from dextrin by an acetobacter strain[10] gave thermogram C. The very sharp endotherm at 220° is its most prominent feature.

The data in Figs. 1 to 5 demonstrate that the dextran thermograms show characteristic contours in the 100 to 310° region. The 200° endotherms are common to the predominantly 1,6-linked dextrans while those near the 225° region occur with enzymatic preparations. Moreover, the thermal peaks near 245° appear to be typical of the most highly 1,3-like linked dextrans. Clinical size preparations, on the other hand, are recognized by a peak at 185°. Significantly, almost all the thermograms show endotherms in the 310 ± 5° region.

Aside from the dominant influence of the type and proportion of glucosidic linkages, further variations appear to be associated with marked changes in solubility, unique viscosity properties, and to a minor extent, purity of the sample. It must be emphasized here that other unknown factors may be involved, especially in view of the structural complexities of the dextrans and more particularly in view of the undeveloped state of this thermal technique.

The differential thermal reactions responsible for the distinct endotherms appear to be similar to those encountered with starch.[3] Analogous evidence given by infrared analysis of the pyrolysis residues, as well as examination of the gaseous pyrolyzates, suggest that transglucosidation[11-13] and dehydration constitute the predominant endothermic processes. Dehydration reactions are, moreover, generally recognized as being stereospecific, particularly when they are catalytic. Consequently, the interpretation of the thermal effects due to chain branching and molecular aggregation may be based predominantly on stereochemical considerations.

The present investigation has shown that there may be some relationships between the thermal property of the bacterial dextrans and their molecular constitution which cannot be deduced readily by other analytical techniques. The results also indicate that differential thermal analysis may become an invaluable aid in elucidating the constitution of other polysaccharides and biologically important polymers.

**Acknowledgment.**—The author thanks Dr. Allene Jeanes of the Northern Utilization Research Branch, United States Department of Agriculture, for her helpful advice and material assistance during this investigation.

OTTAWA, CANADA

[10] E. J. Hehre, *J. Biol. Chem.*, **192**, 161 (1951).

[11] B. Brimhall, *Ind. Eng. Chem.*, **36**, 72 (1944).

[12] F. G. Pantard, *Chemistry & Industry*, 1316 (1953).

[13] I. A. Wolff, *et al.*, *Ind. Eng. Chem.*, **45**, 755 (1953).

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

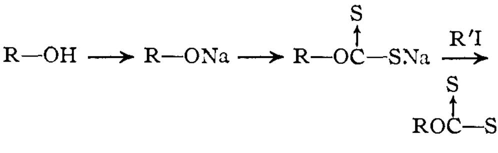
# Dithiocarbonate Esters of Arabinose[1]

By M. L. Wolfrom and A. B. Foster[2]

RECEIVED SEPTEMBER 22, 1955

Certain 2-*O*-(*S*-alkyl dithiocarbonate) esters ("xanthates") of methyl 3,4-*O*-isopropylidene-β-D- and L-arabinopyranoside (I, Ia, II) and of methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-altropyranoside (IV) have been prepared and their behavior on pyrolysis studied. The derivatives did not undergo a Chugaev type elimination reaction, but the 2-*O*-(*S*-methyl dithiocarbonate) of III rearranged to the isomeric 2-*S*-(*S*-methyl dithiocarbonate) (V) on distillation; V was reductively desulfurated and debenzylidenated to 2-deoxy-D-*erythro*-aldopentose ("2-deoxy-D-ribose") in low yield. The relation of the rearrangement (of which other examples are known) to the Chugaev reaction is discussed.

The production of olefins by the controlled thermal decomposition of the *O*-(*S*-alkyl dithiocarbonate) or "xanthate" esters of certain alcohols (Chugaev reaction)[3] is now well known. Numerous examples of the Chugaev reaction have been described in the literature, but the thermal decomposition of 2-*O*-(*S*-alkyl dithiocarbonate) esters of simple carbohydrates has been little studied. In fact, few such esters are known. Freudenberg and Wolf[4] described 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 6-*O*-(*S*-methyl dithiocarbonate), 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose 1-*O*-(*S*-methyl dithiocarbonate) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-*O*-(*S*-methyl dithiocarbonate), of which the latter two derivatives were crystalline. These esters were prepared by the general route (1) as was methyl α-D-glucopyranoside 2-*O*-(*S*-methyl dithiocarbonate).[5] *O*-Acetyl-1-thioaldose 1-*S*-(*O*-alkyl dithiocarbonate) esters have been prepared by the action of potassium *O*-ethyl dithiocarbonate on *O*-acetylglycosyl halides.[6]


$$R{-}OH \longrightarrow R{-}ONa \longrightarrow R{-}O\overset{S}{\overset{\uparrow}{C}}{-}SNa \xrightarrow{R'I} RO\overset{S}{\overset{\uparrow}{C}}{-}SR'$$
(1)

