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SYNTHESIS OF 2,5-DIDEOXY-2-*C*-METHYL-D-ARABINOSE DERIVATIVES FROM METHYL 2,3-ANHYDRO-5-DEOXY-α-D-RIBOFURANOSIDE

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ABSTRACT

Treatment of methyl 2,3-anhydro-5-deoxy-α-D-ribofuranoside with lithium dimethyl cuprate gave methyl 2,5-dideoxy-2-*C*-methyl-α-D-arabinofuranoside (54% yield) and methyl 3,5-dideoxy-3-*C*-methyl-α-D-xylofuranoside (10%). The former was converted into its 3-*O*-acetyl and 3-*O*-benzyl derivatives, which, upon acid hydrolysis, afforded 3-*O*-acetyl- and 3-*O*-benzyl-2,5-dideoxy-2-*C*-methyl-D-arabinofuranose in 60–75% overall yield. Treatment of the 3-*O*-benzyl compound with ethanethiol in the presence of trifluoromethanesulfonic acid afforded 3-*O*-benzyl-2,5-dideoxy-2-*C*-methyl-D-arabinose diethyl dithioacetal (20%) and ethyl 3-*O*-benzyl-2,5-dideoxy-2-*C*-methyl-1-thio-α-D-arabinoside (73%). The former, which was also available from the latter by equilibration in acidic ethanethiol, was acetylated at O-4 and the product converted into the corresponding dimethyl acetal (85% overall yield). This compound was, after debenzylation, hydrolyzed with acid, to provide 4-*O*-acetyl-2,5-dideoxy-2-*C*-methyl-D-arabinose in 70% overall yield.

INTRODUCTION

The stereo- and regio-selectivity of the nucleophilic ring-opening of oxirane rings in pyranosides are in many cases well established, usually giving rise exclusively to the *trans*-diaxial products. Thus, for example, the reaction of lithium dimethyl cuprate with the *allo* oxirane introduced a methyl group, to provide an important building block (the C-9–C-13 segment) in an excellent synthesis of erythronolide A by Hanessian *et al.*[1]. Such chiral synthons that bear a methyl group and a hydroxyl functional group having specific configurations at the vicinal position of the carbon skeleton are of considerable value in connection with schemes for the synthesis of natural products constructed biologically by condensation of propionate units.

By contrast, the opening of the oxirane ring in furanosides by a nucleophile

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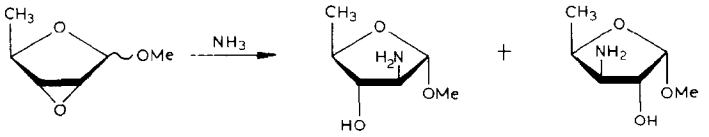
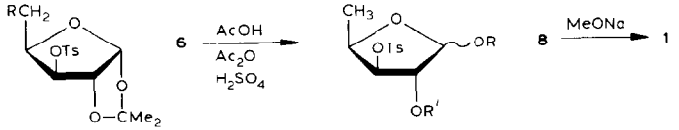
appears to remain ambiguous, as exemplified by the reaction of the α-D-*ribo* epoxide, which takes place either at C-2 or C-3, depending upon steric and polar effects: the reaction of ammonia with methyl 2,3-anhydro-5-deoxy-α-D-ribofuranoside (**1α**) and its anomer (**1β**) respectively occurred[2] at C-2 and C-3, to give methyl 2-amino-2,5-dideoxy-α-D-arabinoside (**2**) and methyl 3-amino-3,5-dideoxy-β-D-xylofuranoside, whereas the epoxide ring of **1α** was later reported[3] to be *equally* attacked by ammonia at C-2 and C-3, to afford a 1:1 mixture of **2** and the α-D-xylofuranoside **3**. We now describe a convenient route for the preparation of 2,5-dideoxy-2-*C*-methyl-α-D-arabinose derivatives as potential building-blocks in the synthesis of macrolides and other natural products*.



