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SYNTHESIS OF 1,2-DIDEOXY-3-HEPTULOSE DERIVATIVES

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ABSTRACT

Reaction of 2,3-*O*-isopropylidene-D-glyceraldehyde with triphenyl(propionylmethylene)phosphorane gave a mixture of (*Z*)- (3) and (*E*)-1,2,4,5-tetradeoxy-6,7-*O*-isopropylidene-D-*glycero*-hept-4-en-3-ulose (4) that was resolved by chromatography. Hydroxylation of **3** with osmium tetraoxide yielded 1,2-dideoxy-6,7-*O*-isopropylidene-D-*lyxo*- (**5**) and -D-*ribo*-3-heptulose (**7**) which were separated by column chromatography. Similarly, **4** gave a mixture of 1,2-dideoxy-6,7-*O*-isopropylidene-D-*arabino*- (**9**) and -D-*xylo*-3-heptulose (**11**) that could be partially resolved by chromatography. On acetonation, **5** and **7** afforded 1,2-dideoxy-4,5-*O*-isopropylidene-D-*lyxo*-3-heptulo-3,6-furanose and 3,7-anhydro-1,2-dideoxy-4,5-*O*-isopropylidene-β-D-*ribo*-3-heptulo-3,6-furanose, respectively, whereas the mixture of **9** and **11** gave 1,2-dideoxy-3,4:5,6-di-*O*-isopropylidene-β-D-*arabino*-3-heptulo-3,7-pyranose, 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-*keto*-D-*arabino*-3-heptulose, and 1,2-dideoxy-3,4:5,7-di-*O*-isopropylidene-α-D-*xylo*-3-heptulo-3,6-furanose. Deacetonation of **5**, **7**, **9**, and **11** gave 1,2-dideoxy-D-*lyxo*-, -D-*ribo*, -D-*arabino*-, and -D-*xylo*-3-heptulose, respectively.

INTRODUCTION

We have reported[1] on the synthesis of enuloses by reaction of *aldehydo* sugars with phosphorus ylids and their use in the synthesis of hexuloses[2], deoxyhexuloses[3], and anhydrohexuloses[4]. We now report on the synthesis of 1,2-dideoxy-hept-4-en-3-uloses and 1,2-dideoxy-3-heptuloses. Of the 3-heptuloses, coriose (D-*altro*-3-heptulose) is the best known, but others have been reported[5].

RESULTS AND DISCUSSION

The reaction of 2,3-*O*-isopropylidene-D-glyceraldehyde (**1**) with triphenyl(propionylmethylene)phosphorane[6] (**2**) severally in methanol and dichloromethane gave mixtures of (*Z*)- (**3**) and (*E*)-1,2,4,5-tetradeoxy-6,7-*O*-isopropylidene-D-*glycero*-

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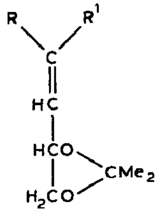
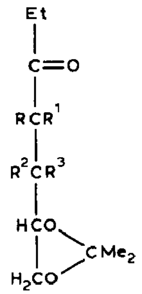
hept-4-en-3-ulose (**4**) in the ratios 1.3:1 and 1:3.6 (isolated products), respectively. The ^{1}H-n.m.r. spectra for **3** and **4** showed $J_{4,5}$ values of 11 and 16 Hz, respectively, in accordance with the *Z* and *E* configurations. The signals for H-5 and H-6 for **3** appeared at δ 6.13 and 5.33, and for **4** at δ 6.75 and 4.68. The ketone carbonyl group deshields H-6 in the *Z* isomer, and H-5 in the *E* isomer. The i.r. absorption for the carbonyl group of **3** occurred at a frequency higher ($\Delta\nu$ 15 cm^{-1}) than that of **4**, reflecting the poorer conjugation in the *Z* isomer. The reverse difference ($\Delta\nu$ 20 cm^{-1}) was found for the C = C absorption. The ϵ value for the u.v. absorption of **3** was less than that of **4**, and indicative of the *Z* configuration. These results accord with those found[1] for analogous compounds.

The difference in the stereoselectivity found in the reaction of **1** and **2** in methanol and dichloromethane accords with previous data[1,4], where the yield of the *Z* isomer was improved by the use of a solvent of higher polarity.

Hydroxylation of **3** with osmium tetraoxide gave a mixture of 1,2-dideoxy-6,7-*O*-isopropylidene-D-*lyxo*- (**5**) and -D-*ribo*-3-heptulose (**7**), and, in the same way, **4** gave a mixture of the D-*arabino* (**9**) and D-*xylo* (**11**) isomers.