Pyrolysis of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-*O*-(*S*-methyl dithiocarbonate)[4] under the conditions originally employed by Chugaev[3] did not give the desired 3,4-unsaturated compound.

The purpose of this investigation was the preparation of other dithiocarbonate ("xanthate") esters of simple carbohydrates, which might reasonably be expected to undergo a Chugaev type reaction (5) and a study of their behavior on pyrolysis.

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[1] A preliminary report of this work appears in *Abstracts Papers Am. Chem. Soc.*, **126**, 23D (1954).

[2] Rockefeller Foundation Fellow, 1953–1954.

[3] L. Chugaev, *Ber.*, **32**, 3332 (1899).

[4] K. Freudenberg and A. Wolf, *ibid.*, **60**, 232 (1927).

[5] T. Lieser and E. Leckzyck, *Ann.*, **519**, 279 (1935); M. L. Wolfrom and M. A. El-Taraboulsi, THIS JOURNAL, **75**, 5350 (1953).

[6] W. Schneider, R. Gille and K. Eisfeld, *Ber.*, **61**, 1244 (1928).

TABLE I

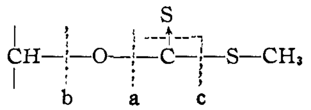
DATA ON THE PREPARATION OF THE *S*-ALKYL XANTHATES

| Compound[a] | Yield, % | M.p., °C. | $[\alpha]^{25}\mathrm{D}$ (*c* 2, benzene) | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|
| Methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-methyl dithiocarbonate)[b] (I) | 70–75 | 119–120 | +217[c] | $C_{11}H_{18}O_5S_2$ | 44.91 | 44.55 | 6.12 | 6.24 |
| Methyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside 2-*O*-(*S*-methyl dithiocarbonate)[b] (Ia) | 72 | 120–121 | +210 | $C_{11}H_{18}O_5S_2$ | 44.91 | 44.74 | 6.12 | 6.35 |
| Methyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside 2-*O*-(*S*-triphenylmethyl dithiocarbonate) (II) | 54 | 169–171 | + 54 | $C_{29}H_{31}O_5S_2$ | 67.01 | 66.66 | 5.87 | 5.75 |
| Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-altropyranoside 2-*O*-(*S*-methyl dithiocarbonate) (IV) | 26 | 113–115 | | $C_{17}H_{22}O_6S_2$ | 53.16 | 52.85 | 6.08 | 5.70 |

[a] Attempts to prepare methyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside 2-*O*-(*S*-*p*-nitrobenzyl dithiocarbonate) and methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-bis-*O*-(*S*-methyl dithiocarbonate) were unsuccessful. [b] Mixed melting point of the D- and L-forms was 97–99°. Recrystallization of equal amounts of the enantiomorphs gave a product of m.p. 97–99°.

The Chugaev reaction involves an elimination of the *O*-(*S*-alkyl dithiocarbonate) group together with an adjacent *cis*-hydrogen atom (5). The reaction is known to proceed readily in cyclohexane derivatives[7] and for this reason analogous pyran derivatives were selected, namely, methyl 3,4-*O*-isopropylidene-β-D- and L-arabinopyranoside (III) in which a substituted *O*-(*S*-alkyl dithiocarbonate) group, at position 2, would be adjacent to a configurationally *cis*-hydrogen. The esters were prepared by the general route (1) in which the use of sodium hydride[8] in the first step was found to be much more expedient than the more conventional use of sodium. The remainder of the sequence is well established. A 70–75% over-all yield of the crystalline 2-*O*-(*S*-methyl dithiocarbonate) (I, Ia) of methyl 3,4-*O*-isopropylidene-β-D- or L-arabinopyranoside and a 54% over-all yield of the 2-*O*-(*S*-triphenylmethyl dithiocarbonate) (II) ester of the L-isomer were thus obtained. The latter derivative was prepared for study because of the known fact[9,10] that the more electrophilic the *S*-alkyl group in the xanthate esters, the greater the instability of the derivative on pyrolysis. In this respect the *S*-triphenylmethyl group is the most effective.[10] A much lower over-all yield (25%) of methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-altropyranoside[11] 2-*O*-(*S*-methyl dithiocarbonate) (IV) was obtained (see Table I). In this compound (IV) the dithiocarbonate group is doubly flanked by *cis*-hydrogen atoms.