1 2 3

RESULTS AND DISCUSSION

5-Deoxy-5-iodo-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[5] (**4**), quantitatively prepared from the 3,5-di-*O*-*p*-tolylsulfonyl compound[6] (**5**), was preferred as the starting material for this synthesis, because 5-deoxy-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-xylofuranose (**6**) was found to be more efficiently obtained by catalytic hydrogenolysis of **4** in the presence of Pd–C than by direct reduction of **5** with lithium aluminum hydride in oxolane[3]. Conversion of **6** into the 1,2-di-*O*-acetyl derivative **7** was achieved in 88–93% yield by acid-catalyzed acetolysis. Treatment of **7** with 1% methanolic hydrochloric acid afforded methyl 5-deoxy-3-*O*-*p*-tolylsulfonyl-α-D-xylofuranoside (**8α**) and its anomer (**8β**) in 45 and 51% yield, respectively, separable by chromatography on a column of silica gel. As **8α** and **8β** were equilibrated by treatment with methanolic acid, either of the anomers was available from the other. These 3-*O*-*p*-tolylsulfonyl com-



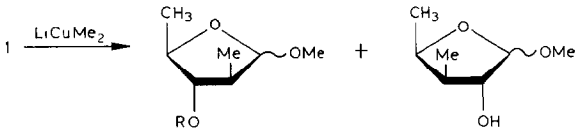
4 R = I
5 R = OTs
6 R = H
Ts = $SO_2C_6H_4Me$-*p*

7 R = R' = Ac
8 R = Me, R' = H

*Part of the results has been reported[4] as a prelimary communication.

pounds were separately treated with methanolic sodium methoxide, to afford methyl 2,3-anhydro-5-deoxy-α-D-ribofuranoside (**1α**) and its anomer (**1β**) in 82 and 60% yield, respectively; these yields are appreciably better than those given by the previous route[2] *via* the corresponding 3-*O*-(methylsulfonyl) derivatives of **8**.

The reaction of **1α** with 2 equivalents of lithium dimethyl cuprate in ether for 3 h at 0° gave, after separation in a column of silica gel with methanol–chloroform as the eluant, methyl 2,5-dideoxy-2-*C*-methyl-α-D-arabinofuranoside (**9α**) and methyl 3,5-dideoxy-3-*C*-methyl-α-D-xylofuranoside (**12α**) in 54 and 10% yield, re-



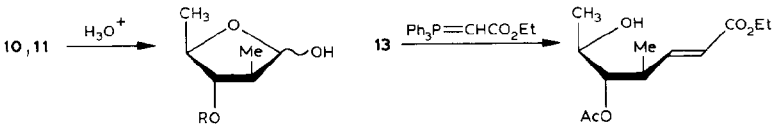
9 R = H
10 R = Ac
11 R = Bn
Bn = $PhCH_2$

12

spectively; the structures of these products were established by their spectra (see Table I for the ^{1}H-n.m.r.-spectral assignments). On the other hand, the reaction of lithium dimethyl cuprate with the anomer **1β** did not produce the expected β anomer (**9β** or **12β**), presumably due to steric hindrance by the 1-β-*O*-methyl group towards nucleophilic attack.

The major product, **9α**, readily led to the 3-*O*-acetyl- and 3-*O*-benzyl-α-D-arabinofuranoside (**10α** and **11α**) in 80 and 83% yield, respectively, by treatment with acetic anhydride–pyridine, or benzyl chloride–calcium sulfate–potassium hydroxide in oxolane. Acid hydrolysis of **10α** and **11α** respectively afforded 3-*O*-acetyl- and 3-*O*-benzyl-2,5-dideoxy-2-*C*-methyl-D-arabinofuranose (**13** and **14**) in 75 and 91% yield.

Ring-opening of these arabinofuranoses (**13** and **14**) by the action of (ethoxycarbonyl)methylenetriphenylphosphorane[7] on **13** in refluxing benzene was examined, but the acyclic *trans*-alkene **15** was obtained in less than 30% yield, suggesting that the furanoid form possesses greater thermodynamic stability than the corresponding acyclic form. This was supported by the result of the conversion of the arabinofuranoses into their acyclic form: compound **14** was treated with an excess of ethanethiol in the presence of trifluoromethanesulfonic acid for 3 h at 20°,



