THE INTRODUCTION OF UNSATURATED LINKAGES INTO SOME CARBOHYDRATES AND ALDITOL DERIVATIVES*

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INTRODUCTION

Corey and Winter\(^2\) reported recently that cyclic thionocarbonates undergo desulphurisation and decarboxylation on treatment with trimethyl phosphite, with the stereospecific introduction of a double bond. This reaction offers a new route to the interesting class of compounds, unsaturated carbohydrates**.

Of the two methods described for the preparation of cyclic thionocarbonates from diols, that utilizing bis(imidazol-1-yl)-thione proceeds in high yield, but suffers from the relative inaccessibility of the reagent. The second method, in which the diol is treated successively with equimolar quantities of \(n\)-butyl-lithium, carbon disulphide, and methyl iodide is facile, but yields are not high. However, recovery of starting material is possible, and it may be recycled.

RESULTS AND DISCUSSION

1,2:5,6-Di-\(O\)-isopropylidene-D-mannitol\(^4\), (I), having a threo-vicinal diol grouping, yielded the 3,4-thionocarbonate (II, \(Y = S\)) described by Baker and Sachdev\(^5\) as one of the products from the reaction of compound (I) with phenyl isothiocyanate. Treatment of the thionocarbonate (II, \(Y = S\)) with refluxing trimethyl phosphite gave crystalline trans-3,4-didehydro-3,4-dideoxy-1,2:5,6-di-\(O\)-isopropylidene-D-threo-hexitol (III). The structures of this, and the other unsaturated compounds reported herein, were confirmed by ozonolysis, and reduction of the ozonides to alcohols which were then characterised as crystalline acyl derivatives. These derivatives were compared with authentic materials, prepared by lead tetraacetate oxidation of the parent diol, followed by reduction, and acylation. Thus, the olefin (III) yielded 1,2-\(O\)-isopropylidene-\(D\)-glycerol (IV, \(R = H\)), which was isolated as its crystalline \(p\)-phenylazobenzoate (IV, \(R = CO\cdot C_6H_4\cdot N\cdot NPh\)). The reduction of the ozonide was performed in two ways. Firstly, a solution of the ozonide in ethyl acetate was shaken in an atmosphere of hydrogen over Adams’

\*A preliminary communication on a part of this work has already been published\(^1\).

\**During the course of this work, the application of the reaction to 1,2-\(O\)-isopropylidene-\(\alpha\)-\(D\)-glucofuranose was reported\(^3\).
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Catalyst, in order to liberate the carbonyl fragment, prior to borohydride reduction. In the second method, the catalytic hydrogenation step was omitted and the ozonide was reduced directly with borohydride. The yields were 31% and 27%, respectively. The low yields in this and other ozonolysis experiments presumably reflect an alternative breakdown pathway of the ozonides.

Reaction of 1,2:5,6-di-O-isopropylidene-D-altitol (talitol)⁶ (V) (erythro-vicinal diol) gave the 3,4-thionocarbonate (VI, Y = S). The structures of this and other new thionocarbonates were confirmed by their conversion (treatment with silver carbonate in methanol) into the corresponding carbonate, in this case, the 3,4-

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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{I}
\]

\[
\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{II}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{III}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{IV}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{V}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{VI}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{VII}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{VIII}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{IX}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{X}
\]

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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{XI}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{XII}
\]

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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{XIII}
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\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{XIV}
\]

\[
\text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{Me}O\]}\hspace{1cm} \text{\[\text{OH}\]}\hspace{1cm} \text{\[\text{Me}\]}\hspace{1cm} \text{\[\text{Me}\]} \tag{XV}
\]

3,4-carbonate (VI, Y = O). This product was identical to that obtained from the parent diol by treatment⁷ with methyl chloroformate in pyridine–carbon tetrachloride, followed by cyclisation of the methyl carbonate with base in N,N-dimethylformamide.

Conversion of the thionocarbonate (VI, Y = S) into cis-3,4-didehydro-3,4-

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dideoxy-1,2:5,6-di-O-isopropylidene-D-\textit{threo}-hexitol (VII) occurred in trimethyl phosphite. Ozonolysis of this olefin, followed by reduction gave compound (IV, \( R = H \)), isolated in 13\% yield as its p-phenylazobenzoate.

In order to investigate the utility of this reaction for the introduction of double bonds into pyranose and furanose sugars, two suitably blocked members of each of these classes, containing 	extit{cis}-vicinal diol groupings were sought. Thus, benzyl 2-\( O \)-benzyl-\( \beta \)-L-arabinopyranoside\textsuperscript{8} (VIII) was converted into the 3,4-thionocarbonate (IX, \( Y = S \)), and thence into the low-melting olefin (X), in good yield. Isolation of the product from ozonolysis of olefin (X), followed by reduction, and benzylation, gave 3-\( O \)-benzoyl-2-\( O \)-benzyl-D-glyceraldehyde (2-benzoyloxyethyl) benzyl acetal (XI, \( R = Bz \)) in 52\% overall yield.

A furanose system which appeared suitable for the introduction of a 2,3-olefinic bond was that reported by Schmidt \textit{et al.}\textsuperscript{9}. These authors described the benzyla- 
tion of 2,3-\( O \)-isopropylidene-L-rhamnose\textsuperscript{*}, a compound believed to exist mainly in the furanose form, with benzyl chloride at 100\° in the presence of potassium hydroxide. They reported that fractional crystallisation of the reaction mixture yielded a compound with m.p. 104\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +30.3\° (an isomer, m.p. 84\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} -15.4\°, was also obtained). The former compound was formulated\textsuperscript{9} as benzyl 5-\( O \)-benzyl-2,3-\( O \)-
isopropylidene-L-rhamnofuranoside, of unspecified anomic configuration, from which, selective removal of the isopropylidene group yielded benzyl 5-\( O \)-benzyl-L-rhamnofuranoside, m.p. 78\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +48.2\°.