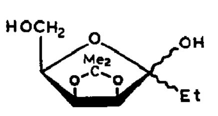


3 R = H, R^1 = COEt
4 R = COEt, R^1 = H



5 R = R^2 = OH, R^1 = R^3 = H
6 R = R^2 = OAc, R^1 = R^3 = H
7 R = R^2 = H, R^1 = R^3 = OH
8 R = R^2 = H, R^1 = R^3 = OAc
9 R = R^3 = OH, R^1 = R^2 = H
10 R = R^3 = OAc, R^1 = R^2 = H
11 R = R^3 = H, R^1 = R^2 = OH
12 R = R^3 = H, R^1 = R^2 = OAc

The mixture of **5** and **7** was resolved by column chromatography. The configuration of **7** was established by acetonation, which gave 3,7-anhydro-1,2-dideoxy-4,5-*O*-isopropylidene-β-D-*ribo*-3-heptulo-3,6-furanose (**14**) identified on the basis of its analytical and spectroscopic data. Thus, the ^{1}H-n.m.r. spectrum of **14** contained a pattern of signals for H-4,5,6,7*endo*,7*exo* identical to that reported[3,7] for 2,6-anhydro-1-deoxy-3,4-*O*-isopropylidene-β-D-psicofuranose. On the basis of the foregoing results, the D-*lyxo* configuration was assigned to **5**. Acetonation of **5** gave a complex mixture of products from which the main component was isolated by column chromatography, and identified as 1,2-dideoxy-4,5-*O*-isopropylidene-D-*lyxo*-3-heptulo-3,6-furanose (**13**). The ^{1}H-n.m.r. spectrum of **13** contained a pattern



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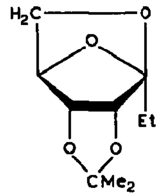

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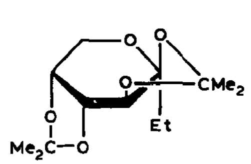

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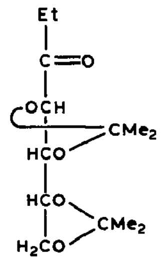

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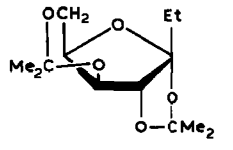

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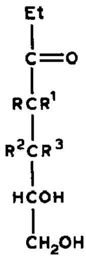

18 $R = R^2 = OH, R^1 = R^3 = H$
19 $R^1 = R^3 = OH, R = R^2 = H$
20 $R = R^3 = OH, R^1 = R^2 = H$
21 $R = R^3 = H, R^1 = R^2 = OH$

of signals similar to that[3b] for the homologous 1-deoxy-3,4-*O*-isopropylidene-D-tagatofuranose.

The mixture of **9** and **11** was only partially resolved by column chromatography (see Experimental). Acetonation of a mixture in which **9** preponderated and column chromatography of the products gave, first, a ~1:1 mixture of 1,2-deoxy-3,4:5,6-di-*O*-isopropylidene-β-D-*arabino*-3-heptulo-3,7-pyranose (**15**) and 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-*keto*-D-*arabino*-3-heptulose (**16**), identified on the basis of the ^{1}H-n.m.r. data (see below). The product of lower mobility was 1,2-dideoxy-3,4:5,7-di-*O*-isopropylidene-α-D-*xylo*-3-heptulo-3,6-furanose (**17**).

The ^{1}H-n.m.r. spectrum of **17** contained resonances for H-4,5,6,7,7′ as two singlets at δ 4.28 and 4.03 with relative intensities of 2:3, in agreement with data for analogous di-*O*-isopropylidene derivatives of 1-deoxy-L-[8] and 1-deoxy-D-sorbose[8] which have α-furanose structures. The $[\alpha]_D$ value (−3°) of **17** was similar to that (−2°) of the homologous di-*O*-isopropylidene derivative[8].

That the component with higher mobility was a mixture of cyclic and acyclic di-*O*-isopropylidene derivatives was demonstrated by the i.r. absorption for carbonyl at 1725 cm^{-1} and the ^{1}H-n.m.r. signals at δ 2.68 (q) and δ 2.03–1.67 (m) for methylene groups α to a ketone and an acetalic carbon atom, respectively. Borohydride reduction of the mixture gave a product with lower mobility, column chromatography of which gave **15**, which contained a cyclic structure since it had no i.r. absorption for hydroxyl or carbonyl. The ^{1}H-n.m.r. resonances for H-4,5,6,7,7′ of **15** were similar to those for the di-*O*-isopropylidene derivative of 1-deoxy-β-D-fructopyranose[8].