13 R = Ac
14 R = Bn

15

TABLE I

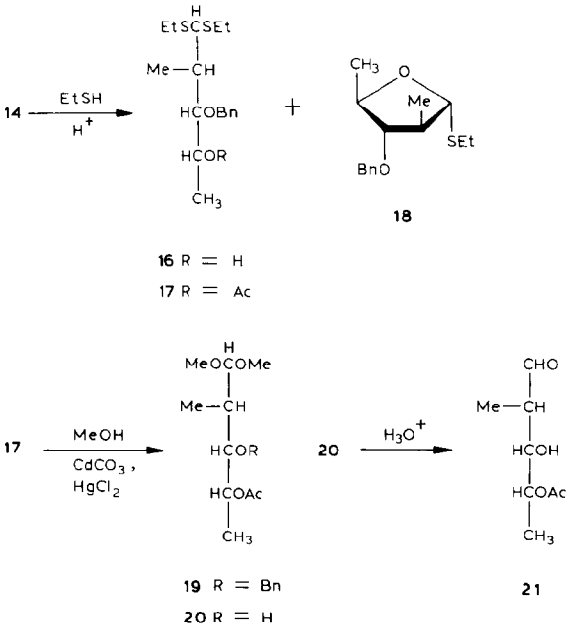
^{1}H-N.M.R PARAMETERS OF COMPOUNDS **1** AND **9–21** IN $CDCl_3$

Compound	Chemical shifts (δ)									Coupling constants (Hz)				
	H-1	*MeO-1*	*H-2*	*Me-2*	*H-3*	*AcO-3*	*H-4*	*AcO-4*	H_3-5	$J_{1,2}$	$J_{2,3}$	$J_{2,Me}$	$J_{3,4}$	$J_{4,5}$
1α	5.09	3.42	3.75	—	3.44	—	4.40	—	1.19	0	2.7	—	0	6.5
1β	4.92	3.40	3.70	—	3.57	—	4.26	—	1.23	1	2.3	—	1	6.5
9α	4.62	3.36	2.14	1.09	3.40	2.8[a]	3.98	—	1.31	1.8	3.5	7.0	4.8	6.5
10α	4.59	3.35	2.1	1.15	4.41	2.07	4.12	—	1.34	1.0	3.2	7.6	5.5	6.1
11α	4.55	3.36	2.24	1.07	3.18	7.32[b] 4.55[c]	4.09	—	1.27	2.0	4.3	7.5	6.3	6.3
12α	4.84	3.48	3.79	2.55[d]	2.28	0.98[e]	4.36	—	1.10	4.5	6.5	7.5[f]	7.0	6.2
13α	5.13	2.0[g]	2.3	1.14	4.45	2.08	4.20	—	1.32	2.0	4	7.5	6.0	6.5
14α	5.02	3.75[g]	2.3	1.05	3.31	7.32[b] 4.52[c]	4.29	—	1.27	6.3	4.2	7.5	4.5	6.5
14β	5.23	3.86[g]	2.3	1.10	3.36	7.32[b] 4.55[c]	4.0	—	1.32	4.5	[h]	7.2	[h]	6.5
15[i]	6.92	5.91[j]	2.5	1.13	4.90	2.14[a]	3.90	1.6[k]	1.25	8.0	[h]	7.5	4.6	6.8
16	3.79 2.63,	1.22[l] 2.64[l]	2.2	1.1	3.80	7.33[b] 4.69[c]	4.01	1.9[k]	1.27	6.6	6.4	6	5.6	6.2
17	3.81 2.63,	1.25[l] 2.69[l]	2.4	1.16	3.96	7.33[b] 4.74[c]	5.10	2.04	1.28	6.5	4.5	6.5	4.5	6.7
18α	4.86	1.26[l] 2.66[l]	2.19	1.17	3.20	7.34[b] 4.57[c]	4.14	—	1.29	5.4	7.0	6.6	5.7	6.6
19	4.23	3.29 3.32	2.03	0.96	3.63 4.54,	7.33[b] 4.62[c,m]	5.05	2.01	1.27	7.5	3.0	7.2	6.2	6.2
20	4.24	3.40 3.44	1.8	0.95	3.85	2.74[a]	4.88	2.03	1.28	5.0	2.0	7.2	7.5	6.1
21	9.71	—	2.45	1.17	4.09	2.3[a]	4.90	2.04	1.30	0	3.8	7.0	7.0	6.0