Repetition of this benzyla- 
tion has now given a product, m.p. 102-104\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +30.1\° (compound \( A \)) which, on partial hydrolysis, gave the 2,3-diol, m.p. 76-78\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +47\° (compound \( C \)). Investigation of the reaction mixture from the benzyla- 
tion, by thin-layer chromatography in benzene, revealed two main components. One (\( R_F 0.3 \)) corresponded to compound \( A \), and a second component had \( R_F 0.6 \). Separation of the two substances on silica gel yielded firstly a compound (\( B \), m.p. 95-97\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{20} -67.6\°), analysing for a benzyl \( O \)-benzyl-\( O \)-isopropylidene-L-rhamnoside, and then compound \( A \). Selective removal of the isopropylidene group of compound \( B \) gave a benzyl \( O \)-benzyl-L-rhamnoside, m.p. 86-88\°, [\( \alpha \)]\textsubscript{D}\textsuperscript{25} -89\° (compound \( D \)).

The structure and anomic configuration of both series of compounds were further investigated. That they differed only in the configuration of the anomic centre was shown when complete hydrolysis of compounds \( A \) and \( B \), followed by reduction, gave the same \( O \)-benzyl-L-rhamnitol. This was identified as the 4-\( O \)-benzyl derivative when two mol. of sodium metaperiodate were consumed in a quantitative determination (the benzyl group must be on the 4 or 5 position). The original two compounds must thus have the pyranose structure. Authentic 5-\( O \)-benzyl-L-rhamnitol, synthesised by benzyla- 
tion of the known 1,2:3,4-di-\( O \)-isopropylidene-L-rhamnitol\textsuperscript{10}, followed by acid hydrolysis, consumed three mol. of periodate per mol.

\textsuperscript{*}See Experimental section for details of this compound.
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Since compounds $C$ and $D$ (derived from compounds $A$ and $B$, respectively, by partial hydrolysis) also differ only in their configuration at the anomeric centre, their structures may be assigned by reference to Hudson's rules\textsuperscript{11}. Thus, the more laevorotatory isomers in the $L$-series, \textit{i.e.} compounds $D$ and $B$, have the $\alpha$-configuration; compounds $C$ and $A$ have the $\beta$-configuration. Therefore compound $A$ is benzyl 4-$O$-benzyl-2,3-$O$-isopropylidene-$\beta$-$L$-rhamnopyranoside, and compound $B$ is the $\alpha$-isomer. The isomer recorded by Schmidt \textit{et al.}\textsuperscript{9} which had m.p. 84°, $[\alpha]_{D}^{20} -15.4^\circ$, was presumably a mixture of compounds $A$ and $B$, since, in the present work, the $\alpha$-anomer could not be obtained pure by fractional crystallisation of the reaction product.

Treatment of benzyl 4-$O$-benzyl-$\beta$-$L$-rhamnopyranoside (XII, compound $C$) in the usual manner gave the thionocarbonate (XIII, $Y = S$), which was converted into benzyl 4-$O$-benzyl-2,3-didehydro-2,3,6-trideoxy-$\beta$-$L$-erythro-hexoside (XIV). The acyclic diol (XV, $R = H$), resulting from ozonolysis and reduction of olefin (XIV), was isolated as its benzoate (XV, $R = Bz$) in only 6\% yield after three crystallisations. (Impure crystalline benzoate was obtained in 10\% yield, but was difficult to purify). Thin-layer chromatography of the crude benzoate (before crystallisation) showed other substances to be present, but in smaller amounts; the olefin (XIV) appeared homogenous in two solvent systems. The benzoate (XV, $R = Bz$) was also obtained from the diol (XII, compound $C$), in the usual manner.

The n.m.r. spectra of the acyclic olefins (III) and (VII) confirmed the stereospecificity of the elimination. Thus, olefin (III) analysed correctly in the olefinic proton region as part of an $A_2X_2$ system, with a coupling constant between olefinic protons of 15.4 c.p.s. The olefin (VII) analysed in a similar manner and had a coupling constant of 10.95 c.p.s. These values are consistent with the expected arrangements, \textit{i.e.} trans- and cis-, respectively, about the double bonds\textsuperscript{12}.

The olefinic protons of the cyclic olefin (X) appeared to be equivalent, since a singlet absorption ($\tau 4.33$) was observed for the two protons. It would appear that $J_{2,3}$ and $J_{4,5}$ are zero, or too small to be resolved. The other cyclic olefin (XIV) showed a quartet (2 protons) at $\tau 4.15$. If the coupling between the olefinic protons and protons on the adjacent carbon atoms is taken as zero [as appears to be true for compound (X)], then the spectrum may be analysed in the olefinic region as a simple AB type ($J, 10.3$ c.p.s.). This coupling constant is in agreement with the cis-arrangement about the unsaturated linkage\textsuperscript{12}.

None of these olefins show absorption in the 1650 cm$^{-1}$ region of the infrared, although this is not to be expected of the acyclic olefins, because of their symmetry. Compounds (III) and (VII) absorbed 1.1 and 1.07 mol. of hydrogen, respectively, over Adams' catalyst; compound (X), in the presence of palladium on charcoal, absorbed 2.5 mol. in 20 min, and 3 mol. after 50 min. In the latter case, uptake continued slowly, presumably due to slow hydrogenation of the aromatic residues. All of the olefins reacted with dilute aqueous potassium permanganate to yield a yellow solution.

