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CRYSTALLINE 2,3:4,5-DI-*O*-ISOPROPYLIDENE-DL-ARABINOSE DIETHYL DITHIOACETAL: SOME REACTIONS OF ACETAL DERIVATIVES OF ARABINOSE*

DEREK HORTON AND OSCAR VARELA
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)
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ABSTRACT

Acetonation of the diethyl dithioacetals of D- and L-arabinose gives the corresponding 2,3:4,5-diisopropylidene acetals (**2a** and **2b**) as oils having $[\alpha]_D$ +82 and −81°, respectively; in admixture, the enantiomers form a well crystallized racemate, m.p. 43–45°. The initial product of acetonation is the 4,5-monoisopropylidene acetal. Demercaptalation of **2a** with mercury(II) chloride–cadmium carbonate gives 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**5**) in high yield, but the literature procedure employing mercury(II) chloride–mercury(II) oxide affords a mixture of **5** and 1,2:3,4-di-*O*-isopropylidene-β-D-arabinopyranose (**6**). A trace of acid readily and completely converts the aldehydo derivative **5** into the cyclic diacetal **6**.

INTRODUCTION

The dithioacetals of sugars are of great utility in a wide range of syntheses[1], and have been extensively utilized in this laboratory, especially for access to aldehydo sugars *via* *O*-substitution and subsequent demercaptalation. In chiral syntheses of non-carbohydrate products from sugar precursors, arabinose is a particularly convenient starting-material, as it is readily available in both enantiomeric forms and thus allows versatility in access to particular target molecules. Such an approach has been used to synthesize optically pure tetra-*C*-substituted cyclopentane derivatives of defined relative and absolute stereochemistry[2].

In work that has utilized the 2,3:4,5-diisopropylidene acetals (**2a** and **2b**) of D- and L-arabinose diethyl dithioacetal as precursors for the corrsponding *O*-substituted aldehydo aldose derivatives, unusual behavior has been encountered in the properties of the acetals **2a** and **2b**, and the demercaptalation of these products has frequently proved difficult to control, leading to mixtures of products.

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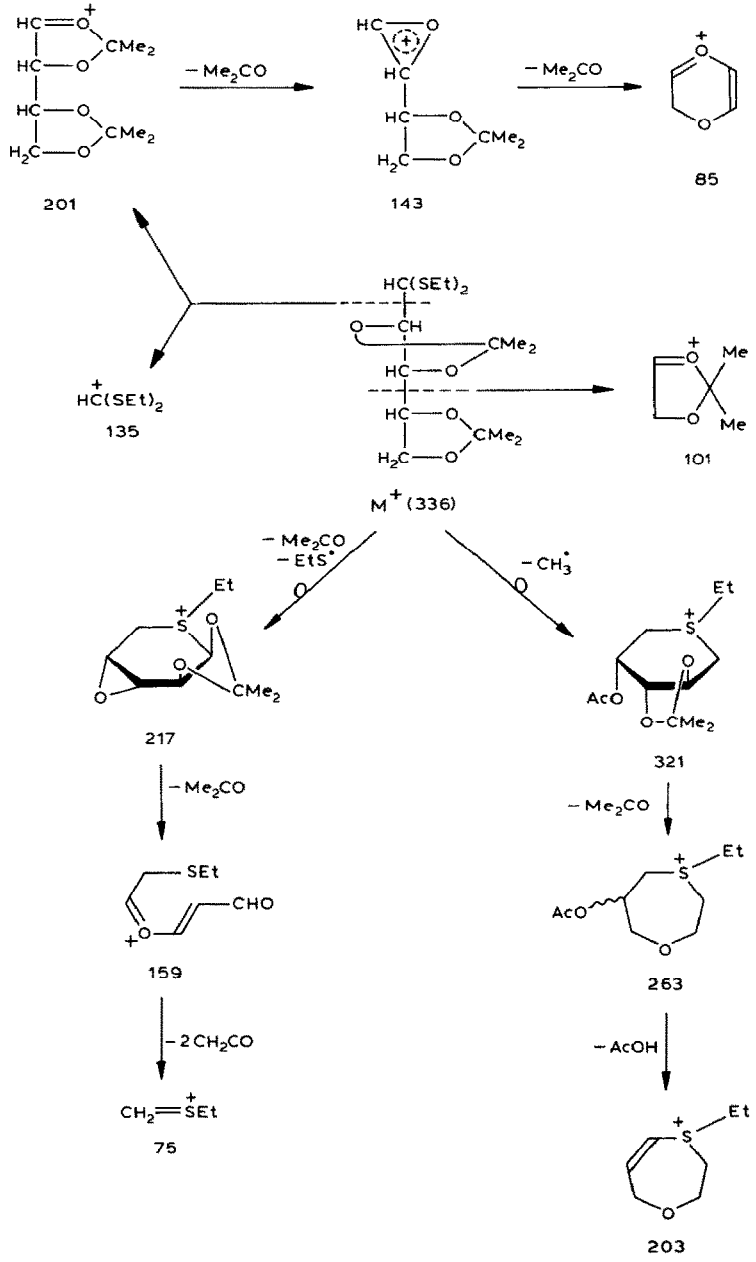
It is shown here that the acetals **2a** and **2b**, obtained as oils of high specific rotation, form in admixture a well crystallized racemate that had been fortuitously encountered as a result of pooling of batches of product prepared from commercial supplies of arabinoses that were mislabelled as to their enantiomeric form. Demercaptalation of the acetals needs to be conducted under carefully controlled conditions if acid-catalyzed conversion of the aldehydo aldose product into the corresponding 1,2:3,4-di-*O*-isopropylidene-β-arabinopyranose is to be prevented.