[a]HO-3. [b]C_6H_5-CH_2-3. [c]Ph-CH_2-3. [d]HO-2. [e]Me-3. [f]$J_{3,Me}$. [g]HO-1. [h]Values uncertain. [i]The numbering of **15** corresponds to those of the other pentoses for the purpose of comparison; additional signals due to SEt group(s), δ 1.31 (t, *J* 7.0 Hz, 3 H) and 4.23 (q, *J* 7.0 Hz, 2 H). [j]O=CC*H*=CH-1 (*J* 18.0 Hz). [k]HO-4. [l]CH_3CH_2S-1 (*J* 7.4 Hz). [m]*J* 10 Hz.

to afford a mixture of 3-*O*-benzyl-2,5-dideoxy-2-*C*-methyl-D-arabinose diethyl dithioacetal (**16**) in 20% yield and the ethyl 1-thio-α-D-arabinoside **18** (73%), separable in a column of silica gel with hexane–ethyl acetate as the eluant. Although many attempts were made to obtain a higher yield of the desired product **16** by employing various other conditions, the foregoing combination has so far resulted in the highest yield As an equilibration between **16** and **18** (~2:7 in favor of the 1-thioglucoside) was caused by the same treatment with acidic ethanethiol, an additional amount of **16** was available from **18** by repeating the procedure.

The reaction of **16** with acetic anhydride–pyridine afforded the 4-*O*-acetyl derivative **17** (96% yield), which was, in turn, converted into the corresponding dimethyl acetal **19** in 92% yield by the usual method. Removal of the benzyl group was effected by catalytic hydrogenolysis in the presence of Pd–C in methanol, giving the dimethyl acetal **20** (70%), which, on hydrolysis with aqueous trifluoroacetic acid, afforded 4-*O*-acetyl-2,5-dideoxy-D-arabinose (**21**) in 80% yield.



Although the yields in some of the steps have not yet been maximized, the present work demonstrates a novel way for preparing various 2,5-dideoxy-2-*C*-methyl-D-arabinose derivatives.

EXPERIMENTAL

General methods. — Melting points were determined with a Yamagimoto MP-S3 instrument and are uncorrected. All reactions were monitored by t.l.c., and the products were detected with ceric sulfate–2M sulfuric acid, or cobalt(II) chloride–acetone, as the indicator. Column chromatography was performed by using Wako C-200. T.l.c. was conducted on plates precoated with silica gel (0.25 mm, Merck). Optical rotations were measured with a Nihon-Bunko DIP-4 polarimeter. I.r. spectra were recorded with a Hitachi 260-10S spectrometer. ^{1}H-N.m.r. spectra were recorded, for solutions in $CDCl_3$, with a Hitachi–Perkin–Elmer R-20A (60 MHz) or JEOL FX100 (100 MHz) spectrometer at 30°. Chemical shifts are recorded as δ values relative to tetramethylsilane (δ 0.0) as the internal standard. Mass spectra were recorded with a Hitachi RM-50GC low-resolution or an A.E.I. MS 50 ultra-high-resolution instrument, and are given in terms of *m/z* (relative intensity) compared with the base peaks.

5-Deoxy-1,2-O-isopropylidene-3-O-p-tolylsulfonyl-α-D-xylose (**6**). — A solution of 5-deoxy-5-iodo-1,2-*O*-isopropylidene-3-*O*-*p*-tolylsulfonyl-α-D-xylofuranose[5] (**4**; 14.0 g) in absolute ethanol (150 mL) was hydrogenolyzed in the presence of 10% Pd–C (1.4 g) and triethylamine (20 mL) at 25°. After the requisite amount

of hydrogen had been consumed, the solid was filtered off, and the filtrate evaporated *in vacuo*. The residue was diluted with water (50 mL) and extracted with 1:1 benzene–light petroleum. Removal of the solvent *in vacuo* gave **6** as a colorless solid (10.0 g, 99%).

