyl D-*lyxo*-hexaosazone replaces the long-used but somewhat inappropriate name phenyl D-galactosazone.

under suitable acidic conditions to yield D-glucose and 2′-naphthyl 1-thio-β-D-glucopyranoside. In like manner the 2′-naphthyl 1-thio-β-D-lactopyranoside yields the same 1-thioglucoside and D-galactose.

BETHESDA, MARYLAND RECEIVED MARCH 6, 1947

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

1,5-Anhydro-D-arabitol

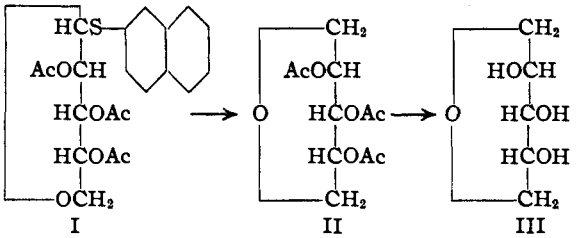
BY HEWITT G. FLETCHER, JR., AND C. S. HUDSON

Until quite recently the chief method of synthesizing the 1,5-anhydrides of the sugar alcohols has been through the catalytic reduction of the acetylated 2-hydroxy-glycals.[1] This synthetic path suffers from two drawbacks: the acetylated 2-hydroxy-glycals are not always readily preparable in substantial yield[2] and their catalytic reduction gives rise to new asymmetry at carbon two, usually necessitating such laborious configurational proofs for the product as was required in the case of 1,5-anhydro-D-mannitol (styracitol), the reduction product of 2,3,4,6-tetraacetyl-2-hydroxy-D-glucal.[1d,3]

In contrast the recently developed process of reductive desulfurization of cyclic 1-thio-sugar derivatives with Raney nickel affords a ready means of synthesizing 1,5-anhydro sugar alcohols of unequivocal structure and configuration. Thus, 1,5-anhydro-D-sorbitol (polygalitol) has been prepared from 2,3,4,6-tetraacetyl-1-thio-β-D-glucopyranose,[1c] octaacetyl-β,β-di-D-glucopyranosyl disulfide[1c] and ethyl tetraacetyl-D-glucopyranosyl xanthate.[4] It has also been prepared in 80% yield from phenyl 1-thio-β-D-glucopyranoside tetraacetate and from *p*-cresyl 1-thio-β-D-glucopyranoside tetraacetate.[5] 1,5-Anhydro-xylitol has likewise been prepared by the reductive desulfurization of phenyl 1-thio-β-D-xylopyranoside triacetate.[1e]

The purpose of the present investigation was to explore this general synthetic method further and, specifically, to apply it to the preparation of one of the pair of unsymmetrical 1,5-anhydropentitols, the 1,5-anhydro-arabitols. The greater availability of pure D-arabinose through the directions of Hockett and Hudson for the Ruff degradation of calcium D-gluconate,[6] led to the choice of the D- rather than of the L-series for this work.

For a 1-thio-D-arabinopyranose derivative we chose the 2′-naphthyl 1-thio-α-D-arabinopyranose triacetate (I), first prepared by Haskins, Hann and Hudson,[7] a readily available and beautifully crystalline compound like the majority of 2′-naphthyl 1-thioglycoside acetates. When treated in absolute alcoholic solutions with Raney nickel this substance gave naphthalene and a sirup, presumably 2,3,4-triacetyl-1,5-anhydro-D-arabitol (II), which could not be induced to crystallize. Catalytic deacetylation of the sirup, however, gave the desired pentitan in crystalline form.



I — 2′-Naphthyl 1-thio-α-D-arabinopyranoside triacetate

II — 2,3,4-Triacetyl-1,5-anhydro-D-arabitol

III — 1,5-Anhydro-D-arabitol

That the original tetrahydropyrane ring of the acetobromo-D-arabinose had remained unchanged in the 2′-naphthyl 1-thio-α-D-arabinoside triacetate and survived in the anhydropentitol was demonstrated by the behavior of the last-named substance toward sodium metaperiodate. On a molar basis the anhydride consumed two atoms of oxygen with the formation of one mole of formic acid. The product is therefore 1,5-anhydro-D-arabitol, III. It was further characterized as its triacetate and tribenzoate.

While a crystalline 1-thio-D-arabinose derivative is most convenient for use in this synthesis it is not indispensable since 1,5-anhydro-D-arabitol triacetate, like 1,5-anhydro-xylitol triacetate,[1e] is somewhat volatile, and can be purified prior to the final deacetylation. Thus both phenyl 1-thio-D-arabinopyranoside triacetate and ethyl triacetyl-D-arabinopyranosyl xanthate, obtained by the condensation of 2,3,4-triacetyl-β-D-arabinopyranosyl bromide with potassium thiophenolate and potassium ethyl xanthate respectively, were obtained only as crude sirups. However, treatment of each of these with Raney nickel gave a sirup which at an elevated temperature and low

(1) *Cf.* (a) L. Zervas, *Ber.*, **63**, 1689 (1930); (b) K. Maurer and K. Plötner, *ibid.*, **64**, 281 (1931); (c) N. K. Richtmyer, C. J. Carr and C. S. Hudson, THIS JOURNAL, **65**, 1477 (1943); (d) R. C. Hockett and Maryalice Conley, *ibid.*, **66**, 464 (1944); (e) H. G. Fletcher and C. S. Hudson, *ibid.*, **69**, 921 (1947).

(2) R. T. Major and E. W. Cook [*ibid.*, **58**, 2333 (1936)], for instance, reported their failure to obtain 2,3,4-triacetyl-2-hydroxy-D-xylal in crystalline form while the present authors have had a similar experience with 2,3,4-triacetyl-2-hydroxy-D-arabinal.

(3) (a) N. K. Richtmyer and C. S. Hudson, *ibid.*, **65**, 64 (1943); (b) L. Zervas and I. Papadimitriou, *Ber.*, **73**, 174 (1940).

(4) H. G. Fletcher, THIS JOURNAL, **69**, 706 (1947).

(5) N. K. Richtmyer and C. S. Hudson, unpublished results from this Laboratory.

(6) R. C. Hockett and C. S. Hudson, THIS JOURNAL, **56**, 1632 (1934).

(7) W. T. Haskins, R. M. Hann and C. S. Hudson, *ibid.*, **69**, 1668 (1947).