Reductive desulfuration of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-methyl dithiocarbonate) (I) with Raney nickel gave the parent alcohol III which was characterized as the known crystalline 2-*p*-toluenesulfonate. The formation of III resulted from cleavage of the C–O linkage **a**. There was no indication in the products of reaction of the presence of methyl 3,4-*O*-isopropylidene-β-D-2-deoxy-D-*erythro*-aldopentoside (resulting from cleavage at **b**) or methyl 3,4-*O*-isopropylidene 2-*O*-methyl-β-D-arabinopyranoside (resulting from cleavage at **c**). These findings are in accord with those of Wolfrom and El-Taraboulsi in the D-glucose structure.[12]



$$\mathrm{CH{-}O{-}\overset{S}{\overset{\uparrow}{C}}{-}S{-}CH_3}$$

The *O*-(*S*-alkyl dithiocarbonates) I, Ia, II and IV were subjected to a variety of thermal treatments and typical experiments are summarized in Table II. Some difficulty was experienced with the derivative of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (I) which sublimed when heated at 120–204° in an open tube at atmospheric pressure. The use of a sealed and evacuated tube under the thermal conditions B and C, did not lead to the elimination of carbon oxysulfide and methyl mercaptan which would indicate the occurrence of a Chugaev-type reaction. As the period or temperature of heating was increased, the amount of unchanged starting material recovered decreased. This is in agreement with the subsequently described finding of the rearrangement of I on distillation. It is of interest to compare the thermal conditions B and C with those used by O'Connor and Nace[8] who found that β-cholestanyl *O*-(*S*-methyl dithiocarbonate) was converted in 94% yield to a mixture of $\Delta^2$- and $\Delta^3$-cholestene when heating at 230° for 2.5 hours at 20 mm. pressure.

The use of the more drastic thermal conditions D on I led to a 36% loss in weight (theoretical loss for elimination of COS and $CH_3SH$, 30.6%), no starting material was recovered and most of the residue was insoluble in benzene. These results would indicate extensive decomposition of the dithiocarbonate ester.

Under thermal conditions (Table II) similar to those used by O'Connor and Nace and mentioned above, II and IV did not undergo any elimination reaction or rearrangement and could be recovered largely unchanged. It is clear from these results that the *S*-alkyl dithiocarbonate esters studied do not undergo elimination reactions under normal Chugaev reaction conditions.

When compound I was subjected to distillation at atmospheric pressure (b.p. 270–280°) the distillate consisted largely of unchanged starting material

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(7) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 120.

(8) G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952).

(9) Irene M. McAlpine, *J. Chem. Soc.*, 1114 (1931).

(10) G. L. O'Connor and H. L. Nace, THIS JOURNAL, **75**, 2118 (1953).

(11) G. J. Robertson and C. F. Griffith, *J. Chem. Soc.*, 1193 (1935).

(12) M. L. Wolfrom and M. A. El-Taraboulsi, *Abstracts Papers Am. Chem. Soc.*, **121**, 8P (1952).