The product of lower mobility was, presumably, a mixture of 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-D-*gluco*- and -D-*manno*-heptitol, since, on oxidation with ruthenium tetraoxide, it yielded a compound (**16**) with i.r. absorption for carbonyl and, under the conditions used in the acetonation of **9** and **11**, it was partially isomerised to **16** but not to **17**.

Hydrolysis of **5**, **7**, **9**, and **11** gave 1,2-dideoxy-D-*lyxo*- (**18**), -D-*ribo*- (**19**), -D-*arabino*- (**20**), and -D-*xylo*-3-heptulose (**21**), respectively. Finally, the equilibrium composition of the mixture **18–21** in aqueous solution was determined by ^{13}C-n.m.r. spectroscopy on the basis of data for 1-deoxy-D-tagatose, literature data[9], and on the results obtained on the formation of complexes with calcium[10]. The proportions of various forms were determined[9] by averaging the signals of each form which were clearly separated from the others.

The ^{13}C-n.m.r. spectrum of 1-deoxy-D-tagatose (Table I) indicated the presence of α- and β-pyranose and α-furanose forms. When calcium chloride was added to the solution, the signals for the β-pyranose form increased in intensity and signals for the β-furanose and *keto*-forms appeared. A down-field shift of the signal of C-3 with respect to that of D-tagatose[9b] occurred, except in the α-furanose form where an up-field shift of the resonances of C-2,3,4,5 occurred. The ^{13}C-n.m.r. spectrum of **18** (see Table II), a homologue of 1-deoxy-D-tagatose, indicated the presence of only α-pyranose (major) and α-furanose forms. On addition of calcium chloride, two new isomers could be detected, presumably the β-furanose and β-pyranose forms, since these isomers are the only ones which have hydroxyl groups suitable for the formation of complexes[10]. Traces of the acyclic forms were detected under both

TABLE I

^{13}C-CHEMICAL SHIFTS AND PROPORTIONS (%) IN THE EQUILIBRIUM OF 1-DEOXY-D-TAGATOSE

Form	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Proportion*	
α-*p*	24.9	99.0	73.8	71.7	66.9	63.0	73.5	41.7[a]
α-*f*	24.6	102.7	75.9	66.6	77.4	63.4	20.2	9.4[a]
β-*p*	25.4	99.5	68.9	73.5	69.9	61.1	6.3	38.2[a]
+ $CaCl_2$[a]	25.7	99.0	69.6	73.4	70.3	60.6		
β-*f* + $CaCl_2$[a]	25.6	103.2	68.2	71.4	80.8	62.2		8.0[a]
keto + $CaCl_2$[a]	28.2	215.0						2.5[a]

[a]2 Equiv. of $CaCl_2{\cdot}2H_2O$.

TABLE II

^{13}C-CHEMICAL SHIFTS AND PROPORTIONS (%) IN THE EQUILIBRIUM OF **18**

Form	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*Proportion*
α-p	7.4	30.2	100.9	71.9	71.1	67.2	63.0	75
$+CaCl_2$[a]	7.5	30.1	100.9	71.8	71.0	67.2	62.9	84.4
α-f	7.7	30.0	104.7	75.5	72.1	76.7	61.3	25
$+CaCl_2$[a]	8.0	30.1	104.6	75.6	72.1	77.3	60.6	8
β-f$+CaCl_2$[a]	7.3	30.5	105.0	69.9	70.8	80.7	63.3	6.3
β-p$+CaCl_2$[a]	7.3	30.9	100.7	65.8	69.5	66.9	62.0	1.1
keto	7.9	34.5	215.2					traces
$+CaCl_2$[a]	8.1	34.4	217.5					traces

[a]2 Equiv. of $CaCl_2 \cdot 2H_2O$.

sets of experimental conditions.

All the 35 signals of the five forms of **19** were discernible and could be assigned (see Table III) by comparison with spectra of D-psicose[9b] and 1-deoxy-L-psicose[9a], and on the basis of the formation of calcium complexes. Thus, there was a remarkable decrease in the intensity of the peaks corresponding to the β-furanose form and an increase in the intensity of those of the other cyclic isomers, mainly those of the α-furanose and β-pyranose forms. This behaviour accords with data previously reported[9]. There was a good correlation of the chemical shifts and, as in the psicose series, the chemical shift of the signal for C-4 (C-3 in a hexulose) was affected by changes at the anomeric carbon atom, the down-field shift being less when hydroxymethyl was replaced by ethyl than by methyl.

The ^{13}C-n.m.r. spectrum of **20** (see Table IV) contained four sets of seven peaks assigned to β-pyanose, β-furanose, α-furanose, and *keto* forms. These results were in good agreement with data[9] in the literature and the above-mentioned effect on C-4 was observed also.