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Levene and Compton have shown that unimolar toluene-p-sulphonylation [at 0° in pyridine-chloroform (5:2; v/v)] of 2,3-O-isopropylidene-L-rhamnose (m.p. 93–94°) yields 2,3-O-isopropylidene-5-O-toluene-p-sulphonyl-L-rhamnofuranose in 40% yield. The formation of anomeric aldopyranose derivatives by the benzylolation of 2,3-O-isopropylidene-L-rhamnose in benzyl chloride at 100° thus warrants further investigation. The formation of different ring isomers may reflect the varying proportions of the two ring forms in equilibrium at 0° and 100°, or may represent a difference in reactivity of ring hydroxyl and side-chain hydroxyl groups to benzylolation and toluene-p-sulphonylation. Another, perhaps more important, factor is the relative stability of the two ring forms in different solvents. Kuhn and Grassner have carried out investigations which suggest that the position of the furanose ⇌ pyranose equilibrium may be significantly different in different solvents. Thus, for D-fructose, they found that the furanose form is favoured to a greater extent in dry N,N-dimethylformamide than in water–N,N-dimethylformamide mixtures; also, mutarotation of D-fructose occurred much more slowly in dry N,N-dimethylformamide than in water–N,N-dimethylformamide mixtures. The isolation of different ring isomers by toluene-p-sulphonylation in pyridine-chloroform, and benzylolation in benzyl chloride, may be an example of the influence of the solvent on the position of the furanose ⇌ pyranose equilibrium.

It is pertinent here to consider the work of Freudenburg and Wolf, who assigned a furanose structure to 2,3-O-isopropylidene-L-rhamnose (m.p. 87–89°, [α]D20 +17.8° (water, equilibrium)). Methylation with methyl iodide–silver oxide, followed by acid hydrolysis, yielded 5-O-methyl-L-rhamnose; a pyranose system would have yielded 4-O-methyl-L-rhamnose. Presumably, methylation proceeds more quickly than the furanose ⇌ pyranose ring interconversion, since it is possible that the final position in this equilibrium may be similar in methyl iodide and benzyl chloride.

Data obtained by Perlin from the n.m.r. spectrum of 2,3-O-isopropylidene-L-rhamnose in deuterium oxide support the furanose assignment already made on chemical evidence, but suggest the presence of a significant proportion of a different species in aqueous solution.

Therefore, for certain compounds which may exhibit this type of ring isomerism, and whose structures are inferred from reactions in solution, it may be necessary to consider the effect of the solvent on the position of the furanose ⇌ pyranose equilibrium.

EXPERIMENTAL

Thin-layer chromatography was carried out on Kieselgel G with detection by sulphuric acid–vanillin. Preparative chromatography was done on B.D.H. silica gel. Routine identifications were based on melting points, mixed melting points, and infrared spectra. Solutions were concentrated in vacuo, and dried with sodium sulphate, unless stated otherwise. Light petroleum refers to the fraction.
of b.p. 60–80°. Proton magnetic resonance spectra were measured at 30° on a Perkin–Elmer R 10 instrument at 60 Mc.p.s. for carbon tetrachloride solutions. An internal reference of tetramethylsilane was used.

1,2: 5,6-Di-O-isopropylidene-D-mannitol 3,4-thionocarbonate (II, Y = S)

To a solution of 1,2:5,6-di-O-isopropylidene-D-mannitol¹⁴ (1) (5.2 g) in sodium-dried tetrahydrofuran (50 ml) was added n-butyl-lithium in hexane (12.5 ml of a 15% solution). After 5 min, carbon disulphide (1.45 ml) was added, and the reaction mixture stored at room temperature for 0.5 h and then heated under reflux for 0.5 h. The mixture was cooled and methyl iodide (1.2 ml) added, and, after 0.5 h at room temperature, the solution was again heated under reflux for 0.5 h. The solution was concentrated to ca. half its original volume, and poured into ice-water (200 ml). The yellow precipitate was collected and recrystallised from ethanol–ethyl acetate to give colourless crystals of the product (1.53 g), m.p. 166–168°, [α]D²⁰ = −15° (c 1.6, chloroform) [lit.⁵, m.p. 160–161°, [α]D = −11° (c 0.3, chloroform)] (Found: C, 51.3; H, 7.0; S, 10.6. C₁₃H₂₉O₆S calc.: C, 51.3; H, 6.6; S, 10.5%). A further yield of product (0.52 g), m.p. 163–165°, was obtained from the mother liquors.

The ice-water filtrate was extracted with chloroform (3 × 50 ml) and the combined, dried extracts were concentrated to give a residue which was crystallised from n-butyl ether to give the starting diol (1.44 g), m.p. 118–121°.

In a later preparation, the diol (5.2 g) yielded the thionocarbonate (3.45 g), m.p. 162–165°, contaminated with a small amount of the cyclic carbonate (C = O, νmax 1800 cm⁻¹) which was difficult to remove by crystallisation.

trans-3,4-Didehydro-3,4-dideoxy-1,2: 5,6-di-O-isopropylidene-D-threo-hexitol (III):

A solution of 1,2:5,6-di-O-isopropylidene-D-mannitol 3,4-thionocarbonate (2.0 g) in trimethyl phosphate (30 ml, redistilled before use) was heated under reflux for 70 h in an atmosphere of nitrogen. To the vigorously stirred solution was added 6N sodium hydroxide solution until, after prolonged stirring, the solution remained alkaline (40 ml). The mixture was extracted with chloroform (4 × 30 ml), and the combined extracts were washed with water (2 × 20 ml) and dried. Removal of the solvent afforded a residue which was crystallised from light petroleum to give the title compound (1.04 g, 67%), m.p. 80–82°, [α]D²⁰ +57.3° (c 1.3, chloroform) (Found: C, 62.7; H, 8.7. C₁₂H₂₀O₄ calc.: C, 63.1; H, 8.8%).