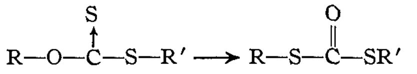
TABLE II

THERMAL TREATMENT OF THE *O*-(*S*-ALKYL DITHIOCARBONATE) ESTERS

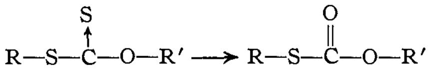
| Compound | | Reaction conditions | Temp., °C. | Time, hr. | Observation |
|---|---|---|---|---|---|
| Methyl 3,4-*O*-isopropylidene β-D-(or L)-arabinopyranoside 2-*O*-(*S*-methyl dithiocarbonate)[a] (I, Ia) | (A) | Open tube, atm. press. | 120–205 | 1 | Starting mater. subl. unchanged |
| | (B) | Sealed tube *in vacuo* | 200–210 | 1 | No evol. of CH$_3$SH + COS; 230 mg. recovd. |
| | (C) | Sealed tube *in vacuo* | 210–218 | 4 | No evol. of CH$_3$SH + COS; 153 mg. recovd. |
| | (D) | Sealed tube *in vacuo* | 253–254 | 5 | Loss in wt. 107 mg.; no starting mater. recovd.; residue largely insol. in benzene |
| Methyl 3,4-*O*-isopropylidene β-L-arabinopyranoside 2-*O*-(*S*-triphenylmethyl dithiocarbonate) (II) | | Open tube at 10–15 mm. | 200–230 | 1–3 | No loss in wt.; 50–80% recov. |
| Methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-altropyranoside[11] 2-*O*-(*S*-methyl dithiocarbonate) (IV)[b] | | Open tube at 10–15 mm. | 203–207 | 2 | No loss in wt.; 60 mg. recovd. |

[a] Sample wt., 300 mg. [b] Sample wt., 80 mg.

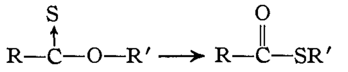
which crystallized and was easily separated. It is probable that the non-crystalline fraction of the distillate contained a rearranged product, presumably the substance V. This assumption was based on the fact that reductive desulfuration of the non-crystalline fraction with Raney nickel gave known methyl 3,4-*O*-isopropylidene-β-2-deoxy-D-*erythro*-aldopentoside (VI). Hydrolysis of VI gave 2-deoxy-D-*erythro*-aldopentose ("2-deoxy-D-ribose"), characterized by ionophoresis and by the formation of the crystalline anilide. The inferred rearrangement I → V is not without precedent. Thus Freudenberg and Wolf[4] obtained crystalline 1,2:5,6-di-*O*-isopropylidene α-D-1-thioglucofuranose 3-*S*-(*S*-methyl dithiocarbonate) in 30% yield on distillation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-*O*-(*S*-methyl dithiocarbonate) at atmospheric pressure (2). Similar rearrangements of such esters have been noted by Laakso[13] and in the closely analogous thionocarbonates (3)[14] and thiono esters (4).[15]


(2)

$$R{-}O{-}\overset{\overset{S}{\uparrow}}{C}{-}S{-}R' \longrightarrow R{-}S{-}\overset{\overset{O}{\|}}{C}{-}SR' \qquad (2)$$


(3)

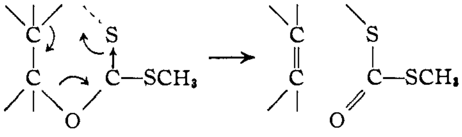
$$R{-}S{-}\overset{\overset{S}{\uparrow}}{C}{-}O{-}R' \longrightarrow R{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' \qquad (3)$$


(4)

$$R{-}\overset{\overset{S}{\uparrow}}{C}{-}O{-}R' \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}SR' \qquad (4)$$

The isolation of 2-deoxy-D-*erythro*-aldopentose ("2-deoxy-D-ribose") as described herein constitutes a new synthesis of this biologically important sugar. Because of the low over-all yield the synthesis is of little value as a preparative method.

The mechanism of the Chugaev reaction has been studied extensively[16] and it is currently thought that the β-*cis* elimination which occurs involves a cyclic transition state complex in which the thiono sulfur bonds to the β-hydrogen. O'Connor and Nace[8] have shown that the reaction is strictly unimolecular and that the transition state complex is highly ordered (negative entropy of activation). Thus the geometry of the transition state would appear to be of importance. It is possible that the failure of the dithiocarbonate esters described in this paper to undergo a Chugaev-type elimination reaction may have been due in part to interference with the probably critical geometry of the transition state by the heavy substitution of the pyran ring. Alternatively, the occurrence of an elimination reaction in the *O*-(*S*-alkyl dithiocarbonate) derivatives I, II and IV would lead to an enol ether and not an olefin and it is possible that the hydrogen β-*cis* to the *O*-(*S*-alkyl dithiocarbonate) group is inactivated by the oxygen functions attached to the same carbon atom.