*Methyl 2,3-anhydro-5-deoxy-3-*O-p-*tolylsulfonyl-α-*D-*ribofuranoside* (**1α**) *and its anomer* (**1β**). — These compounds were prepared from **6** in three steps *via* **7** and **8** by applying the method used by Kuzuhara and Emoto[2] for the corresponding 3-*O*-(methylsulfonyl) compound. 1,2-Di-*O*-acetyl-5-deoxy-3-*O*-*p*-tolylsulfonyl-D-xylofuranose (**7**), prepared by heating **6** (6.5 g) in 20:2:1 acetic acid–acetic anhydride–conc sulfuric acid (150 mL) for 16 h at 20° (88–93% yield), was stirred with methanol (150 mL) containing 1% of hydrochloric acid for 16 h at 20°, and then the resulting mixture was separated into the α anomer (**8α**) in 45% yield and the β anomer (**8β**; 51%) by chromatography on silica gel, using, as the eluant, chloroform which was gradually changed to 1:19 MeOH–$CHCl_3$.

Sodium (0.26 g, 11 mmol), dissolved in absolute methanol (7 mL), was added to a cold solution of **8α** (2.27 g, 7.5 mmol) in absolute methanol (7 mL), and the mixture was kept for 4 days at 5°. After addition of cold methanol (15 mL) and solid ammonium chloride (3 g), the solution was evaporated *in vacuo*, and the residue extracted with CH_2Cl_2. The extract was evaporated, and the residue chromatographed in a column of silica gel with hexane → 40% EtOAc–hexane, giving **1α** (0.80 g, 85% yield) as colorless needles; m.p. 24° (from pentane, lit.[2] m.p. 21–23°); R_F 0.45 (1:1 EtOAc–hexane); for ^{1}H-n.m.r. data, see Table I.

Similarly, the anomer **8β** gave a 60% yield of **1β** as a colorless liquid (lit.[2] m.p. 2–3°); R_F 0.70 (1:1 EtOAc–hexane).

*Methyl 2,5-dideoxy-2-*C-*methyl-α-*D-*arabinofuranoside* (**9α**) *and methyl 3,5-dideoxy-3-*C-*methyl-α-*D-*xylofuranoside* (**12α**). — A solution of **1α** (770 mg, 5.9 mmol) in dry ether (8 mL) was added dropwise to a cold solution of lithium dimethyl cuprate that had been prepared by adding 1.3M methyllithium (18.5 mL, 24 mmol) in ether to copper(I) iodide (2.41 g, 12 mmol) suspended in dry ether (14 mL) at 0° under argon. Then ether (30 mL) and saturated, aqueous ammonium chloride (to decompose the excess of reagent) were slowly added. The precipitate was filtered off, the filtrate extracted with ether, and the extracts were combined, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was chromatographed in a column of silica gel with $CHCl_3$ → 3:97 MeOH–$CHCl_3$, giving **9α** (453 mg, 52%) and **12α** (84 mg, 10%), both as colorless syrups.

9α: R_F 0.40 (1:19 MeOH–$CHCl_3$); $[\alpha]_D^{15}$ +102° (*c* 1.29, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3500 cm^{-1} (OH); *m/z* 146 (M^+); for ^{1}H-n.m.r. data, see Table I.

12α: R_F 0.45 (1:19 MeOH–$CHCl_3$); $[\alpha]_D^{15}$ +148° (*c* 1.35, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3540 cm^{-1} (OH); *m/z* 146 (M^+); for ^{1}H-n.m.r. data, see Table I.

Similar treatment of **1β** with 2 equivalents of lithium dimethyl cuprate in ether did not produce the expected anomer (**9β** or **12β**).

*Methyl 3-*O-*acetyl-2,5-dideoxy-2-*C-*methyl-α-*D-*arabinofuranoside* (**10α**). — A mixture of **9α** (40 mg), pyridine (0.2 mL), and acetic anhydride (0.1 mL) was

kept for 36 h at 5°, diluted with cold water (5 mL), and extracted with 1:1 benzene–light petroleum. The extracts were combined, dried (Na_2SO_4), and evaporated, and the residue was chromatographed in a column of silica gel with hexane → 1:19 EtOAc–hexane, giving **10α** (42 mg, 80%) as a colorless syrup: R_F 0.4 (1:4 EtOAc–hexane); $[\alpha]_D^{15}$ +101° (*c* 1.15, $CHCl_3$); ν_{max}^{film} 1730 cm^{-1} (C=O); *m/z* 188 (M^+); for ^{1}H-n.m.r. data, see Table I.