The ^{13}C-n.m.r. spectrum of **21** (see Table V) contained seven intense peaks,

TABLE III

^{13}C-CHEMICAL SHIFTS AND PROPORTIONS (%) IN THE EQUILIBRIUM OF **19**

Form	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*Proportion*
α-f	8.1	30.4	105.6	73.0	71.7	83.5	62.4	38
β-f	7.9	28.2	109.0	75.4	71.5	83.1	64.0	10
α-p	7.7	31.1	100.2	69.9	71.1	66.1	59.2	27
β-p	7.0	30.2	101.2	72.5	67.0	68.8	65.4	19
keto	6.8	33.3	215.7	79.1	73.6	72.3	64.9	6

TABLE IV

^{13}C-CHEMICAL SHIFTS AND PROPORTIONS (%) IN THE EQUILIBRIUM OF **20**

Form	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*Proportion*
β-p	7.7	31.1	100.3	69.9	70.5	70.4	64.0	41.5
β-f	7.3	30.9	104.0	78.8	75.7	81.2	63.2	37
α-f	7.2	28.4	108.3	83.2	77.2	82.0	62.4	13
keto	7.9	32.6	216.7	78.4	72.0	71.6	63.7	8.5

TABLE V

^{13}C-CHEMICAL SHIFTS AND PROPORTIONS (%) IN THE EQUILIBRIUM OF **21**

Form	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-7*	*Proportion*
α-p	7.2	31.0	99.9	73.6	74.8	70.5	62.6	~100

even after 80,000 scans, which were asssigned to the α-pyranose form on the basis of a comparison with data for L-sorbose[9b] and its 1-deoxy derivative[9a].

EXPERIMENTAL

General methods. — Solutions were dried over $MgSO_4$ before concentration under diminished pressure. ^{1}H-N.m.r. spectra (80 MHz, $CDCl_3$, internal Me_4Si) were recorded with a Bruker WP-80 CW spectrometer and ^{13}C-n.m.r. spectra [20.11 MHz, internal 1,4-dioxane (δ 67.4 relative to external Me_4Si)] were obtained at 32° with a Bruker WP-80 SY spectrometer with deuterium lock. Most solutions were 1.5–2.0M in deuterium oxide. I.r. spectra were recorded with a Perkin-Elmer 782 instrument and mass spectra with a Hewlett-Packard 5970 mass spectrometer. Optical rotations were measured for solutions in chloroform (1-dm tube) with a Perkin-Elmer 141 polarimeter. R_F values are reported for t.l.c. performed on Silica Gel G (Merck) with ether–hexane (3:2) and detection by charring with sulfuric acid. Column chromatography was performed on silica gel (Merck, 7734). Descending p.c. was performed on Whatman No. 1 paper with *A*, 1-butanol-ethanol-water (28:7:13); *B*, 1-butanol–ethanol–water (4:1:5, upper layer); and *C*, 2% of phenylboronic acid in *B*; and detection with silver nitrate[11]. With solvent *C*, Britton's method[12] was used prior to detection.

The non-crystalline compounds for which elemental analyses were not obtained were shown to be homogeneous by chromatography and were characterised by n.m.r. and mass spectrometry.