RESULTS AND DISCUSSION

Various catalysts have been used for the acetonation of arabinose diethyl dithioacetal in acetone solution; these include copper(II) sulfate[3], sulfuric acid–copper(II) sulfate[4], sulfuric acid–copper(II) sulfate–diphosphorus pentaoxide[5], and sulfuric acid alone[6,7]. The 2,3:4,5-diisopropylidene acetal is subsequently isolated pure from the product mixture by distillation or chromatography. In our work, D-arabinose diethyl dithioacetal was acetonated with the use of sulfuric acid, and the mixture made neutral with aqueous ammonia; column-chromatographic purification afforded ~90% of pure 2,3:4,5-di-*O*-isopropylidene-D-arabinose diethyl dithioacetal (**2a**) as an oil having $[\alpha]_D$ +82° in methanol, in accord with literature[3–5] values; this compound has resisted all attempts, by a number of workers in this laboratory over a 20-year period, to induce crystallization. Similar acetonation of the L dithioacetal (**1**) gave the enantiomeric diisopropylidene acetal **2b**, likewise always as an oil, whose specific rotation (−81° in methanol) was in agreement with literature values[6,7].

When **2a** and its enantiomer (**2b**) were mixed in equal amounts, and the mixture dissolved in pentane, a crystalline precipitate formed upon cooling the solution for a few h. Recrystallization from pentane afforded large, colorless, optically inactive prisms, m.p. 43–45°, whose i.r., ^{1}H- and ^{13}C-n.m.r., and mass spectra were identical to those of the separate, syrupy enantiomers; the crystals gave an acceptable elemental analysis. The observed behavior demonstrates that a racemic compound[8] is formed, and explains why scaled-up preparations of putative **2a** and **2b** isolated in this laboratory on various occasions have afforded semi-crystalline distillates of impeccable chromatographic homogeneity and n.m.r.-spectral characteristics showing no evidence of impurity, but which displayed anomalously low magnitudes of optical rotation[9]. The preparations had used pooled samples of dithioacetal precursors obtained from diferent commercial lots of D- and L-arabinose. It was subsequently found that a commercial batch supplied as L-arabinose was, in fact, (−)-D-arabinose (in the early literature termed "*l*-arabinose"), and thus the semicrystalline product of anomalously low rotation was a mixture of the racemate **2a,b** with one of the pure enantiomers. These observations indicate the need for caution in verifying the enantiomeric identity of arabinose samples from commercial sources.

