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Note

Methoxymercuration adducts of 4,6-*O*-benzylidene-D-allal, and their demercuration products

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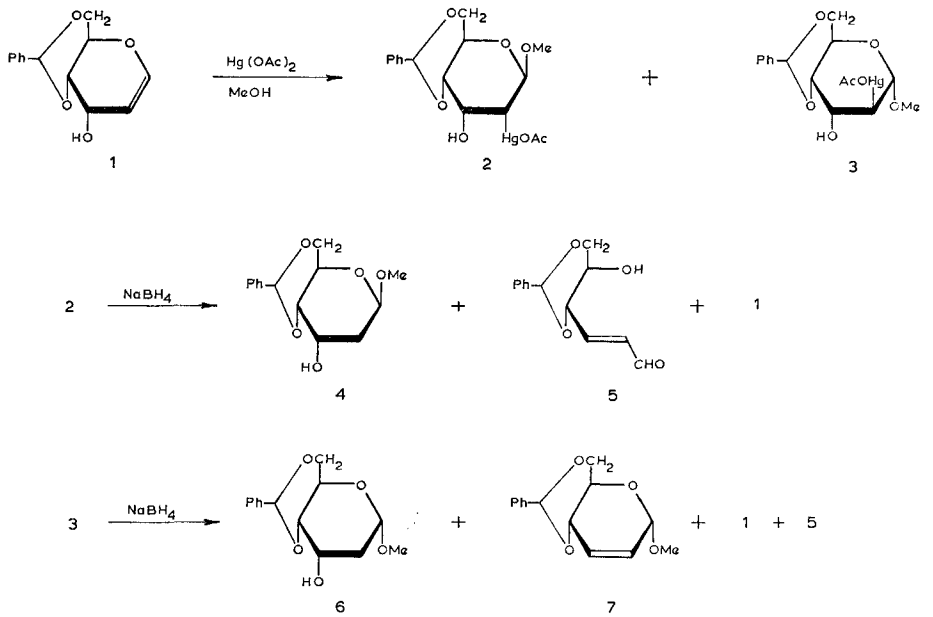
This report describes the methoxymercuration of 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol (4,6-*O*-benzylidene-D-allal, **1**) to afford the β-D-*allo* (**2**) and α-D-*altro* (**3**) adducts in 40 and 53% yield, respectively. Demercuration was effected by sodium borohydride, to give the anomeric methyl 4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hexopyranosides **4** (from **2**) and **6** (from **3**) in yields of 72 and 40%, together with various elimination products.

A program[1,2] in this laboratory is concerned with the synthesis of various deoxy and amino sugars as potential replacements for daunosamine[3] (3-amino-2,3,6-trideoxy-L-*lyxo*-hexose), the carbohydrate component in the antitumor antibiotics daunorubicin[4,5] and adriamycin[5,6], in order to provide access to substitutional and/or configurational analogs of these anthracycline antibiotics that might possibly have better therapeutic indices than the parent drugs.

In this connection, the anomeric methyl 4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hexopyranosides **4** and **6** were required as starting materials. The α anomer **6** is readily obtained[7] by reductive cleavage of the epoxide ring in methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**8**) with lithium aluminum hydride. As the epoxide[8] **8** was available in quantity, and may be converted[9–11] in high yield into 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hex-1-enitol (**1**), it was decided to evaluate the methoxymercuration–demercuration reaction-sequence[12] with the glycal **1** as a possible route to the β anomer **4**.

Methoxymercuration of the benzylidene glycal **1** yielded two isomeric addition-products having the β-D-*allo* (**2**) and α-D-*altro* (**3**) configurations, as indicated by their ^{1}H-n.m.r. spectroscopic data (see Table I), in particular the observed proton–proton coupling-constants, bearing in mind that both compounds are constrained into the $^4C_1$(D) conformation through the 4,6-*O*-benzylidene group (*trans*-decalin type of system). Because of the extremely low solubility of **3** in the reaction medium (and in most other organic solvents), the two isomers could be quantitatively separated simply by filtering off the precipitate, to give analytically pure **3** in 53% yield. The filtrate afforded **2** as the sole crystalline product, and it was obtained in 40% yield.