(5)

It has been suggested[17] that the Chugaev reaction may involve a rearrangement to the dithiol carbonate (2) prior to elimination. This would seem improbable since the dithiol carbonates are known to be more stable than the corresponding *S*-alkyl dithiocarbonate esters.[13] Further, from an infrared study, O'Connor and Nace[8] concluded that no rearranged product was present in quantity as the Chugaev reaction proceeded. Thus it would appear that the rearrangement (3) encountered by Freudenberg and Wolf[4] and in this paper are not partially complete Chugaev-type reactions but alternative reactions. It is significant that the thermal conditions necessary to effect the rearrangements of the types 2, 3 and 4[4,13–15] are generally more drastic than those necessary to bring about the Chugaev reaction in suitable derivatives.[8]

## Experimental

**Methyl 3,4-*O*-Isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-Methyl Dithiocarbonate) (I).**—A solution of 10.6 g. of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside[18] in 300 ml. of dry benzene was added to a suspension of 6 g. (5 moles) of sodium hydride in 50 ml. of dry benzene.[8] Vigor-

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[13] P. V. Laakso, *Suomen Kemistilehti*, **16B**, 19 (1943); *C. A.*, **40**, 4687 (1946).

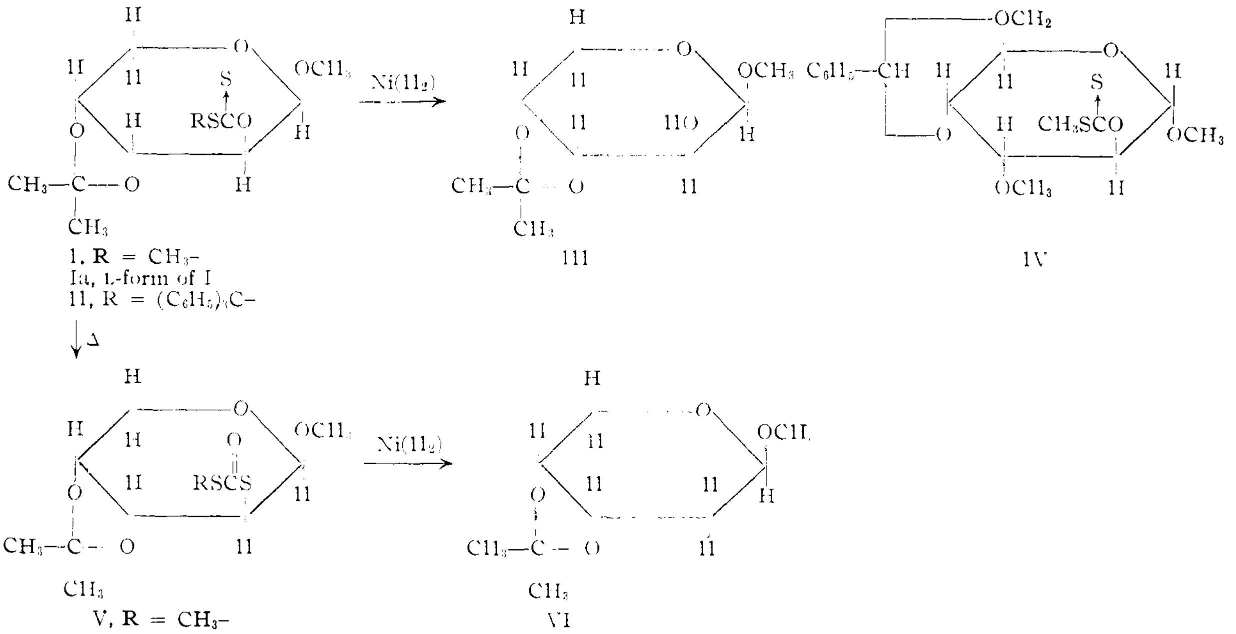
[14] A. Schönberg and L. v. Vargha, *Ber.*, **63**, 178 (1930); A. Schönberg, L. v. Vargha and W. Paul, *Ann.*, **483**, 107 (1930).

[15] S. A. Karjala and S. M. McElvain, THIS JOURNAL, **55**, 2966 (1933).