Reaction of 2,3-O-isopropylidene-D-glyceraldehyde (**1**) *with triphenyl(propionylmethylene)phosphorane* (**2**). — (*a*) To a stirred solution of **1** (10.8 g, 83 mmol) in dry methanol (50 mL) at room temperature was added dropwise a solution of the ylid 2[6] (26.5 g, 79.5 mmol) in the same solvent (50 mL). T.l.c. then revealed two new compounds, R_F 0.68 and 0.53. The mixture was left for 24 h at room temperature and then concentrated, and the solid residue was extracted with hexane (4×25 mL). The combined extracts were cooled for 1 h at 5°, filtered, and concentrated. Column chromatography (ether–hexane, 1:6) of the residue gave, first, (*Z*)-1,2,4,5-tetradeoxy-6,7-*O*-isopropylidene-D-*glycero*-hept-4-en-3-ulose (3; 6.9 g, 47%), isolated as a mobile oil, $[\alpha]_D$ +150° (*c* 1.25); ν_{max}^{film} 2998, 2942, and 2882 (C–H), 1696 (ketone, C=O), 1622 (C=C), 1382 and 1373 (CMe_2), 1260, 1214, 1156, 1059, 991 (=C–H), and 861 cm^{-1} (1,3-dioxolane ring); λ_{max}^{MeOH} 229 nm (ε, 6600). ^{1}H-N.m.r. data: δ 6.22 (m, 2 H, H-4,5), 5.33 (m, 1 H, H-6), 4.42 (dd, 1 H, $J_{6,7}$ 7, $J_{7,7'}$ 8 Hz, H-7), 3.54 (dd, 1 H, $J_{6,7'}$ 7 Hz, H-7'), 2.50 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 1.43 and 1.35 (2 s, 6 H, CMe_2), and 1.05 (t, 3 H, H-1,1,1); δ (acetone-d_6) 6.35 (d, 1 H, $J_{4,5}$ 11 Hz, H-4), 6.13 (dd, 1 H, $J_{5,6}$ 5 Hz, H-5), 5.25 (dt, 1 H, $J_{6,7}$ = $J_{6,7'}$ = 7 Hz, H-6), 4.30 (dd, 1 H, $J_{7,7'}$ 8 Hz, H-7), 3.46 (dd, 1 H, H-7'), 2.53 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 1.35 and 1.30 (2 s, 6 H, CMe_2), and 0.99 (t, 3 H, H-1,1,1). Mass spectrum: *m/z* 169 ($M^{+\cdot}$ –Me), 155 ($M^{+\cdot}$ –Et), 154, 128, 127 ($M^{+\cdot}$ –EtCO), 126 ($M^{+\cdot}$ –Me_2CO), 125 ($M^{+\cdot}$ –EtCOH), 111, 109 ($M^{+\cdot}$ –Me–AcOH), 98, 97, 96, 81, 72, 69 ($M^{+\cdot}$ –EtCO –Me_2CO), 59 (Me_2COH^+), 57 ($EtCO^+$), and 43 (Ac^+, base peak).

Eluted second was (*E*)-1,2,4,5-tetradeoxy-6,7-*O*-isopropylidene-D-*glycero*-hept-4-en-3-ulose (4; 5.14 g, 35%), isolated as a mobile oil, $[\alpha]_D$ +32° (*c* 1.35); ν_{max}^{film} 2990, 2942, and 2883 (C–H), 1681 (ketone, C=O), 1642 (C=C), 1384 and 1373 (CMe_2), 1254, 1219, 1156, 1063, 979 (=C–H), and 845 cm^{-1} (1,3-dioxolane ring); λ_{max}^{MeOH} 220 nm (ε, 11,000). ^{1}H-N.m.r. data: δ 6.75 (dd, 1 H, $J_{4,5}$ 16, $J_{5,6}$ 5.3 Hz, H-5), 6.34 (dd, 1 H, $J_{4,6}$ 1.3 Hz, H-4), 4.68 (m, 1 H, H-6), 4.19 (dd, 1 H, $J_{6,7}$ 6.5, $J_{7,7'}$ 8 Hz, H-7), 3.66 (dd, 1 H, $J_{6,7'}$ 7 Hz, H-7'), 2.55 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 1.43 and 1.39 (2 s, 6 H, CMe_2), and 1.08 (t, 3 H, H-1,1,1). Mass spectrum: *m/z* 171 ($M^{+\cdot}$ +2–Me), 170 ($M^{+\cdot}$ +1–Me), 169 ($M^{+\cdot}$ –Me), 155 ($M^{+\cdot}$ –Et), 154, 128, 127 ($M^{+\cdot}$ –EtCO), 125 ($M^{+\cdot}$ –EtCOH), 113, 111, 109 ($M^{+\cdot}$ –Me–AcOH), 99, 98, 97, 96, 95, 85, 84, 83, 82, 81, 79, 72, 71, 70, 69 ($M^{+\cdot}$ –EtCO–Me_2CO), 59 ($MeCOH^+$), 57 ($EtCO^+$), and 43 (Ac^+, base peak).

(*b*) To a solution of 1 (765 mg, 6 mmol) in dichloromethane (12.5 mL) at room temperature was added a solution of 2 (2 g, 6 mmol) in the same solvent (12.5 mL). After 30 min, the procedure in (*a*) then gave 3 (200 mg, 18%) and 4 (720mg, 65%).