The acetoxymercurial adducts underwent extremely rapid, reductive demercuration* when treated with sodium borohydride in methanol–aqueous sodium hydroxide. In the reaction with **2**, the corresponding 2-deoxy-β-D-glycoside **4** was obtained in high yield (72%), together with a small proportion of an α,β-unsaturated aldehyde (**5**) and traces of the glycal **1**. When the reduction procedure was applied to the α-D-*ribo* mercurial adduct **3**, the corresponding 2-deoxy-α-D-glycoside **6** was formed in only moderate yield (40%), together with substantial proportions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**) and the glycal **1**; the *aldehydo* sugar **5** was detected only as a minor contaminant (2%) in this mixture of products.



The identities of the demercuration products **1**, **6**, and **7** were established by the good agreement of their physical constants with those reported in the literature for the same compounds prepared by independent routes. Furthermore, n.m.r. (Table I) and mass-spectrometric (see Experimental section) data fully supported the structures assigned.

The 2-deoxy-β-D-*ribo*-glycoside **4**, m.p. 96–97° and $[\alpha]_D$ −34° (in chloroform), appears to be new. It gave an acceptable elemental analysis, and its n.m.r. spectrum in benzene-d_6 (Table I) was essentially first-order, displaying, in particular, the signal for the anomeric proton as a well-resolved doubled doublet ($J_{1,2e}$ 2.4, $J_{1,2a}$ 9.5 Hz); the remainder of the spectrum closely resembled that of the α anomer **6** (Table I). The

*Results of the photochemical demercuration (*cf.*, ref. 13) will be reported elsewhere.

mass spectrum of **4** (see Experimental section) was identical with that of **6**, except for the intensities of certain fragment-ions. As well as a fairly intense, molecular ion (*m/e* 266, 6.4% of the base peak), the spectrum showed, in particular, a characteristic[14] fragment at *m/e* 179 (36%), and ions at *m/e* 149 (14%) and 117 (100%) attributable to the typical process of *h*-rupture[15].

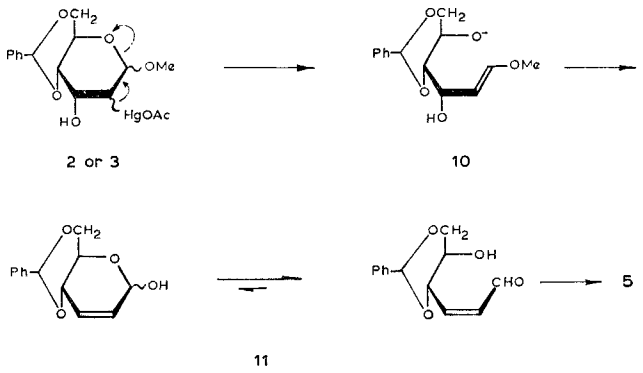
The chromatographically slowest-migrating component from both reactions appeared to be the α,β-unsaturated aldehyde **5**, as indicated from its characteristic, intense i.r. absorption at 1685 cm^{-1} and a weak absorption (shoulder) at 1650 cm^{-1}, complemented by a maximum at 228 nm in its u.v. spectrum. The n.m.r. spectrum (Table I) in chloroform-*d* provided independent evidence[16] for the proposed, open-chain structure of **5**, in particular, the doublet at extremely low field for H-1 (δ 9.58), the well-resolved multiplets for H-2 and H-3 (δ 6.47 and 7.05, as verified by double-irradiation experiments), the benzylidene-proton resonance at δ 5.56 (confirming that the 1,3-dioxane ring was still intact), and the presence of a hydroxyl group (signal at δ 2.59, that disappeared upon addition of D_2O); the large value for $J_{2,3}$ (16 Hz) indicated[16] the *trans* disposition of the alkene protons. Mass spectrometry (*m/e* 234, M^+; see Experimental section) and the elemental composition further supported the structure assigned.