Ozonolysis of the olefin was carried out as follows. Purified ethyl acetate (40 ml) was cooled to −78° (acetone–Drikold) and ozonised oxygen bubbled through until a permanent blue colour was obtained. The olefin (0.10 g) in ethyl acetate (3 ml) was added, when most of the blue colour was discharged. The solution was removed from the cold bath and, after 10 min, excess of ozone removed by a stream of nitrogen. The solution was shaken in an atmosphere of hydrogen in the presence of Adams' catalyst for 1 h. The filtered solution was concentrated (bath temperature <30°), and the residue taken up in water (15 ml) and ethanol (5 ml). Potassium borohydride (0.1 g) was added and the solution stored overnight

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at room temperature, then a further quantity of potassium borohydride (0.1 g) was added. After 0.5 h, the solution was neutralised to pH 7.5 with glacial acetic acid, and the solution extracted continuously with chloroform for 6 h. The dried extract gave, on concentration, a residue (0.079 g) which was dissolved in pyridine (2.5 ml) and treated overnight with \( p \)-phenylazobenzoyl chloride (0.37 g) in pyridine (5 ml). Isolation of the product in the usual manner gave, from methanol, 2,3-\( O \)-isopropylidene-1-\( O \)-\( p \)-phenylazobenzoyl-d-glycerol (0.073 g, 24% based on olefin), m.p. 91–92°, mixed m.p. 91–93°, infrared spectrum indistinguishable from that of the authentic compound. A further quantity (0.02 g), m.p. 88–91°, was obtained from the mother liquor.

A second ozonolysis, in which the catalytic hydrogenation step was omitted, gave the same \( p \)-phenylazobenzoate in 27% yield.

\[
2,3-O-\text{Isopropylidene}-1-\text{O-}p\text{-phenylazobenzoyl-d-glycerol} \quad (IV, R = CO\cdot C_6H_4N\cdot NPh)
\]

\[2,3-O-\text{Isopropylidene}-d\text{-glycerol}\] (0.46 g) was treated with \( p \)-phenylazobenzoyl chloride (0.97 g) in pyridine (10 ml), and yielded the product, (0.97 g, 77%), m.p. 92–94°, \( [\alpha]_{D}^{21} +8.2° \) (c 1.4, acetone) (Found: C, 67.25; H, 5.7; N, 8.3. \( C_{19}H_{26}N_{2}O_{4} \) calc.: C, 67.0; H, 5.9; N, 8.2%).

\[1,2:5,6-\text{Di-O-isopropylidene-d-altritol 3,4-thionocarbonate} \quad (VI, Y = S)\]

\[1,2;5,6-\text{Di-O-isopropylidene-d-altritol (talitol)} \] (V) was prepared as previously described, and in one preparation exhibited anomalous behaviour on determination of the melting point. If heating was commenced below 35°, the compound had m.p. 62–64°, as previously recorded. If placed in the heating block above 45°, melting was immediate. On thin-layer chromatography in each of three different solvent systems, the compound appeared homogeneous. The unusual melting point behaviour was ascribed to dimorphism.

The diol (4.4 g) in tetrahydrofuran (40 ml) was treated successively with \( n \)-butyl-lithium in hexane (10.5 ml), carbon disulphide (1.22 ml), and methyl iodide (1.01 ml). The isolation procedure was similar to that described above for the mannitol thionocarbonate and yielded, after two crystallisations from light petroleum–benzene, the title compound (1.75 g, 52% on utilised diol), m.p. 120–122°, \( [\alpha]_{D}^{21} -53.2° \) (c 2.14, chloroform). (Found: C, 51.4; H, 6.55; S, 10.65. \( C_{19}H_{20}O_{6}S \) calc.: C, 51.3; H, 6.6; S, 10.5%). Extraction of the aqueous filtrate with chloroform gave the starting diol (1.5 g).

\[\text{cis-3,4-Didehydro-3,4-dideoxy-di-O-isopropylidene-d-threo-hexitol} \quad (VII)\]

Treatment of the altritol thionocarbonate (1.38 g) in trimethyl phosphite (30 ml), as described above for the mannitol derivative, yielded the title compound as a colourless liquid (0.8 g, 77%), b.p. 84–86°/1 mm, \( [\alpha]_{D}^{21} -8.1° \) (c 2.2, chloroform), \( n_D^{26} 1.4499. \) (Found: C, 63.1; H, 8.7. \( C_{12}H_{20}O_{4} \) calc.: C, 63.1; H, 8.8%).

Ozonolysis of the olefin, as described above, followed by reduction (with catalytic hydrogenation), yielded a residue (0.067 g, 60%) which was \( p \)-phenyl-
azobenzoylated to give 2,3-O-isopropylidene-1-O-phenylazobenzoyl-D-glycerol (0.038 g, 13% based on olefin), showing a double m.p. at 83° and 92–94°. The infrared spectrum and that of the authentic material were identical. The material showing double melting-point behaviour was redissolved in methanol and seeded with authentic compound, m.p. 92–94°. The material obtained had m.p. 92–94° (without preliminary melting at 83°), and, with the authentic compound, mixed m.p. 92–94°.

1,2:5,6-Di-O-isopropylidene-D-altroitol 3,4-carbonate (VI, Y = O)

(a) From the diol. 1,2:5,6-Di-O-isopropylidene-D-altroitol (V) (2.02 g) in pyridine (20 ml) was cooled in an ice-salt bath and a solution of methyl chloroformate (0.66 ml) in carbon tetrachloride (25 ml) added dropwise with stirring over 15 min. The mixture was stored overnight at 0° and then poured into a stirred mixture of ice-water (50 ml) and chloroform (50 ml). The organic layer was separated, and the aqueous layer further extracted with chloroform (3 × 20 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate and water. Concentration of the dried solution gave a residue from which last traces of pyridine were removed by the repeated addition and distillation of toluene. Dry N,N-dimethylformamide (20 ml) and a catalytic quantity of sodium methoxide (ca. 0.025 g) were added, and the mixture heated at 100° for 15 min. The residue obtained on concentration was dissolved in chloroform, washed with dilute acetic acid and water, and then dried. Removal of the solvent and crystallisation of the residue from methanol gave the 3,4-carbonate (0.55 g, 25%), m.p. 175–177°, [α]D21 −78.3° (c 1.7, chloroform) (Found: C, 54.3; H, 7.1. C13H20O7 talc.: C, 54.15; H, 7.0%).