Hydroxylation of 3. — To a solution of 3 (3.22 g, 17.5 mmol) in methanol (50 mL) was added a solution of potassium chlorate (1.15 g, 9.4 mmol) in water (25 mL). The mixture was acidified (pH ~ 4) with acetic acid (0.7 mL), aqueous 1% osmium tetraoxide (7 mL) was added, and the mixture was left for 5 h at room temperature. T.l.c. then revealed the disappearance of 3, and two products, R_F 0.21 and 0.12. The mixture was neutralised (anhydrous $NaHCO_3$) and concentrated, the residue was extracted with ethyl acetate (3 × 40 mL), and the combined extracts were concentrated. Column chromatography (ether–hexane, 1:1 → 2:1) of the residue gave, first, 1,2-dideoxy-6,7-*O*-isopropylidene-D-*lyxo*-3-heptulose (5; 2.06 g, 54%), m.p. 44–45° (from hexane), $[\alpha]_D$ +60° (*c* 1.2); ν_{max}^{KBr} 3341 (OH), 2995, 2942, and 2895 (C–H), 1724 (ketone, C=O), 1386 and 1375 (CMe_2), 1214, 1162, 1068, and 869 cm^{-1} (1,3-dioxolane ring). N.m.r. data: ^1H ($CDCl_3$ + D_2O), δ 4.34 (dt, 1 H, $J_{5,6}$ 4, $J_{6,7}$ = $J_{6,7'}$ = 7 Hz, H-6), 4.13 (d, 1 H, $J_{4,5}$ 8 Hz, H-4), 4.08 (dd, 1 H, $J_{7,7'}$ 8.5 Hz, H-7), 3.86 (dd, 1 H, H-7'), 3.46 (dd, 1 H, H-5), 2.84 (dq, 1 H, $J_{1,2}$ 7, $J_{2,2'}$ 14 Hz, H-2), 2.60 (dq, 1 H, H-2'), 1.43 and 1.36 (2 s, 6 H, CMe_2), and 1.07 (t, 3 H, H-1,1,1). Before exchange with D_2O, signals at δ 3.50 and 2.75 (2 d, $J_{4,OH}$ = $J_{5,OH}$ = 6.5 Hz, HO-4,5) were observed; ^{13}C, δ 212.65 (C-3), 109.46 (CMe_2), 77.26 (C-4), 76.15 (C-5), 72.58 (C-6), 66.40 (C-7), 33.90 (C-2), 26.40 and 25.16 ($C\mathit{Me}_2$), and 7.34 (C-1).

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.30; H, 8.41.

Conventional acetylation of **5** (275 mg, 1.26 mmol) in dry pyridine (4 mL) and acetic anhydride (2 mL) yielded, after column chromatography (ether–hexane, 1:3), the 4,5-diacetate **6** (280 mg, 74%), R_F 0.39, m.p. 58–60°, $[\alpha]_D$ +5° (*c* 1.13); ν_{max}^{KBr} 2988, 2940, 2920, and 2883 (C–H), 1751 (ester, C=O), 1741 (ketone, C=O), 1373 (CMe_2), 1220, 1066, and 851 cm^{-1} (1,3-dioxolane ring). ^1H-N.m.r. data: δ 5.28 (t, 1 H, $J_{4,5}$ = $J_{5,6}$ = 5 Hz, H-5), 5.13 (d, 1 H, H-4), 4.33 (dt, 1 H, $J_{6,7}$ = $J_{6,7'}$ = 6.3 Hz, H-6), 4.05 (dd, 1 H, $J_{7,7'}$ 8.3 Hz, H-7), 3.75 (dd, 1 H, H-7'), 2.73–2.35 (m, 2 H, H-2,2'), 2.11 and 2.06 (2 s, 6 H, 2 Ac), 1.38 and 1.30 (2s, 6 H, 6 Me_2), and 1.03 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1).

Anal. Calc. for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34. Found: C, 55.82; H, 7.16.

Eluted second was 1,2-dideoxy-6,7-*O*-isopropylidene-D-*ribo*-3-heptulose (**7**; 925 mg, 24%), m.p. 44–46° (from hexane), $[\alpha]_D$ −59° (*c* 1.25); ν_{max}^{KBr} 3514 and 3455 (OH), 2996, 2983, 2946, and 2878 (C–H), 1699 (ketone C=O), 1384 and 1373 (CMe_2), 1264, 1232, 1211, 1161, 1140, 1106, 1070, and 842 cm^{-1} (1,3-dioxolane ring). N.m.r. data: ^1H, δ 4.29 (bt, 1 H, $J_{4,OH}$ = $J_{4,5}$ = 4 Hz, H-4), 4.20–3.69 (m, 4 H, H-5,6,7,7'), 3.84 (d, 1 H, HO-4), 2.81 (d, 1 H, $J_{5,OH}$ 7 Hz, HO-5), 2.63 (m, 2 H, H-2,2'), 1.38 and 1.30 (2 s, 6 H, CMe_2), and 1.11 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1). ^{13}C, δ 210.00 (C-3), 109.70 (CMe_2), 78.24 (C-4), 74.21 (C-5), 74.00 (C-6), 66.97 (C-7), 32.61 (C-2), 26.33 and 25.00 ($C\mathit{Me}_2$), and 7.40 (C-1).