Demercuration of compound **2**, having the acetoxymercuri group equatorially attached, evidently follows the normal reduction-mode, giving rise to elimination products to only a minor extent. It is noteworthy that, with two possible leaving-groups of similar character (hydroxyl and methoxyl), only one possible alkene (the glycal **1**) is formed, namely, the one arising through *trans*-diequatorial elimination. In contrast, compound **3**, having an axially exposed mercuri substituent, flanked diaxially by two potential leaving-groups, is much more prone to elimination reactions, and gives both alkenes **1** and **7** in substantial yields that, when combined, equal the yield of the "normal" product **6**.

The formation of the *aldehydo* derivative **5** poses an interesting problem. An analogous product, together with the corresponding allylic alcohol, was observed by Takiura and Honda[17] upon demercuration of 2-(acetoxymercuri)-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (**9**). Although a reducing sugar might be postulated as precursor for compound **5**, it may be ruled out for several reasons; the methoxymercuration was conducted under rigorously anhydrous conditions; the addition products **2** and **3** were of undoubted purity [by elemental analysis, and n.m.r. and i.r. spectroscopy (no C=O absorption[17] at ~1700 cm^{-1})]; and finally, no allylic alcohol could be detected in the mixture of products, according to t.l.c. by comparison with a reference sample (prepared from **5** by reduction with sodium borohydride). The absence of allylic alcohol, despite the large excess of reducing reagent employed in the demercuration reactions, stands in contrast to Honda's analogous experiments[17] with the hydroxymercuration adduct **9**.

A glycal–pseudoglycal rearrangement[18], with subsequent isomerization[19] to the more stable *E* isomer, is not very probable, either. A high concentration of glycal **1** in the mixture of products arising from **3** would then suggest, contrary to the experi-

mental findings, that there would be higher yields of the aldehyde **5** as compared to the reaction with **2**, where hardly any glycal **1** is formed at all; in the latter instance, however, a considerable proportion of the aldehyde **5** was isolated.



Scheme 1

A possible route (Scheme 1) to compound **5**, directly from the mercurial adducts, would involve cleavage of the C-1–O-5 bond, particularly favored in the β-D-*allo* derivative **2** because of the *trans*-diaxial arrangement, but also feasible with the α-D-*altro* isomer **3** (*gauche* relationship). Subsequent hydrolysis of the resulting enol ether **10**, and β-elimination under neutral or slightly acidic (silica gel) conditions, would lead to the (*Z*)-hex-2-enopyranose derivative **11**, which tends[20] to exist in the open-chain, *aldehydo* form, rather than as the pyranoid structure, and undergoes[19] photochemical (or* less effectively, thermal) conversion into the more stable *E* isomer **5**. This hypothetical mechanism would be compatible with all the aforementioned observations.

EXPERIMENTAL

General methods. — Evaporations were performed under diminished pressure at a bath temperature below 50°. Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. A Perkin–Elmer Model 141 polarimeter and 1-dm tubes were used for measurement of specific rotations. I.r. spectra were recorded with a Perkin–Elmer Model 457 grating i.r. spectrophotometer, with the compounds dispersed in potassium bromide. U. v. spectra were recorded with a Cary Model 14 recording spectrophotometer. ^{1}H-N.m.r. spectra were recorded at 100 MHz with a Varian HA-100 spectrometer; chemical shifts refer to an internal standard of tetramethylsilane ($\delta = 0.00$), and are listed, together with spin-coupling values (Hz) in

*A referee suggested that the rearrangement of the (*Z*)-hex-2-enopyranose **11** into the *E* isomer **5** might well proceed *via* a dienol intermediate.