The electron-impact, mass spectrum of **2a** (or **2b**) showed (see Scheme 1) the



Scheme 1. Mass-spectral fragmentation of **2a**; *m/z* values are given below the ions.

molecule-ion (*m/z* 336) as 35% of the base peak (*m/z* 43, CH_3CO^+, 100%). Supportive evidence for the 2,3:4,5 substitution-mode in acetal **2a,b** was provided by the ions at *m/z* 135 [$(EtS)_2CH^+$] and 201 (formed by C-1–C-2 cleavage), and *m/z*

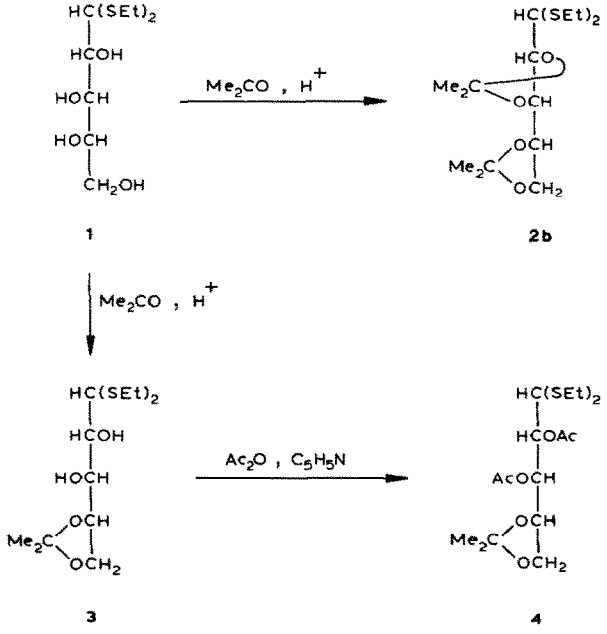
101, arising from C-3–C-4 cleavage. From *m/z* 201, loss of acetone gives the ion *m/z* 143, from which further elimination of acetone or of ketene affords *m/z* 85 or 101, respectively. From the molecule-ion, successive losses of a methyl group followed by acetone, acetic acid, or both, generate *m/z* 263, 261, and 203. Similar fragmentation-modes have been proposed for related isopropylidene acetals[10]. Alternatively, rearrangement of the molecule-ion with loss of acetone and an ethylthio radical would yield the cation having *m/z* 217, and further eliminations of acetone and 2 molecules of ketene would produce the fragments at *m/z* 159 and 75. The intense peak at *m/z* 59 may be attributed to protonated acetone.

The ^{13}C-n.m.r. spectrum of **2a,b** provided further verification that the isopropylidene groups are engaged in 1,3-dioxolane rings; as demonstrated by Buchanan *et al.*[11], the chemical shifts both of the quaternary and the methyl carbon atoms are sensitive to the ring size and conformation of the acetal. They proposed[11] δ 108.1–111.4 for the acetal carbon atom and δ 23.3–28.3 for the methyl group of a 2,2-dimethyl-1,3-dioxolane ring. The corresponding resonances for **2a,b** lie within these ranges. For the sugar-chain backbone, the C-5 (δ 67.5) and C-1 (δ 52.5) signals were readily recognized, as were the methyl-group signals of the dithioacetal (δ 14.2); the carbon signals of the CH_2 groups of the ethylthio groups overlapped with the methylene-group signals of the dioxolane rings.