Methyl 3-O-benzyl-2,5-dideoxy-2-C-methyl-α-D-xylofuranoside (**11α**). — A mixture of **9α** (215 mg, 1.47 mmol), benzyl chloride (0.5 mL, 4.3 mmol), calcium sulfate (0.3 g), 85% potassium hydroxide (0.95 g, ~17 mmol), and dry oxolane (3 mL) was refluxed under argon for 26 h, cooled, diluted with ether (10 mL) and cold water (5 mL) at <5°, and the pH brought to ~8. The aqueous layer was extracted with ether, and the ethereal layers were combined, dried (Na_2SO_4), and evaporated *in vacuo*. Chromatography of the residue in a column of silica gel with 1:1 benzene–hexane → 1:4 EtOAc–benzene afforded **11α** as a pale-yellow syrup (288 mg, 83%); R_F 0.55 (1:9 EtOAc–benzene); for ^{1}H-n.m.r. data, see Table I.

3-O-Acetyl-2,5-dideoxy-2-C-methyl-D-arabinofuranose (**13**). — A solution of **10α** (21 mg) in 49:49:2 acetonitrile–water–trifluoroacetic acid (1.2 mL) was stirred for 30 min at 0°, and then for 22 h at 20°; the pH was brought to 5.5 (Bromocresol Green) with solid sodium hydrogencarbonate, and the mixture extracted with several portions of CH_2Cl_2. The extracts were combined, dried (Na_2SO_4), and evaporated *in vacuo*, and the residue was chromatographed in a column of silica gel with benzene → 1:4 EtOAc–benzene, giving **13** as a colorless syrup (14.5 mg, 75%); R_F 0.2 (1:9 EtOAc–benzene); for ^{1}H-n.m.r. data, see Table I.

3-O-Benzyl-2,5-dideoxy-2-C-methyl-α,β-D-arabinofuranose (**14α,β**). — This compound was prepared according to the procedure described for **13**; thus, from 173 mg of **11α** was obtained 148 mg (91%) of **14** as a colorless syrup, R_F 0.15 (1:9 EtOAc–hexane); for ^{1}H-n.m.r. data, see Table I; the product consisted of an ~4:1 mixture of the α and β anomers (based on the n.m.r. spectrum).

Ethyl 5(S)-acetoxy-6(R)-hydroxy-4(R)-methyl-2(E)-heptenoate (**15**). — A solution of **13** (14.5 mg) and (ethoxycarbonyl)methylenetriphenylphosphorane[7] (38 mg) in dry benzene (1.3 mL) was refluxed under argon for 13 h, and then cooled, and chromatographed in a column of silica gel with hexane → 2:3 EtOAc–hexane, giving **15** as a colorless syrup (6.5 mg, 30%); R_F 0.7 (3:2 EtOAc–hexane); *m/z* 380 (M^+); for ^{1}H-n.m.r. data, see Table I.

3-O-Benzyl-2,5-dideoxy-2-C-methyl-D-arabinofuranose diethyl dithioacetal (**16**) *and ethyl 3-O-benzyl-2,5-dideoxy-2-C-methyl-1-thio-α-D-arabinofuranoside* (**18**). — A mixture of **14** (174 mg), ethanethiol (10 mL), and trifluoromethanesulfonic acid (~0.1 mL) was stirred under argon for 10 min at 0°, and then for 3 h at 20°, diluted with ether (10 mL) and water (3 mL) at 0°, and the acid neutralized with solid sodium hydrogencarbonate. The aqueous layer was extracted with ether, and the extracts were combined, dried (Na_2SO_4), and evaporated *in vacuo*; the residue was chromatographed in a column of silica gel with hexane → 1:4 EtOAc–hexane, giving **16** (50 mg, 20%) and **18** (153 mg, 73%).