Table I; the assignments were confirmed in many instances by decoupling experiments. T.l.c. was performed on precoated plates of Silica Gel 60 (E. Merck, Darmstadt); zones were detected by u.v. light, and by spraying with sulfuric acid and subsequent heating. Solvent volumes are v/v; petroleum ether refers to the fraction boiling at 65–110°. Column chromatography was performed with silica gel (Merck No. 7734; 63–200 μm), providing 40 ml of column volume/g of mixture separated. Microanalyses were performed by W. N. Rond of this Department, except for the mercury-containing compounds **2** and **3**, which were analyzed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-9 double-focusing, high-resolution spectrometer operating at an ionizing potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 120°. The spectra of all compounds studied displayed intense peaks of aromatic ions (*m/e* 107, 106, 105, 91, 79, and 77); the notations h_1 and h_2 in the assignments refer to the *h*-rupture process proposed by Chizhov *et al.*[15]. 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; v, very; w, weak. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

*Methoxymercuration of 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-*D*-ribo-hex-1-enitol* (**1**). — Mercuric acetate (4.14 g, 13 mmol) and the glycal[10] **1** (3.01 g, 12.86 mmol) were dissolved in abs. methanol (40 ml). After 18 h at 0°, the white precipitate that had almost immediately formed was filtered off and dried, to give analytically pure *methyl 2-(acetoxymercuri)-4,6-*O*-benzylidene-2-deoxy-α-*D*-altropyranoside* (**3**); yield 3.6 g (53%), m.p. 191–192° (dec.), $[\alpha]_D^{22}$ −14° (*c* 0.5, pyridine); ν_{max}^{KBr} 3500 (OH), 1630–1580 (HgOAc), and 765 and 705 cm^{-1} (aryl); X-ray powder diffraction data: 7.08 s (1), 13.69 m, 7.05 w, 5.84 m, 5.17 s (3), 4.91 w, 4.39 s, 3.95 s (2,2), and 3.67 s (2,2).

Anal. Calc. for $C_{16}H_{20}HgO_7$ (524.92): C, 36.61; H, 3.84; Hg, 38.21. Found: C, 36.44; H, 3.98; Hg, 40.45.

The syrupy residue obtained on evaporation of the mother liquor from the foregoing was dissolved in dichloromethane, and the solution was washed with water and dried (magnesium sulfate). After distilling off the solvent, the remaining syrup crystallized upon trituration with ethanol. Recrystallization from ethanol afforded pure *methyl* 2-*(acetoxymercuri)-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranoside* (**2**); yield 2.7 g (40%), m.p. 97–103°, $[\alpha]_D^{22}$ −20° (*c* 1, chloroform); ν_{max}^{KBr} 3450 (OH), 1630–1570 (HgOAc), and 750 and 695 cm^{-1} (aryl); X-ray powder diffraction data: 13.08 s (3,3), 11.78 s (3,3), 9.87 m, 8.19 w, 7.53 w, 6.63 w, 5.94 m, 4.77 s (1), 4.48 w, and 4.30 s (2).

Anal. Calc. for $C_{16}H_{20}HgO_7$ (524.92): C, 36.61; H, 3.84; Hg, 38.21. Found: C, 36.54; H, 4.07; Hg, 39.35.

*Reaction of the β-*D*-allo acetoxymercuri derivative* **2** *with sodium borohydride.* — A solution of sodium borohydride (300 mg, 7.9 mmol) in M aqueous sodium hydroxide (20 ml) was added dropwise to a cooled (0°) solution of **2** (2.17 g, 4.13 mmol) in a