(b) From the thionocarbonate. 1,2:5,6-Di-O-isopropylidene-D-altroitol 3,4-thionocarbonate (0.1 g) in methanol (20 ml) was stirred vigorously with silver carbonate for 2 h. The filtered solution was concentrated, clarified with charcoal in methanol, and crystallised from the same solvent to give the title compound (0.04 g, 42%), m.p. 175–177° (mixed m.p. 175–177°), infrared spectrum indistinguishable from that of the authentic compound.

Benzyl 2-O-benzyl-β-L-arabinopyranoside (VIII)

The hydrolysis is a modification of that due to Wold. A mixture of benzyl 2-O-benzyl-3,4-O-isopropylidene-β-L-arabinopyranoside (11.24 g) in water (80 ml) and glacial acetic acid (20 ml) was boiled under reflux for 2 h with vigorous stirring; complete solution was not achieved. The crystalline mass obtained on cooling was collected and dried in vacuo over phosphorus pentoxide to give the product (8.0 g, 85%), m.p. 130–131°, [α]D26 +194° (c 0.75, chloroform) (Found: C, 69.35; H, 6.65. C16H22O5 calc.: C, 69.1; H, 6.7%).

Benzyl 2-O-benzyl-β-L-arabinopyranoside 3,4-thionocarbonate (IX, Y = S)

The mixture obtained by treatment of benzyl 2-O-benzyl-β-L-arabinopyranoside (6.6 g) in tetrahydrofuran (50 ml) successively with n-butyl-lithium solution (12.3 ml),
carbon disulphide (1.45 ml), and methyl iodide (1.25 ml) was poured into water to give a yellow solid which was collected and dissolved in chloroform (60 ml). Light petroleum (60 ml) was added and, after storage at 0° for 1 h, the unchanged starting diol (2.2 g) was collected. The filtrate was concentrated, and the residue crystallised from benzene–light petroleum to give a further quantity of diol (0.77 g). The solvent was removed from the mother liquor, and the material crystallised from ethanol to give the title compound (2.95 g, 73% on utilised diol), m.p. 99–101°, \([\alpha]_D^{18} + 175°\) (c 1.3, chloroform). (Found: C, 64.7; H, 5.7; S, 8.5%. C_{20}H_{20}O_{3}S calc.: C, 64.5; H, 5.4; S, 8.6%).

**Benzyl 2-O-benzyl-3,4-didehydro-3,4-dideoxy-\(\alpha\)-D-\(\alpha\)-cyano-pentoside (X)**

Reaction of the above thionocarbonate (2.2 g) in trimethyl phosphite (35 ml) yielded, on crystallisation from ethyl acetate–light petroleum, the product (1.24 g, 73%), m.p. 33–35°, \([\alpha]_D^{18} + 115°\) (c 1.9, chloroform) (Found: C, 76.55; H, 6.8. C_{19}H_{20}O_{2} calc.: C, 77.0; H, 6.8%).

Ozonolysis of the olefin in the manner already described (without catalytic hydrogenation), followed by reduction, and benzoylation of the diol (0.097 g) so produced, gave 3-O-benzoyl-2-O-benzyl-D-glyceraldehyde (2-benzoyloxyethyl) benzyl acetal (XI) (0.094 g, 52% on olefin), m.p. 78–79°, alone or in admixture with the authentic compound. The infrared spectrum was indistinguishable from that of the authentic compound.

3-O-Benzoyl-2-O-benzyl-D-glyceraldehyde (2-benzoyloxyethyl) benzyl acetal (XI, \(R = Bz\))

To a stirred solution of benzyl 2-O-benzyl-\(\beta\)-L-arabinopyranoside (0.66 g) in purified ethyl acetate (20 ml) was added lead tetra-acetate (0.886 g) over 15 min. The precipitated lead acetate was removed and the filtrate concentrated. The residue was dissolved in ethanol (20 ml) and water (10 ml), and potassium borohydride (0.7 g) added. After 12 h at room temperature, the solution was brought to pH 7.5 with glacial acetic acid and, after evaporation of the ethanol, was extracted with chloroform (4 × 50 ml). The combined extracts were washed with water (20 ml), dried, and concentrated to give the syrupy diol (XI, \(R = H\)) (0.59 g). Benzylation in pyridine gave the product (0.35 g, 66%), m.p. 79–80°, \([\alpha]_D^{37} + 40.3°\) (c 1.3, chloroform) (Found: C, 73.5; H, 5.95. C_{28}H_{32}O_{7} calc.: C, 73.3; H, 6.0%).

**Benzyl 2-O-benzyl-\(\beta\)-L-arabinopyranoside 3,4-carbonate (IX, \(Y = O\))**

(a) From the diol. Benzyl 2-O-benzyl-\(\beta\)-L-arabinopyranoside (1.1 g) was treated with methyl chloroformate (0.29 ml) in pyridine (15 ml) and carbon tetrachloride (10 ml), as previously described for the preparation of the altritol derivative. The product obtained after the cyclisation of the acyclic carbonate in \(N, N\)-dimethylformamide was crystallised from ethyl acetate–light petroleum to give the starting diol (0.39 g). The mother liquor was concentrated and the residue crystallised from methanol to yield a product (0.37 g, 48% on unrecovered diol), m.p. 83–89°.
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which was recrystallised from methanol to give the title compound, m.p. 88–90°*, 
\([\alpha]_D^{20} +166^\circ (c 1.0, \text{ chloroform})\) (Found: C, 67.0; H, 5.7. \(C_{20}H_{20}O_8\) calc.: C, 67.4; 
H, 5.7%).