16: R_F 0.4 (1:4 EtOAc–hexane); *m/z* (relative intensity) 328 (1.43, M^+), 205 (17.4, M − 2 EtSH + H), 161 (4.38, M − 2 EtSH − Ac), 131 (11.8, M − 2 EtSH − Ac − HCHO), and 91 (100, C_7H_7); for ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{17}H_{28}O_2S_2$: mol. wt., 328.1530. Found*: mol. wt., 328.1527.

18: R_F 0.7 (1:4 EtOAc–hexane); *m/z* 266 (M^+); for ^{1}H-n.m.r. data, see Table I.

*4-O-Acetyl-3-O-benzyl-2,5-dideoxy-2-C-methyl-*D*-arabinose diethyl dithioacetal* (**17**). — A mixture of **16** (101 mg), dry pyridine (5 mL), and acetic anhydride (2.5 mL) was stirred under argon overnight at 18°, evaporated *in vacuo*, and the residue, diluted with cold water (2 mL), was extracted with 1:1 benzene–light petroleum. The extracts were combined, and evaporated *in vacuo*, and the residue was chromatographed in a column of silica gel with hexane → 1:19 EtOAc–hexane, giving **17** as a colorless syrup (110 mg, 97%); R_F 0.55 (1:4 EtOAc–hexane); $[\alpha]_D^{15}$ −0.88° (*c* 1.13, $CHCl_3$); for ^{1}H-n.m.r. data, see Table I.

*4-O-Acetyl-3-O-benzyl-2,5-dideoxy-2-C-methyl-*D*-arabinose dimethyl acetal* (**19**). — A mixture of **17** (75 mg, 0.20 mmol), mercury(II) chloride (277 mg, 1.0 mmol), and cadmium(II) carbonate (100 mg, 0.58 mmol) in absolute methanol (2 mL) was refluxed under argon for 12 h, cooled, filtered, and the filtrate evaporated *in vacuo*. A solution of the residue in $CHCl_3$ (10 mL) was washed with brine, evaporated *in vacuo*, and the residue chromatographed in a column of silica gel with hexane → 1:19 EtOAc–hexane, giving **19** (58 mg, 92%) as a colorless syrup; R_F 0.40 (1:4 EtOAc–hexane); $[\alpha]_D^{15}$ +1.02° (*c* 1.96, $CHCl_3$); *m/z* 278 (0.97, M − MeOH), 246 (1.41, M − 2 MeOH), 91 (85.3, C_7H_7), and 75 (100, MeOAc + H); for ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{16}H_{22}O_4$ (M − MeOH): mol. wt., 278.1518. Found*: mol. wt., 278.1520.

*4-O-Acetyl-2,5-dideoxy-2-C-methyl-*D*-arabinose dimethyl acetal* (**20**). — A solution of **19** (32 mg) in absolute methanol (0.5 mL) was hydrogenolyzed at room temperature in the presence of 10% Pd–C (12 mg), the suspension filtered, the filtrate evaporated, and the residue purified by chromatography in a column of silica gel with hexane → 1:4 EtOAc–hexane, giving **20** (20 mg, 88%) as a colorless syrup; R_F 0.15 (1:4 EtOAc–hexane); for ^{1}H-n.m.r. data, see Table I.

*4-O-Acetyl-2,5-dideoxy-2-C-methyl-*D*-arabinose* (**21**). — A solution of **20** (19 mg) in 49:49:2 acetonitrile–water–trifluoroacetic acid (2 mL) was stirred for 15 min at 0°, and for 4 h at 15°, the acid neutralized at 5° with solid $NaHCO_3$, and the mixture extracted with CH_2Cl_2. The extract was evaporated *in vacuo*, and the residue chromatographed in a column of silica gel with hexane → 1:4 EtOAc–hexane, giving **21** as a colorless liquid (12 mg, 80%); R_F 0.35 (2:3 EtOAc–hexane); *m/z* 175 (40.7, M + 1), 157 (25.1, M − OH), 128 (65.1, M − HCO_2H), 115 (85.2, M −

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AcO), 97 (49.0, M − AcOH − OH), and 86 (100, M − AcOH − CO); for ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_8H_{15}O_4$ (M + 1): mol. wt., 175.0970. Found*: mol. wt., 175.0973.

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