TABLE I

100-MHZ, N.M.R.-SPECTRAL DATA FOR COMPOUNDS **1–7**

Compound[a]	*Chemical shifts* (δ)[b] (*first-order couplings, Hz, in parentheses*)[c]											
	H-1 ($J_{1,2}$)	*H-2*[d] ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-5* ($J_{5,6'}$)	*H-6* ($J_{5,6}$)	*H-6'* ($J_{6,6'}$)	*Aryl*	*PhC–H*	*OMe*	*OH*[e]	*Others*[f]
1	6.41 d (6.0)	4.96 t (6.0)	4.19 m (3.4)	3.77 dd (9.8)	4.16 m (9.5)	4.45 dd (4.8)	3.77 t (9.8)	7.60–7.20 m	5.62 s	—	2.59	—
2[g]	4.87 d (10.2)	2.59 dd (3.0)	4.20–3.84 m (3.0)	3.52 dd (9.2)	4.20–3.84 m (9.5)	4.32 dd	3.70 t (9.5)	7.58–7.26 m	5.56 s	3.42 s	4.05	1.97 s (HgOAc)
3[g,h]	5.26 s (W_h 3.5)	3.43 d (3.0)	←	4.80–4.30 m	→		3.89 t (10.0)	7.75–7.15 m	5.73 s	3.26 s	4.88	2.11 s (HgOAc)
4[i,j]	4.82 dd (2.4)	2.11 ddd (3.8)	3.86 m (2.8)	3.12 dd (9.2)	3.96 m (9.4)	4.23 dd (4.9)	3.53 t (9.9)	7.70–7.10 m	5.29 s	3.25 s	2.28	1.62 m (H-2*a*)
5	9.58 d (7.8)	6.47 m (16.0)	7.05 dd (4.0)	←	4.40–3.60 m	→		7.58–	5.56 s	—	2.59	—
6[i,k]	4.32 dd (1.3)	1.84 ddd (3.2)	4.26–3.90 m (2.8)	3.15 dd (9.0)	← 4.26–3.90 m → (11.8)		3.53 t (11.8)	7.70–7.05 m	5.41 s	2.88 s	3.95	1.39 dt (H-2*a*)
7	4.90 s (W_h 4.5)	5.72 m (~10)	6.14[d] d	←	4.43–3.74 m	→		7.60–7.20 m	5.58 s	3.47 s	—	—

[a] In chloroform-*d*, unless otherwise stated. [b] Signal multiplicities: d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet. [c] W_h stands for line width at half height. [d] Refers to the equatorially disposed hydrogen atom in the 2-deoxyglycosides **4** and **6**. [e] Broadened signal. [f] Assignments in parentheses. [g] Satellite peaks as a result of ^1H–^{199}Hg coupling (*cf.*, refs. 13 and 21) were not recorded. [h] In pyridine-d_5. [i] In benzene-d_6. [j] $J_{1,2a}$ 9.5 Hz; $J_{2e,2a}$ 14.5 Hz; $J_{2a,3}$ 3.0 Hz. [k] $J_{1,2a}$ 3.6 Hz; $J_{2e,2a}$ 15.0 Hz; $J_{2a,3}$ 3.6 Hz.

mixture of methanol (30 ml) and M aqueous sodium hydroxide (10 ml). After 30 min at 0°, mercury was filtered off, and the base neutralized by dropwise addition of acetic acid. The solvent was then evaporated, water (20 ml) was added to the residue, and the suspension was extracted with dichloromethane (three 35-ml portions). The combined organic phase was washed with water, dried (magnesium sulfate), and evaporated. The resulting, crystalline residue was shown by t.l.c. (3:2 benzene–ether) to be a mixture of two major components, which were separated by column chromatography on silica gel with the t.l.c. solvent as eluant.

The first compound (R_F 0.32) emerging from the column crystallized after evaporating off the solvent, and was identified as *methyl 4,6-O-benzylidene-2-deoxy-β-D-ribo-hexopyranoside* (**4**); yield 790 mg (72%) after recrystallization from ether–petroleum ether, m.p. 96–97°, $[\alpha]_D^{22}$ −34° (*c* 1, chloroform); ν_{max}^{KBr} 3500 (OH), and 740 and 695 cm^{-1} (aryl); *m/e* (rel. intensity): 266 (6.4, M^+), 248 (0.1, $M-H_2O$), 223 (32, $M-CH_2CHO^{14}$; m* at 187.0, calc. 186.95), 179 (36)[14], 149 (14, h_2), 117 (100, h_1), 99 (78, h_1-H_2O; m* at 83.8, calc. 83.77); X-ray powder diffraction data: 11.94 s, 9.11 w, 8.00 m, 5.84 s (2), 5.42 s, 4.89 m, 4.56 w, 4.24 vs (1), 3.67 m, and 3.50 s (3).