(b) From the thionocarbonate. Treatment of benzyl 2-O-benzyl-\(\beta\)-L-arabino-
pyranoside 3,4-thionocarbonate (0.25 g) in methanol (10 ml) and benzene 10 ml) 
with silver carbonate, in the same way as for the altritol thionocarbonate derivative, 
gave, from methanol, the carbonate (0.054 g, 23%), m.p. 86.5–87° (mixed 
m.p. 87–89°), infrared spectrum indistinguishable from that of the authentic com-
pound.

Benzylation of 2,3-O-isopropylidene-\(L\)-rhamnose

2,3-O-Isopropylidene-\(L\)-rhamnose was prepared by the method already 
described\[20\], except that the residue obtained on concentration of the chloroform 
solution was not distilled. Instead, it was partitioned between ethyl acetate (100 ml) 
and saturated aqueous sodium hydrogen carbonate (35 ml). The aqueous layer 
was extracted with ethyl acetate (2 × 75 ml), and the combined organic solutions 
were washed with water (2 × 10 ml) and dried. Concentration of the solution 
gave a residue which was crystallised from ethyl acetate–light petroleum to yield 
2,3-O-isopropylidene-\(L\)-rhamnose (15.4 g), m.p. 84–86°, \([\alpha]_D^{25} +17.6^\circ\) (0.5 h) \(\rightarrow\) 
+20.7° (15 h) (c 2.8, water)\[**\]. Further product (9.7 g) was obtained from the mother 
liquor and had m.p. 82–90°. Material of variable m.p. (83–90°) was obtained on 
recrystallisation; the m.p. was not consistently raised by further recrystallisations. 
After storage for several months over phosphorus pentoxide, the material had 
m.p. 90–93°.

The benzylation of 2,3-O-isopropylidene-\(L\)-rhamnose\[***\] (m.p. 84–86°) was 
carried out as described by Schmidt et al.\[9\]. The isomer, m.p. 102–104°, \([\alpha]_D^{20} +30.1^\circ\) 
(c 2.0, acetone) (lit\[9\], m.p. 104°, \([\alpha]_D^{20} +30.3^\circ\) in acetone) was obtained by fractional 
crystallisation of the reaction product. Two components of the crude benzylation 
product were detected by thin-layer chromatography in benzene. One (\(R_F\) 0.3) 
corresponded to the isomer with m.p. 102–104°, and the other had \(R_F\) 0.6, and 
was present apparently in the lesser amount. A preparative separation of the crude 
product (13.7 g) was carried out on silica gel (1.1 kg) using benzene–ether 
(24:7:0.3, v/v) and collecting 500 ml fractions. Fractions 18–32 gave the compound 
with \(R_F\) 0.6 (4.8 g), which on recrystallisation from methanol gave benzyl 4-O-
benzyl-2,3-O-isopropylidene-\(\alpha\)-L-rhamnopyranoside (1.9 g), m.p. 95–97°, \([\alpha]_D^{25} -67.6^\circ\)

*The analytical sample showed a double melting point. On first determination, it had m.p. 84–86° 
and, after resolidification, m.p. 88–90°.

**Freudenberg and Wolf\[15\] describe two isomers of this compound; one had m.p. 87–89°, 
\([\alpha]_D^{25} +13.5^\circ\) (5 min) \(\rightarrow\) +17.8° (equilibrium, water), and the second had m.p. 79–80°, 
\([\alpha]_D^{25} +10.9^\circ\) (5 min) \(\rightarrow\) +17.6° (equilibrium, water). Both isomers give 5-O-methyl-\(L\)-rhamnose 
on methylation followed by hydrolysis\[15,21\], and have been formulated as \(\beta\)- and \(\alpha\)-rhamnofuranose 
derivatives, respectively\[21\].

***Schmidt et al.\[9\] gave no constants for this compound, but gave reference to its method of prepa-
ration, from which it may be assumed that it had m.p. 90–91°.

*Carbohydrate Res., 1 (1965) 214–228*
Further elution with benzene–ether (1:1, v/v) yielded the material with $R_f$ 0.3 (7.0 g), which was crystallised from methanol to give benzyl 4-O-benzyl-2,3-O-isopropylidene-β-L-rhamnopyranoside (3.7 g), m.p. 102–104°.

**Acid hydrolysis of benzyl 4-O-benzyl-2,3-O-isopropylidene-α- and β-L-rhamnopyranoside**

(a) *Removal of the isopropylidene group.* A mixture of benzyl 4-O-benzyl-2,3-O-isopropylidene-α-L-rhamnopyranoside (0.86 g) and 0.05N hydrochloric acid (9 ml) was heated under reflux at 100°, and enough ethanol (ca. 10 ml) added to achieve solution. After 1 h, the solution was neutralised with sodium hydrogen carbonate and cooled to give colourless crystals which were collected and dried over phosphorus pentoxide *in vacuo*. Recrystallisation of the dried material from ethyl acetate–light petroleum gave benzyl 4-O-benzyl-α-L-rhamnopyranoside (0.47 g, 61%), m.p. 86–88°, $[\alpha]^D_{\text{D}} +88.8°$ (c 3.5, acetone) (Found: C, 69.7; H, 7.1%. $\text{CsH}_{24}\text{O}_5$ talc.: C, 69.7; H, 7.0%).

Similar treatment of benzyl 4-O-benzyl-2,3-O-isopropylidene-β-L-rhamnopyranoside (3.95 g) gave benzyl 4-O-benzyl-β-L-rhamnopyranoside (2.94 g, 83%), m.p. 76–78°, $[\alpha]^D_{\text{D}} +47°$ in acetone; lit.°, m.p. 77.5°, $[\alpha]^D_{\text{D}} +48.2°$ in acetone.