[16] See reference 8 and other references cited therein.

[17] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 60 (1951).

[18] J. Honeyman, *J. Chem. Soc.*, 990 (1946).


I, R = $CH_3$-
Ia, L-form of I
II, R = $(C_6H_5)_3C$-
III
IV
V, R = $CH_3$-
VI

ous evolution of hydrogen occurred and the mixture was well stirred and boiled under reflux for 18 hr. The deep red solution was cooled, decanted from excess sodium hydride and treated with 20 ml. of carbon disulfide. Immediate separation of the red gelatinous sodium salt of the sugar dithiocarbonate occurred. The mixture was boiled under reflux for 1 hr. and was then treated with excess methyl iodide. After a further 5 hr. of refluxing, the reaction mixture was filtered, partially decolorized with carbon and concentrated to small volume. Addition of excess hexane gave colorless prisms; yield 11.1 g. (72%). Pure material was obtained on recrystallization from benzene-hexane; m.p. 119–120°,[19] $[\alpha]^{25}D$ −217° (*c* 2.48, benzene). By essentially the same procedure, the derivatives listed in Table I were prepared.

**Reductive Desulfuration of Methyl 3,4-*O*-Isopropylidene-β-L-arabinopyranoside 2-*O*-(*S*-Methyl Dithiocarbonate) (Ia).**—A solution of 1.31 g. of Ia in 200 ml. of an ethanol–benzene mixture (equal parts by volume) was boiled under reflux with freshly prepared Raney nickel[20] from 30 g. of alloy. The mixture was filtered and the nickel was washed several times with hot methanol. Evaporation of the combined filtrate and washings gave a sirup, yield 0.48 g. (52.8%), b.p. 80–85° (bath temperature) (0.05 mm.), $n^{31}$ 1.4600, $[\alpha]^{31}D$ +192° (*c* 1.4, chloroform). Honeyman[18] records b.p. 82° (bath temperature) (0.1 mm.), $[\alpha]D$ +199.1° in chloroform for methyl 3,4-*O*-isopropylidene-β-L-arabinopyranoside. The product from the reductive desulfuration gave a crystalline *p*-toluenesulfonate in good yield, m.p. 131–132° alone or in admixture with authentic methyl 3,4-*O*-isopropylidene-2-*O*-*p*-toluenesulfonyl-β-L-arabinopyranoside.[18]

**Isomerization of Methyl 3,4-*O*-Isopropylidene-β-D-arabinopyranoside 2-*O*-(*S*-Methyl Dithiocarbonate) (I).**—Isomerization of I was effected by distillation at atmospheric pressure.[4] The distillate was allowed to stand for 24 hr. to permit as complete crystallization as possible of unchanged starting material. Extraction of the distillate with hexane which contained 10% of benzene or ethanol removed sirupy material. Concentration of the extracts normally afforded a small extra amount of starting material. The results of a series of distillations are recorded in Table III.

**Reductive Desulfuration of the Non-crystalline Distillate from I.**—A solution of 15.77 g. of the non-crystalline distillate from I (see Table III) in 500 ml. of an ethanol–hexane mixture (equal parts by volume) was boiled under reflux for 5 hr. with Raney nickel freshly prepared from 100 g. of alloy.[20] The mixture was filtered and the nickel was exhaustively extracted with methanol using a Soxhlet apparatus. The extract was combined with the earlier filtrate, concentrated, and the residue distilled, using a Widmer flask with a 15 cm. column. Methyl 2-deoxy-3,4-*O*-isopropylidene-β-D-*erythro*-aldopentopyranoside was obtained; yield 2.52 g., b.p. 65–70° (bath temperature) (0.1 mm.), $n^{25}$ 1.4438, $[\alpha]^{25}D$ −42.5° (*c* 1.75, chloroform). Allerton and Overend[21] record b.p. 110–115° (bath temperature) (12 mm.), $n^{20}$ 1.4456, $[\alpha]D$ −47.8° (water) for the product obtained by the isopropylidenation of methyl 2-deoxy-β-D-ribopyranoside.