The ^{1}H-n.m.r. spectrum of **2a** (or of **2b**) afforded additional consolidation of the structure and conformation, as well as correlation with the X-ray crystallographic analysis[12] of a related compound, the *Z*-enol acetate of the aldehydo sugar (**5**) derived from **2a**. The large value (7.3 Hz) of $J_{3,4}$ indicated the antiparallel disposition of H-3 and H-4 in the most populated conformational state, as observed[12] crystallographically for the *Z*-enol acetate of **5**. The value of $J_{2,3}$ is similar to that observed by Hall and co-workers[13] for related compounds; its magnitude depends on the extent of twist in the dioxolane ring. An essentially gauche disposition of H-1 and H-2 was indicated by the small value (2.5 Hz) of $J_{1,2}$, although there is probably some degree of torsion along C-1–C-2 to alleviate 1,3-parallel interactions involving one of the ethylthio groups in either of the two idealized, staggered conformations having H-1 and H-2 gauche-disposed.

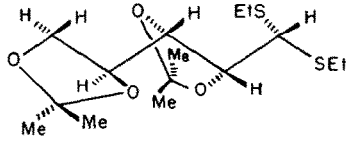
Accompanying the diacetal **2b** in the acetonation of **1** was a by-product identified as 4,5-*O*-isopropylidene-L-arabinose diethyl dithioacetal (**3**). The formation of a monoacetal derivative of D-arabinose diethyl dithioacetal had earlier been reported by Zinner and co-workers[5]. It is to be expected that monoacetonation would favor attack at the primary hydroxyl group, by analogy with detailed studies[14,15] on the acetonation of alditols under neutral or acid-catalyzed conditions, and the formation of **3** here is interpreted as the initial stage of the acetonation reaction under kinetic control.

The ^{1}H-n.m.r. spectrum of **3** was rather complex, but its diacetate **4** gave an essentially first-order spectrum. The downfield shifts of H-2 and H-3 relative to the diacetal confirmed that C-2 and C-3 of **3** are hydroxylated. The magnitudes of the coupling constants observed for **4** were similar to those for tetra-*O*-acetyl-D-

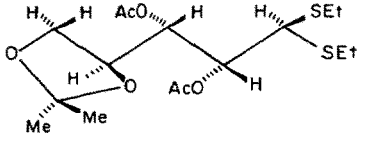


arabinose diethyl dithioacetal[16], but with $J_{1,2}$ and $J_{3,4}$ being somewhat smaller, and $J_{2,3}$ somewhat larger, suggesting that the five-membered ring involving C-4 and C-5 causes a slight distortion from the planar, zigzag, backbone chain that is normally[17] adopted by acyclic *arabino* derivatives.

The ^{13}C-n.m.r. spectra of **3** and **4** accorded with expectations, broadly resembling that of the diacetal **2a,b**. The diacetate **4** showed an acetyl-carbonyl resonance at 169.9 p.p.m. and a resonance at 109.6 p.p.m. for the quaternary carbon atom of the acetal group; the latter value is as expected for a 2,2-dimethyl-1,3-dioxolane[11].



2b



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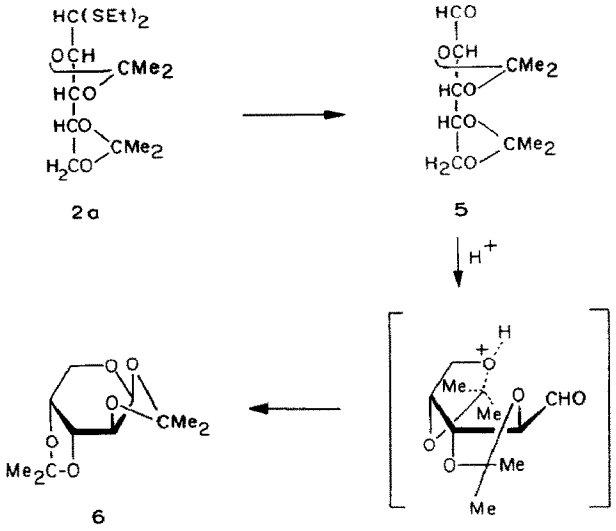
Demercaptalation of **2a** with mercury(II) chloride–cadmium carbonate in acetone according to the general procedure of Wolfrom *et al.*[18] gave 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**5**) in good yield. In contrast, use of the literature procedure[4,19] for demercaptalation of **2a** by use of mercury(II) chloride–