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.45; H, 8.62.

Conventional acetylation of **7** (370 mg, 1.7 mmol) in dry pyridine (4 mL) and acetic anhydride (2 mL) yielded, after column chromatography (ether–hexane, 1:3), the syrupy acetate **8** (370 mg, 72%), R_F 0.39, $[\alpha]_D$ −13° (*c* 1.15); ν_{max}^{film} 2991, 2941, and 2889 (C–H), 1758 (ester and ketone, C=O), 1374 (CMe_2), 1219, 1155, 1072, 1060, and 842 cm^{-1} (1,3-dioxolane ring). ^1H-N.m.r. data: δ 5.47 (d, 1 H, $J_{4,5}$ 2.7 Hz, H-4), 5.33 (dd, 1 H, $J_{5,6}$ 6.6 Hz, H-5), 4.30 (m, 1 H, H-6), 4.06 (dd, 1 H, $J_{6,7}$ 6, $J_{7,7'}$ 8.7 Hz, H-7), 3.81 (dd, 1 H, $J_{6,7'}$ 5 Hz, H-7'), 2.79–2.33 (m, 2 H, H-2,2'), 2.18 and 2.05 (2 s, 6 H, 2 Ac), 1.34 and 1.32 (2 s, 6 H, CMe_2), and 1.06 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1).

Hydroxylation of **4**. — A solution of **4** (3.41 g, 18.5 mmol) in methanol (50 mL) was treated with potassium chlorate (1.21 g, 10 mmol), acetic acid (0.8 mL), and aqueous 1% osmium tetraoxide (8 mL). Following the above procedure, the product isolated (3.59 g) contained two components (R_F 0.20 and 0.18). Column chromatography (ether–hexane, 1:1) of this mixture gave, first, a product (1.52 g), m.p. 84–86°, which, after two recrystallisations from hexane, afforded 1,2-dideoxy-6,7-*O*-isopropylidene-D-*arabino*-3-heptulose (9), m.p. 87–88°, $[\alpha]_D$ +85° (*c* 1.27); ν_{max}^{KBr} 3488 (OH), 2995, 2981, 2908, and 2888 (C–H), 1723 (ketone, C=O), 1385 and 1373 (CMe_2), 1223, 1165, 1151, 1085, 1069, 868, and 847 cm^{-1} (1,3-dixolane ring). N.m.r. data: ^1H, δ 4.41 (bd, 1 H, $J_{4,OH}$ 4 Hz, H-4), 4.25–3.77 (m, 4 H, H-5,6,7,7′), 3.98 (d, 1 H, HO-4), 2.55 (m, 2 H, H-2,2′), 2.22 (d, 1 H, $J_{5,OH}$ 10 Hz, HO-5), 1.45 and 1.35 (2 s, 6 H, CMe_2), and 1.12 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1); ^{13}C, δ 211.02 (C-3), 109.33 (CMe_2), 76.22 (C-4), 75.46 (C-5), 72.55 (C-6), 66.74 (C-7), 31.13 (C-2), 26.89 and 25.02 (CMe_2), and 7.37 (C-1).

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.55; H, 8.56.

Conventional acetylation of 9 (70 mg, 0.32 mmol) in dry pyridine (1 mL) and acetic anhydride (0.5 mL) yielded, after column chromatography (ether–hexane, 1:2), the syrupy 4,5-diacetate 10 (90 mg, 94%), R_F 0.38, $[\alpha]_D$ +65° (*c* 1.27); ν_{max}^{film} 2990 and 2945 (C–H), 1757 (ester, C=O), 1740 (ketone, C=O), 1375 (CMe_2), 1216, 1075, 1028, and 843 cm^{-1} (1,3-dioxolane ring). ^1H-N.m.r. data: δ 5.34 (dd, 1 H, $J_{4,5}$ 2.3, $J_{5,6}$ 6 Hz, H-5), 5.28 (d, 1 H, H-4), 4.25 (m, 1 H, H-6), 4.03 (dd, 1 H, $J_{6,7}$ 5.7, $J_{7,7'}$ 8.3 Hz, H-7), 3.82 (dd, 1 H, $J_{6,7'}$ 5 Hz, H-7′), 2.70–2.35 (m, 2 H, H-2,2′), 2.15 and 2.01 (2 s, 6 H, 2 Ac), 1.41 and 1.31 (2 s, 6 H, CMe_2), and 1.02 (t, 3 H, $J_{1,2}$ 8 Hz, H-1,1,1).