(b) *Complete hydrolysis followed by reduction.* A solution of benzyl 4-O-benzyl-2,3-O-isopropylidene-α-L-rhamnopyranoside (1 g) in ethanol (20 ml) and N sulphuric acid (58 ml) was heated at 100°. Aliquots were taken at intervals and their rotations measured. After 6 h, the rotation was constant ($[\alpha]_{D}$−24°) and sodium hydrogen carbonate was added until the solution was neutral. After the addition of potassium borohydride (0.5 g), the solution was stored overnight at room temperature. Glacial acetic acid was added until the pH was 7.5, and the solution was then concentrated. After repeated evaporation of methanol from the residue, it was dissolved in water (30 ml) and the solution was extracted continuously with chloroform for 5.5 h. On concentration, the dried extract gave an oil which crystallised from ethyl acetate to give a solid (0.25 g), m.p. 86–89°; two further recrystallisations from the same solvent gave 4-O-benzyl-L-rhamnitol, m.p. 90–91°, $[\alpha]^D_{\text{D}} −7.0°$ (c 1.4, ethanol) (Found: C, 61.3; H, 8.0. C₁₃H₂₀O₅ calc.: C, 60.9; H, 7.9%). The compound reacted with 1.98 mol. of sodium metaperiodate per mol. in a quantitative determination.

Similarly, benzyl 4-O-benzyl-2,3-O-isopropylidene-β-L-rhamnopyranoside yielded 4-O-benzyl-L-rhamnitol, m.p. 90–91°, alone or in admixture with the compound from the above preparation. The infrared spectra of the products from the two preparations were indistinguishable.

5-O-Benzyl-L-rhamnitol

1,2:3,4-Di-O-isopropylidene-L-rhamnitol¹⁰ (2.5 g) in benzyl chloride (10 ml) was stirred with powdered potassium hydroxide (5 g) at 100° for 5 h. Water (50 ml) was then added and the reaction mixture was extracted with chloroform (4 × 50 ml). The combined extracts were washed with water (20 ml) and the solution dried

*Carbohydrate Res.*, 1 (1965) 214–228
(K$_2$CO$_3$) overnight. Concentration, finally at 80°/2 mm, gave a liquid which showed one main component ($R_F$ 0.53) on thin-layer chromatography (CHCl$_3$), a small amount of starting material, and a fast-running compound ($R_F$ 0.86). The liquid was distilled (b.p. 140-160°/0.6 mm) to yield a product containing no starting material, but which was still contaminated with the material with $R_F$ 0.86. Chromatography on silica gel (35 g), using chloroform and collecting 20 ml fractions, gave the fast-running compound (0.05 g) in fractions 4-7. Elution with chloroform–ethanol (4:1, v/v) gave the chromatographically pure product (0.22 g). In a large scale preparation, the crude benzylolation product (2.55 g) yielded, after chromatography, the required compound ($R_F$ 0.53) (1.46 g, yield reduced by spillage), which was distilled to give 5-O-benzyl-1,2:3,4-di-O-isopropylidene-L-rhamnitol (1.1 g), b.p. 154-156°/0.6 mm, $n_D$ 1.4851, $[a]_D^{20}$ 0.0° (c 0.96, chloroform) (Found: C, 67.6; H, 8.1. Cl$_{19}$H$_{28}$O$_5$ talc.: C, 67.8; H, 8.4).

The above compound (0.61 g) in aqueous acetic acid (12 ml, 1:1, v/v) was boiled under reflux for 4 h. Concentration yielded a residue from which water was removed by repeated addition and evaporation of absolute alcohol. Alcohol was removed similarly with ethyl acetate. Crystallisation of the material from ethyl acetate gave 5-O-benzyl-L-rhamnitol (0.25 g, 54%), m.p. 143-146°, $[a]_D^{20}$ +24.4° (c 1.2, ethanol) (Found: C, 60.7; H, 8.1. Cl$_{13}$H$_{20}$O$_5$ calc.: C, 60.9; H, 7.9%). The compound reacted with 2 mol. of sodium metaperiodate per mol.

Benzyl 4-O-benzyl-β-L-rhamnopyranoside 2,3-thionocarbonate (XIII, Y = S)

Benzyl 4-O-benzyl-β-L-rhamnopyranoside (2.94 g) in tetrahydrofuran (50 ml) was treated successively with n-butyl-lithium (5.3 ml), carbon disulphide (0.63 ml), and methyl iodide (0.54 ml), as described for the preparation of the mannitol thionocarbonate. The mixture was poured into ice-water (150 ml) and extracted with chloroform (3 x 50 ml). The extract was washed with water (10 ml), dried, and concentrated. The residue was dissolved in chloroform (10 ml) and light petroleum (40 ml) and, after storage at 0° overnight, the precipitated material was collected. Recrystallisation from absolute ethanol gave the product (0.79 g, 38% based on utilised dial), m.p. 141-142°, $[a]_D^{20}$ +49.7° (c 1.4, chloroform) (Found: C, 65.0; H, 6.05; S, 8.4. C$_{21}$H$_{22}$O$_5$S calc.: C, 65.25; H, 5.7; S, 8.3%).

Evaporation of the solvent from the mother liquor, and crystallisation of the residue from ethyl acetate–light petroleum gave the starting diol (1.1 g).