Anal. Calc. for $C_{14}H_{18}O_5$ (266.30): C, 63.15; H, 6.81. Found: C, 62.92; H, 6.74.

In the mother liquor of **4**, a trace of the glycal **1** (R_F 0.37) could be detected; it was isolated by preparative t.l.c., yield 20 mg (2%), indistinguishable (by mixed m.p. and i.r. spectroscopy) from the product described in the next section.

The other component, having R_F 0.12, was obtained as a crystalline solid upon evaporation of the solvent, and was recrystallized from ether–petroleum ether, to yield pure (E)-aldehydo-*4,6-O-benzylidene-2,3-dideoxy*-D-erythro-*hex-2-enose* (**5**); yield 80 mg (8.3%), m.p. 120–121°, $[\alpha]_D^{22}$ −58.3° (*c* 0.36, chloroform); ν_{max}^{KBr} 3500 (OH), 1685 and 1650 (C=C–CHO), and 750 and 705 cm^{-1} (aryl); λ_{max}^{MeOH} 228 nm (ε 11,100); *m/e* (rel. intensity): 234 (0.3, M^+), 216 (0.03, $M-H_2O$), 205 (0.03, $M-\cdot CHO$), 149 (21, h_2), 85 (5, h_1); X-ray powder diffraction data: 9.45 s (3,3), 6.43 vw, 5.88 s (2), 5.47 s, 4.83 m, 4.49 m, 4.18 s (3,3), 4.04 s, 3.80 s, 3.66 s, 3.52 vs (1), and 3.36 s.

Anal. Calc. for $C_{13}H_{14}O_4$ (234.26): C, 66.66; H, 6.02. Found: C, 66.70; H, 5.87.

Reaction of the α-D-altro *acetoxymercuri derivative* **3** *with sodium borohydride.* — Similarly to the foregoing procedure, a solution of compound **3** (4.5 g, 8.6 mmol) in a mixture of methanol (60 ml) and M aqueous sodium hydroxide (25 ml) was treated with sodium borohydride (700 mg, 18.5 mmol, dissolved in 30 ml of M aqueous sodium hydroxide) for 30 min at 0°. The mixture was processed as before, giving a crystalline residue (~2 g) that was shown by t.l.c. (3:2 benzene–ether) to be a mixture of four major components (R_F 0.58, 0.37, 0.22, and 0.12), which were fractionated by column chromatography on silica gel with the t.l.c. solvent as eluant.

The fastest-migrating component (R_F 0.58; 500 mg, 23.5%) crystallized upon evaporation of the solvent, and was recrystallized from ethanol to afford *methyl 4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside* (**7**); m.p. 117–119°, $[\alpha]_D^{22}$ +134.6° (*c* 1, chloroform); ν_{max}^{KBr} 745 and 695 cm^{-1} (aryl); *m/e* (rel. intensity): 248 (0.8, M^+), 217 (2.8, $M-MeO\cdot$), 205 (0.04, $M-\cdot CH_2CHO^{14}$), 171 (2, $M-Ph\cdot$), 149 (100, h_2; m* at 89.5, calc. 89.52), 99 (69, h_1), 91 (40, $PhCH_2^+$; m* at 55.6, calc. for

149→91: 55.58); X-ray powder diffraction data: 11.18 s (3), 5.80 s (2), 5.55 m, 5.05 m, 4.28 w, 3.98 s (1,1), 3.79 s (1,1), 3.66 w, 3.53 w, and 3.29 m.