mercury(II) oxide, even with later modifications[9], was less satisfactory. The latter procedure is rapid and the starting material is consumed in <2 h (the cadmium carbonate-mediated reaction requires 12 h), but a mixture of two products is invariably formed, one being the expected aldehyde, and the other was here characterized as 1,2:3,4-di-*O*-isopropylidene-β-D-arabinopyranose (**6**). The proportion of the latter decreases when the reaction is conducted with larger volumes of solvent (acetone) and the suspension is stirred energetically. Compound **6** appears to arise through acid-catalyzed rearrangement of the aldehyde **5**, as treatment of the pure aldehyde **5** in acetone with cation-exchange resin led to quantitative conversion into **6**. Such a transformation presumably involves successive hydrolysis of the 4,5-acetal, tautomeric cyclization to the aldopyranoses, acetal migration to a conformationally more-stable *cis*-monoacetal, and subsequent reacetonation; the possibility exists that the isopropylidene groups are not completely detached during the process, but form transient monosubstituted intermediates.

Favored hydrolysis of the 4,5-*O*-isopropylidene group from **5** was to be expected, based on the generalization that the more-rapidly formed ring of a sugar diacetal may be selectively hydrolyzed[1] by aqueous acid; the terminal acetal ring of **2a** or **2b** may be selectively cleaved under very mild conditions[5,20]. During the conditions of demercaptalation, the hydrochloric acid liberated[6] would be expected to be neutralized by the base used, but, evidently, mercury(II) oxide is much less effective for this process than cadmium carbonate. Efficient stirring, and use of the

latter acid-acceptor, permitted preparation of pure aldehyde **5** in 73% yield, and none of the rearrangement product **6** could be detected. The rearrangement is not detectably catalyzed by silica gel, either under the conditions of t.l.c. or of column chromatography therewith.

The absence of furanoid products in the acid-catalyzed rearrangement of **5** to **6** is not unexpected, as conventional[21], or kinetic[22], acetonation of arabinose leads exclusively to pyranose derivatives. In this conversion, as in related, acid-catalyzed, acetal rearrangements[23–25], the driving force appears to be conversion into a thermodynamically more-stable product.

EXPERIMENTAL

General methods. — T.l.c. was performed on precoated glass plates (0.25 mm) of silica gel 60F-254 (E. Merck, Darmstadt, G.F.R.). Spots were detected by spraying the plates with 5% sulfuric acid, followed by heating. Silica gel 60 (Merck, 230–400 mesh) was used for column chromatography. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Specific rotations were determined with a Perkin–Elmer Model 141 polarimeter. I.r. spectra were recorded with a Perkin–Elmer 457 grating spectrophotometer. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-9 double-focusing, high-resolution spectrometer (70 eV). N.m.r. spectra were recorded by Dr. O. Mols with Bruker WP-200 or WM-300 spectrometers, at 200 or 300 MHz for protons, and 50.3 MHz for carbon-13. Chemical shifts refer to an internal standard of tetramethylsilane (δ 0.00); signal multiplicities are given as d, doublet; m, multiplet; q, quartet; s, singlet; and t, triplet. X-Ray powder diffraction data give interplanar spacings (Å) for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; w, weak; v, very. Elemental analyses were performed by Dr. O. Mols.