Benzyl 4-O-benzyl-2,3-didehydro-2,3,6-trideoxy-β-1-erythro-hexoside (XIV)

Treatment of benzyl 4-O-benzyl-β-L-rhamnopyranoside 2,3-thionocarbonate (0.76 g) with trimethyl phosphite (15 ml), in the manner previously described, gave a liquid which was distilled to yield the title compound (0.35 g, 57%), b.p. 200-210°/1 mm, $[a]_D^{25}$ -73.5° (c 1.7, chloroform) (Found: C, 77.0; H, 7.0. C$_{20}$H$_{22}$O$_5$ calc.: C, 77.4; H, 7.2%). The olefin appeared homogeneous by thin-layer chromatography in chloroform and benzene. On storage at -15°, the product solidified.
Ozonolysis of the olefin (0.10 g), as described previously (without catalytic hydrogenation), gave a liquid (0.073 g) which was benzoylated in the usual manner. Thin-layer chromatography of the crude benzoate showed the presence of several components, with the expected product predominating. The crude product was treated in methanol with charcoal and the solution stored at $-15^\circ$, when crystallisation occurred slowly. The solid (0.018 g) was collected, and two crystallisations from ethyl acetate–light petroleum gave 4-\textit{O}-benzoyl-2-\textit{O}-(2-benzoyloxy-\textit{r}-benzoyloxy-\textit{ethyl})-3-\textit{O}-benzyl-\textit{l}-deoxy-\textit{d}-erythritol (XV, $R = \text{Bz}$) (0.010 g, 6\% on olefin), m.p. 60–61° (mixed m.p. 60–62°). The infrared spectrum was indistinguishable from that of the authentic sample. No other product separated out on storage of the mother liquor at $-15^\circ$ for several weeks.

4-\textit{O}-Benzy\textit{l}-2-\textit{O}-(2-benzoyloxy-\textit{r}-benzoyloxy-\textit{ethyl})-3-\textit{O}-benzyl-\textit{l}-deoxy-\textit{d}-erythritol (XV, $R = \text{Bz}$)

Benzyl 4-\textit{O}-benzyl-\textit{p}-\textit{L}-rhamnopyranoside (0.24 g) was oxidised with lead tetra-acetate (0.31 g) in purified ethyl acetate (20 ml). Filtration and concentration of the reaction mixture gave a syrup. Toluene (5 ml) was distilled from the residue which was then dissolved in water (20 ml) and ethanol (20 ml), and sufficient sodium hydrogen carbonate added to make the solution alkaline. After the addition of potassium borohydride (0.3 g), the solution was stored at room temperature overnight. Glacial acetic acid was then added to adjust the pH to 7.5, and ethanol was removed by evaporation of the solution to half its original volume. Extraction with chloroform (5 x 20 ml), followed by concentration of the dried extract, gave a syrup (0.16 g) which was benzoylated in the usual manner. Crystallisation of the product twice from ethyl acetate–light petroleum yielded material (0.14 g, 55\%), m.p. 59–62°. Two further crystallisations from methanol yielded the title compound, m.p. 60–62°, $[\alpha]_D^{28} +2.9^\circ$ (c 1.55, chloroform) (Found: C, 73.7; H, 6.2. C$_{34}$H$_{34}$O$_7$ calc.: C, 73.6; H, 5.8\%).

Benzyl 4-\textit{O}-benzyl-\textit{p}-\textit{L}-rhamnopyranoside 2,3-carbonate (XIII, $Y = O$)

(a) \textit{From the diol}. Benzyl 4-\textit{O}-benzyl-\textit{p}-\textit{L}-rhamnopyranoside (1.24 g) was treated in pyridine (15 ml) and carbon tetrachloride (20 ml) with methyl chloroformate (0.31 ml) in carbon tetrachloride (15 ml), and the cyclic carbonate prepared and isolated as described previously. Attempted preferential crystallisation of the cyclic carbonate from methanol was unsuccessful. The reaction product was therefore chromatographed on silica gel (100 g) using chloroform–ether (9:1, v/v). The cyclic carbonate was eluted first and crystallised from ethyl acetate–light petroleum to yield the title compound (0.08 g, 14\% on utilised diol), m.p. 92–93°, $[\alpha]_D^{23} +31.7^\circ$ (c 1.9, chloroform) (Found: C, 67.8; H, 5.9. C$_{34}$H$_{33}$O$_6$ calc.: C, 68.1; H, 6.00).

Further elution of the column with chloroform–ether (1:1, v/v) gave the starting diol (0.71 g).

(b) \textit{From the thionocarbonate}. A solution of benzyl 4-\textit{O}-benzyl-\textit{p}-\textit{L}-rhamnopyranoside 2,3-thionocarbonate (0.117 g) in methanol (5 ml) and benzene
(5 ml) was shaken vigorously with silver carbonate (0.36 g) for 5 h. The filtered solution was concentrated, and the material crystallised from ethyl acetate-light petroleum to yield the carbonate (0.024 g, 21%), m.p. 91–93° (mixed m.p.), infrared spectrum indistinguishable from that of the authentic compound.

Test for unsaturation with aqueous potassium permanganate

Each of the four olefinic compounds described herein reacted with aqueous potassium permanganate to yield yellow solutions. Vigorous shaking was necessary due to the low solubility of the compounds in aqueous media.

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SUMMARY

The degradation of thionocarbonates, prepared from vicinal diols in the alditol series, and of cis-vicinal diols when part of an aldopyranose, has been investigated as a means of introducing unsaturation into molecules of the carbohydrate type.

The O-benzylation of mono-O-isopropylidene-L-rhamnose has been shown to give the anomeric benzyl 4-O-benzyl-2,3-O-isopropylidene-L-rhamnopyranosides. This contrasts with O-toluene-p-sulphonylation in pyridine, and O-methylation by Purdie's method, both of which yield 5-substituted 2,3-O-isopropylidene-L-rhamnofuranose derivatives.

REFERENCES

9 O. Th. Schmidt, E. Flankenhorn, and F. Kübler, Ber., 75 (1942) 579.
15 K. Freudenberg and A. Wolf, Ber., 59 (1926) 836.