Anal. Calc. for $C_{14}H_{16}O_4$ (248.28): C, 67.73; H, 6.50. Found: C, 67.50; H, 6.60.

For this compound, the following data have been reported: m.p. 119–120°, $[\alpha]_D$ +130 ±2° in chloroform[22] and[11] m.p. 119.5–120°, $[\alpha]_D$ +129° in chloroform.

The second fraction (R_F 0.37) furnished, after distilling off the solvent, crystalline *1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-*D-ribo-*hex-1-enitol* (**1**), which was recrystallized from ether–hexane; yield 305 mg (15%), m.p. 84–85°, $[\alpha]_D^{22}$ +196.3° (*c* 1, chloroform) and +213.7° (*c* 1.1, ethanol) (lit.[10] m.p. 84–85°; m.p. 83.5°, $[\alpha]_D$ +209.5° in ethanol[11]; m.p. 84–84.5°, $[\alpha]_D$ +210° in ethanol[9]; and[23] m.p. 83–84°, $[\alpha]_D$ +195° in chloroform); ν_{max}^{KBr} 3170 (OH), 1640 (C=C), and 755 and 705 cm^{-1} (aryl); *m/e* (rel. intensity): 234 (27, M^+), 205 (1.2, M − ·CHO; m* at 179.6, calc. 179.59), 162 (15, M − CHO–CH_2–CHO; m* at 112.1, calc. 112.15; and 205 − CH_3CO·; m* at 128.0, calc. 128.02), 128 (0.8, M − PhCHO), 99 (27, 128 − ·CHO; m* at 76.5, calc. 76.57), 71 (26, CHO–CH_2–CO^+; m* at 50.9, calc. for 99→71: 50.92), 57 (10, 162 − PhCO·); X-ray powder diffraction data: 12.44 s (3), 9.60 w, 7.13 w, 5.88 w, 5.48 w, 5.29 w, 4.99 s (2), 4.77 m, 4.42 s (1), and 3.97 m.

Anal. Calc. for $C_{13}H_{14}O_4$ (234.25): C, 66.66; H, 6.02. Found: C, 66.46; H, 5.90.

Evaporation of the third fraction (R_F 0.22) afforded a crystalline solid that was recrystallized from ethanol to give *methyl 4,6-*O*-benzylidene-2-deoxy-*α*-*D*-ribo-hexopyranoside* (**6**); yield 910 mg (40%), m.p. 125–126°, $[\alpha]_D^{22}$ +140.3° (*c* 1, chloroform) (lit.[24] m.p. 124–125°, $[\alpha]_D$ +145° in chloroform; m.p. 127–129°, $[\alpha]_D$ +140° in chloroform[25]; and[2] m.p. 127–128°, $[\alpha]_D$ +146° in chloroform); ν_{max}^{KBr} 3500 (OH), and 770 and 700 cm^{-1} (aryl); *m/e* (rel. intensity): 266 (58, M^+), 265 (13.6), 235 (10, M − MeO·), 223 (9, M − ·CH_2CHO[14]; m* at 187.0, calc. 186.95), 179[14] (100; m* at 120.5, calc. 120.45), 149 (12, h_2), 117 (70, h_1; m* at 51.5, calc. 51.46), 99 (70, $h_1 - H_2O$; m* at 83.8, calc. 83.77); X-ray powder diffraction data: 7.86 m, 6.04 m, 4.80 s (1), 5.75 s (2), 3.89 s (3), and 3.48 m.

Anal. Calc. for $C_{14}H_{18}O_5$ (266.30): C, 63.15; H, 6.81. Found: C, 63.27; H, 7.05.

The last fraction, having R_F 0.12, was shown to contain (E)-aldehydo-*4,6-*O*-benzylidene-2,3-dideoxy-*D*-erythro-hex-2-enose* (**5**), identical (by mixed m.p., and i.r.- and n.m.r.-spectroscopic data) with the product obtained in the foregoing reaction; yield 50 mg (2.5%).

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