2,3:4,5-Di-O-isopropylidene-D-arabinose diethyl dithioacetal (**2a**). — The procedure used was essentially that previously employed in this laboratory[9]. To vacuum-dried D-arabinose diethyl dithioacetal (**1**; 10 g, 39 mmol) suspended in dry acetone (140 mL) was added sulfuric acid (0.25 mL). The mixture was stirred for 24 h at room temperature, made neutral with aqueous ammonia, filtered, and the filtrate evaporated to dryness. Extraction of the residue with hexane, and evaporation of the extract, gave a light-brown syrup (12.8 g, 98%), t.l.c. of which with 5:1 benzene–methanol showed **2a** as the main component (R_F 0.78) together with a minor component (R_F 0.44). The two components were separated pure from 1.0 g of the mixture on a short column eluted with 5:1 hexane–ethyl acetate, to give **2a** as a colorless syrup (0.91 g) that could not be induced to crystallize; $[\alpha]_D$ +82° (*c* 1.0, methanol); lit.[3] +57.8 ±2° (methanol), lit.[5] +86.0° (methanol), and lit.[4] +83.0° (methanol).

The slower-migrating component was isolated crystalline, and identified as 4,5-*O*-isopropylidene-D-arabinose diethyl dithioacetal (**3**).

2,3:4,5-Di-O-isopropylidene-L-arabinose diethyl dithioacetal (**2b**). — The procedure used for the D enantiomer was employed, but starting with the L enantiomer of **1**. Product **2b** was an oil having $[\alpha]_D$ −81° (*c* 1.0, methanol); lit.[6] −79.2° (chloroform), and lit.[7] −82° (methanol). The enantiomers **2a** and **2b** gave identical i.r. and ^{1}H-n.m.r. spectra.

Crystalline 2,3:4,5-di-O-isopropylidene-DL-arabinose diethyl dithioacetal (**2a,b**). — Compounds **2a** (100 mg) and **2b** (100 mg) were mixed, and dissolved in pentane (2 mL). Crystals separated from the solution after refrigeration for a few h; yield 150 mg. Recrystallization from pentane afforded the pure racemate **2a,b** as large, colorless, optically inactive prisms; m.p. 43–45°; ^{1}H-n.m.r. (Me_2SO-d_6): δ 4.23 (dd, $J_{2,3}$ 7.2 Hz, H-2), 4.15–4.03 (m, 2 H, H-4,5), 4.03 (d, $J_{1,2}$ 2.5 Hz, H-1), 3.91 (t, $J_{3,4}$ 7.3 Hz, H-3), 3.81 (dd, $J_{4,5'}$ 4.4, $J_{5,5'}$ 8.0 Hz, H-5'), 2.65 (m, 4 H, 2 SCH_2CH_3), 1.34, 1.32, 1.30, 1.26 (s, 12 H, 2 CMe_2), and 1.18 (m, 6 H, 2 SCH_2CH_3); ^{13}C-n.m.r. ($CDCl_3$): δ 110.3, 109.8 (CMe_2), 84.6, 79.2, 77.2 (C-2,3,4), 67.7 (C-5), 52.5 (C-1), 27.1, 26.9, 26.4, 25.1 (× 2), 24.8 (CMe_2 and SCH_2CH_3), and 14.2 (× 2, SCH_2CH_3); *m/z*: 338 (4%), 337 (6), 336 (M^+, 35), 321 (5), 263 (3), 261 (1), 217 (33), 203 (9), 201 (2), 177 (4), 159 (15), 143 (96), 135 (90), 101 (22), 87 (18), 85 (15), 75 (18), 59 (55), and 43 (100); X-ray powder diffraction data: 10.5 s (2), 8.78 m, 7.51 m, 6.94 vs (1), 6.63 m, 5.82 w, 5.14 m, 4.78 m, 4.47 s (3), 4.29 s, and 4.01 m.

Anal. Calc. for $C_{15}H_{28}O_4S_2$: C, 53.39; H, 8.32. Found: C, 53.30; H, 8.21.

The ^{1}H- and ^{13}C-n.m.r. spectra of **2a,b** were identical with the respective spectra of the separate enantiomers, as were the i.r. spectra (KBr pellets) of **2a,b** in the region 4000–600 cm^{-1}.