TABLE III

DISTILLATION[a] OF METHYL 3,4-*O*-ISOPROPYLIDENE-β-D-ARABINOPYRANOSIDE 2-*O*-(*S*-METHYL DITHIOCARBONATE)

| Sample, g. | Distillate, g. | Recovd. starting mater., g. | Decompn. loss G. | Decompn. loss %[c] | Non-crystalline distillate[b] G. | Non-crystalline distillate[b] %[c] |
|---|---|---|---|---|---|---|
| 2.38 | 1.43 | 0.52 | 0.95 | 40[d] | 0.91 | 38 |
| 4.00 | 2.97 | 0.70 | 1.03 | 26 | 2.27 | 57 |
| 5.23 | 4.11 | 1.72 | 1.12 | 21 | 2.39 | 44 |
| 5.00 | 4.20 | 1.89 | 0.80 | 16 | 2.31 | 46 |
| 5.23 | 4.17 | 1.77 | 1.06 | 20 | 2.40 | 44 |
| 4.35 | 3.71 | 1.53 | 0.64 | 15 | 2.18 | 50 |
| 24.00 | 19.45 | 10.00 | 4.55 | 19 | 9.45 | 39 |
| 18.00 | 13.82 | 7.50 | 4.12 | 23 | 6.32 | 35 |

[a] See Experimental section for details. [b] The weights recorded in this column represent a mixture of starting material and isomerized product. [c] Basis starting material. [d] This result appears anomalous.

**Hydrolysis of Methyl 2-Deoxy-3,4-*O*-isopropylidene-β-D-*erythro*-aldopentoside (VI).**—A solution of 296 mg. of VI in 15 ml. of 0.02 *N* aqueous methanolic (7:3, v./v.) hydrochloric acid was boiled under reflux for 80 min. Anions were then removed by means of Duolite A-4,[22] the solution was concentrated by freeze-drying and finally dried by standing over phosphoric anhydride in a vacuum desiccator to give a pale yellow sirup which was reducing toward Fehling solution; yield 130 mg. Ionophoresis of the product[23] in sodium borate buffer at *p*H 10 under a potential of 800 volts (final current 35 milliamperes) indicated the presence of a single substance which moved identically with authentic 2-deoxy-D-*erythro*-aldopentose ("2-deoxy-D-ribose").[24]

A solution of 110 mg. of the sirupy 2-deoxy-D-*erythro*-

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[19] All melting points are uncorrected.

[20] H. Adkins and A. A. Pavlic, This Journal, **69**, 3039 (1947).

[21] R. Allerton and W. G. Overend, *ibid.*, 1480 (1951).

[22] A product of the Chemical Process Co., Redwood City, Calif.

[23] A. B. Foster, *Chemistry & Industry*, 880 (1952); *J. Chem. Soc.*, 982 (1953); A. B. Foster and M. Stacey, *J. Appl. Chem. (London)*, **3**, 19 (1953).

[24] Sample kindly provided by Dr. J. C. Sowden of Washington University, St. Louis, Mo.

aldopentose in 5 ml. of ethanol containing 0.1 g. of freshly distilled aniline was boiled under reflux for 3 hr. Thereafter the solution was partially decolorized with carbon and concentrated to 1 ml.; 2-deoxy-D-*erythro*-aldopentose anilide crystallized slowly; yield 20 mg. The crude material was recrystallized from ethanol; m.p. 163–164° unchanged on admixture with an authentic specimen of 2-deoxy-D-*erythro*-aldopentose anilide[24,25] of m.p. 165–167°.

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[25] W. G. Overend, M. Stacey and L. F. Wiggins, *J. Chem. Soc.*, 1358 (1949).

COLUMBUS 10, OHIO

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[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, TECHNICAL UNIVERSITY, BUDAPEST]

# Identification of Aldoses in the Form of Formazans via their Phenylhydrazones

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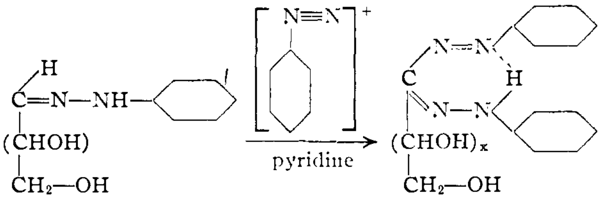
Aldoses have been identified by the use of the formazan reaction. By coupling with diazonium solutions, crystalline sugar formazans with characteristic physical properties have been prepared from the reaction of the corresponding aldose and phenylhydrazine without isolation of the intermediate phenylhydrazone. The optimal conditions for formazan formation have been established.