4,5-O-Isopropylidene-L-arabinose diethyl dithioacetal (**3**). — To a solution of L-arabinose diethyl dithioacetal (1.00 g, 3.9 mmol) in dry acetone (20 mL) containing sulfuric acid (0.05 mL) was added molecular sieves (0.5 g). The mixture was stirred for 4 h at room temperature, made neutral with aqueous ammonia, filtered, and the filtrate evaporated. The residue was extracted with boiling ether, and the filtered extract diluted with hexane. Colorless needles were obtained after storage for a few h at room temperature; yield 0.97 g (84%). Recrystallization from ether–hexane gave pure **3** having m.p. 76°, $[\alpha]_D^{25}$ +70.2° (*c* 1.0, chloroform) {lit.[5] m.p. 70–72°, $[\alpha]_D^{20}$ −68.9° (chloroform) for the enantiomer}; ^{1}H-n.m.r. (C_6D_6): δ 4.17–3.93 (m, 6 H, H-1,2,3,4,5,5'), 3.13 (d, OH), 2.49–2.33 (m, 4 H, 2 SCH_2CH_3), 2.20 (broad d, OH), 1.44, 1.30 (s, 6 H, CMe_2), and 1.06–0.92 (m, 6 H, 2 SCH_2CH_3); ^{13}C-n.m.r. ($CDCl_3$): δ 109.5 (CMe_2), 76.4, 71.1, 70.4 (C-2,3,4), 67.1 (C-5), 55.8 (C-1), 26.7, 25.5, 25.2, 23.6 (CMe_2 and SCH_2CH_3), 14.4, and 14.3 (SCH_2CH_3).

Anal. Calc. for $C_{12}H_{24}O_4S_2$ (296.44): C, 48.62; H, 8.16. Found: C, 48.51; H, 8.18.

2,3-Di-O-acetyl-4,5-O-isopropylidene-L-arabinose diethyl dithioacetal (**4**). — Acetic anhydride (1 mL) was added to a solution at 0° of compound **3** (200 mg) in pyridine (3 mL), and the mixture was stirred overnight at room temperature. Methanol was added, and the solution was evaporated, to afford a pale-brown

syrup that was purified on a short column, with 4:1 benzene–ethyl acetate as eluant, to give **4** as a colorless syrup; $[\alpha]_D^{25}$ −18° (*c* 1.0, chloroform); lit.[5] $[\alpha]_D$ +28.2° for the D enantiomer; ^{1}H-n.m.r. (C_6D_6): δ 5.98 (dd, $J_{3,4}$ 7.1 Hz, H-3), 5.67 (dd, $J_{2,3}$ 3.2 Hz, H-2), 4.18 (d, $J_{1,2}$ 7.1 Hz, H-1), 4.11 (dd, $J_{4,5}$ 5.8 Hz, H-4), 4.01 (dd, $J_{5,5'}$ 8.3 Hz, H-5), 3.85 (dd, $J_{4,5'}$ 6.2 Hz, H-5'), 2.64–2.42 (m, 4 H, 2 SCH_2CH_3), 1.82, 1.74 (s, 6 H, 2 Ac), 1.38, 1.24 (s, 6 H, CMe_2), and 1.06 (t, 6 H, 2 SCH_2CH_3); ^{13}C-n.m.r. ($CDCl_3$): δ 169.9 (C=O), 109.6 (CMe_2), 75.0, 72.6, 71.4 (C-2,3,4), 66.1 (C-5), 51.9 (C-1), 26.4, 25.3, 25.2, 25.1, 20.9, 20.7 (Me of CMe_2, Ac, plus SCH_2CH_3), and 14.1 (SCH_2CH_3).

Anal. Calc. for $C_{16}H_{28}O_6S_2$ (380.51): C, 50.50; H, 7.42. Found: C, 50.40; H, 7.47.

*2,3:4,5-Di-*O*-isopropylidene*-aldehydo-D-*arabinose* (**5**). — *A.* A modification[9] of the method of Zinner and co-workers[4] was first employed. A solution of the crude dithioacetal **2a** (11.7 g, 35 mmol) in acetone (200 mL) was stirred, and yellow mercury(II) oxide (21 g, 97 mmol), mercury(II) chloride (21 g, 77 mmol), and water (20 mL) were added in succession. The mixture was heated for 2 h at 56°, and then filtered into a receiver containing mercury(II) oxide (6 g). The resultant suspension was heated for 0.5 h at 56°, evaporated, and the residue extracted with dichloromethane (300 mL). The extract was washed twice with 5% aqueous potassium iodide (100-mL portions) and then with water (100 mL), and the dried (magnesium sulfate) extract was evaporated to a syrup (6.3 g) that contained two components having t.l.c. mobilities of 0.75 and 0.60 (3:1 benzene–ether). Fractional distillation of the syrup at 80°/4.0 Pa gave pure aldehyde **5** (3.3 g, 41%); $[\alpha]_D^{25}$ −15° (*c* 2, chloroform); lit.[26] −17.1° and[27] −18.2° in chloroform; R_F 0.60; ^{1}H-n.m.r. (Me_2CO-d_6): δ 9.71 (d, $J_{1,2}$ 2.0 Hz, H-1), 4.37 (dd, $J_{2,3}$ 5.0 Hz, H-2), 4.20–3.80 (m, 4 H, H-3,4,5,5'), 1.41, 1.32, and 1.29 (12 H, 2 CMe_2).

The preparation of aldehyde **5** was performed exactly as just described, except that the product-mixture was resolved by column chromatography with 9:1 benzene–ethyl acetate as the eluant. Fractions containing the product having R_F 0.75 were evaporated, and the resultant syrup crystallized spontaneously at room temperature to give a compound identified as 1,2:3,4-di-*O*-isopropylidene-β-D-arabinopyranose (**6**); yield 3.8 g (47%). Recrystallization from methanol–water gave pure **6**; m.p. 41–42°, $[\alpha]_D^{25}$ +14° (*c* 1, chloroform).

The aldehyde **5** was recovered from the column in ~35% yield as a slightly yellow syrup whose $[\alpha]_D$ value and ^{1}H-n.m.r. spectra were identical with those already described.

B. The aldehyde **5** was prepared from the dithioacetal **1** by the general demercaptalation procedure of Wolfrom and co-workers[18], employing mercury(II) chloride and cadmium carbonate; chromatographic purification of the product-mixture gave compound **5** in 73% yield.

*Conversion of 2,3:4,5-di-*O*-isopropylidene*-aldehydo-D-*arabinose* (**5**) *into 1,2:3,4-di-*O*-isopropylidene-β-*D*-arabinopyranose* (**6**). — A solution of aldehyde **5** (150 mg) in acetone (5 mL) was stirred for 18 h at room temperature with Dowex

50W (H^+) cation-exchange resin (100 mg); t.l.c. then showed complete conversion of **5** into **6**, and this was obtained in 84% yield after removal of the resin. Recrystallization from methanol–water gave pure **6**, m.p. 41–42°, $[\alpha]_D^{25}$ −4° (*c* 1, water), $[\alpha]_D^{25}$ +14° (*c* 1, chloroform), in agreement with literature data[22,28]; λ_{max}^{KBr} 7.26 μm (CMe_2), OH absorption absent; ^{1}H-n.m.r. ($CDCl_3$): δ 5.49 (d, $J_{1,2}$ 4.8 Hz, H-1), 4.56 (dd, $J_{3,4}$ 7.7 Hz, H-3), 4.30 (dd, $J_{2,3}$ 2.2 Hz, H-2), 4.22 (m, $J_{4,5}$ 2.2 Hz, H-4), 3.83 (dd, $J_{5,5'}$ 12.9 Hz, H-5), 3.65 (dd, $J_{4,5'}$ 1.1 Hz, H-5′), 1.53, 1.48, 1.35, and 1.33 (s, 12 H, 2 CMe_2).

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