In earlier communications[1,2] we have reported that when allowed to react in pyridine solution with cold solutions of diazonium compounds, aldose phenylhydrazones yielded brilliant red, readily crystallized sugar formazans. Owing to their melting point and characteristic crystalline forms, these new nitrogenous sugar derivatives can be used to advantage in identifying aldoses.



Aldose phenylhydrazone Aldose diphenylformazan

TABLE I

| | M.p., °C. | Crystalline form |
|---|---|---|
| D-Glucose diphenylformazan | 177–178 | Red ndls., freq. rosettes |
| D-Galactose diphenylformazan | 167–168 | Bronze-red tablets |
| D-Mannose diphenylformazan | 174–175 | Bunches of microscopic russet ndls. |
| L-Arabinose diphenylformazan | 173–174 | Bunches of fine br.-red ndls. |
| L-Rhamnose diphenylformazan | 175–176 | Brill. red ndl. cryst. |
| D-Xylose diphenylformazan | 123–124 | Lanceolate red ndls. |

Because they contain no active methine groups[3,4] the ketose phenylhydrazones do not yield formazans; this reaction is therefore suitable for distinguishing aldoses from ketoses. It is more specific than the osazone test, frequently used in the identification of sugars, for it yields a different formazan for each aldose, while the latter does not differentiate between epimers.

For the purposes of identifying aldoses, we have simplified this reaction. The sugar phenylhydrazones derived from the reaction mixtures of the sugar and phenylhydrazine are not isolated but, after addition of pyridine, are immediately coupled to give the formazan.

In a previous paper[2] it has been reported that on standing sugar phenylhydrazone solutions suffer a considerable diminution of their capacity for coupling, a phenomenon connected with optically observable structural changes. Obviously, two processes are taking place in the reaction of the sugar and phenylhydrazine, which from the point of view of formazan formation have opposing effects: (i) the formation of phenylhydrazone; (ii) the transformation of this into a form unsuitable for coupling.

To decide on the usefulness of the simplified reaction in aldose identification, formazan formation from the corresponding aldoses has been studied as a function of time. For each sugar the reaction with phenylhydrazine has been examined in three different solvents, *viz.*, (i) water, (ii) 50% alcohol–water, (iii) pyridine. After identical periods of time, all three solutions were coupled to yield the formazan in a pyridine medium by the addition of diazotized aniline. The data in the tables reveal that on the whole the yield was highest in pyridine solution, between the 24th and 48th hour. With mannose the nearly insoluble phenylhydrazone separates very soon; therefore in this case the formazan reaction was done with the separated phenylhydrazone and, of course, showed no deviation as a function of time.

Experiments on the separation of mixtures of sugar formazans by means of chromatography are in progress.

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## Experimental

**Reagents.**—D-Glucose puriss. "Gyogyert"; D-galactose puriss. "Riedel"; D-mannose "Hoffmann-LaRoche"; L-arabinose p. u. sci. "Riedel"; L-rhamnose "B.D.H."; D-xylose puriss. "Fluka"; L-sorbose pur. "Merck"; D-fructose p. u. sci. "Schuchardt."

**Melting Points.**—All m.p.'s were determined in capillary tubes and are uncorrected. As the m.p. changes considerably with the manner of heating,[5] our bath was heated rapidly to within about 10° of the m.p. Thereafter its temperature was raised slowly, so that the mercury column was unchanging at the moment of melting.

**Preparation of Diazonium Solution.**—A solution of 9.3 g. of aniline in a mixture of 25 ml. of concd. hydrochloric acid and an equal amount of water was diazotized at 0–5° with

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[1] G. Zemplén and L. Mester, *Acta Chim. Acad. Sci. Hung.*, **2**, 9 (1952).

[2] L. Mester and Á. Major, THIS JOURNAL, **77**, 4297 (1955).

[3] H. v. Pechmann, *Ber.*, **25**, 3181 (1892).

[4] S. Hünig and O. Boes, *Ann.*, **579**, 28 (1953).

[5] H. v. Pechmann, *Ber.*, **27**, 1682 (1894).