Eluted second was 1,2-dideoxy-6,7-*O*-isopropylidene-D-*xylo*-3-heptulose (11, 135 mg), m.p. 107–108° (from ether–hexane), $[\alpha]_D$ −48° (*c* 1.12); ν_{max}^{KBr} 3449 and 3381 (OH), 2989, 2946, and 2901 (C–H), 1716 (ketone, C=O), 1383 and 1373 (CMe_2), 1260, 1217, 1155, 1110, 1072, and 865 cm^{-1} (1,3-dioxolane ring). N.m.r. data: ^1H, δ 4.31 (q, 1 H, $J_{5,6} = J_{6,7} = J_{6,7'} = 6$ Hz, H-6), 4.12 (dd, 1 H, $J_{4,OH}$ 4.7, $J_{4,5}$ 2.3 Hz, H-4), 4.10 (dd, 1 H, $J_{7,7'}$ 8 Hz, H-7), 3.92 (ddd, 1 H, $J_{5,OH}$ 6.6 Hz, H-5), 3.85 (dd, 1 H, H-7′), 3.68 (d, 1 H, HO-4), 2.78 (dq, 1 H, $J_{1,2}$ 7, $J_{2,2'}$ 15 Hz, H-2), 2.58 (d, 1 H, HO-5), 2.47 (dq, 1 H, H-2′), 1.45 and 1.38 (2 s, 6 H, CMe_2), and 1.02 (t, 3 H, H-1,1,1); ^{13}C, δ 210.31 (C-3), 109.92 (CMe_2), 77.20 (C-4), 76.68 (C-5), 72.36 (C-6), 66.03 (C-7), 31.76 (C-2), 26.61 and 25.26 (CMe_2), and 7.33 (C-1).

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.36; H, 8.60.

A mixture (1.24 g) of 9 and 11 was also obtained.

Conventional acetylation of 11 (25 mg, 0.11 mmol) in dry pyridine (0.5 mL) and acetic anhydride (0.2 mL) yielded, after column chromatography (ether–hexane, 1:1), the syrupy 4,5-diacetate 12 (25 mg, 76%), R_F 0.40, $[\alpha]_D$ −40° (*c* 1.23); ν_{max}^{film} 2990, 2945, and 2891 (C–H), 1757 (ester, C=O), 1750 (ketone, C=O), 1374 (CMe_2), 1218, 1156, 1132, 1077, 1030, and 849 cm^{-1} (1,3-dioxolane ring). ^1H-N.m.r. data: δ 5.23 (dd, 1 H, $J_{4,5}$ 3.3, $J_{5,6}$ 5.7 Hz, H-5), 5.07 (d, 1 H, H-4), 4.15 (q, 1 H, $J_{6,7} = J_{6,7'} = 5.7$ Hz, H-6), 4.00–3.70 (m, 2 H, H-7,7′), 2.72 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 2.10 and 2.02 (2 s, 6 H, 2 Ac), 1.35 and 1.25 (2 s, 6 H, CMe_2), and 1.01 (t, 3 H, H-1,1,1).

Acetonation of 5. — A solution of 5 (600 mg, 2.75 mmol) in dry acetone (20 mL) and conc. sulfuric acid (0.1 mL) was stirred for 24 h at room temperature with anhydrous copper sulfate (2 g). T.l.c. then showed a complex mixture in which the substance with R_F 0.09 preponderated. The mixture was neutralised (K_2CO_3), filtered, and concentrated. Column chromatography (ether–hexane, 1:3) of the residue yielded syrupy 1,2-dideoxy-4,5-*O*-isopropylidene-D-*lyxo*-3-heptulo-3,6-furanose (**13**; 60 mg, 10%), $[\alpha]_D$ +9° (*c* 1); ν_{max}^{film} 3381 (OH), 2987, 2945, and 2890 (C–H), 1382 and 1374 (CMe_2), 1214, 1166, 1097, 1077, 979, and 882 cm^{-1} (1,3-dioxolane ring). ^{1}H-N.m.r. data: δ 4.83 (dd, 1 H, $J_{4,5}$ 6, $J_{5,6}$ 4 Hz, H-5), 4.46 (d, 1 H, H-4), 4.21 (dt, 1 H, $J_{6,7}$ 5.3 Hz, H-6), 3.86 (d, 2 H, H-7,7), 3.80 and 2.35 (2 bs, 2 H, HO-3,7), 1.78 (m, 2 H, H-2,2′), 1.45 and 1.30 (2 s, 6 H, CMe_2), and 1.00 (t, 3 H, $J_{1,2}$ 7.5 Hz, H-1,1,1).

Acetonation of **7**. A solution of **7** (400 mg, 1.83 mmol) in dry acetone (20 mL) and conc. sulfuric acid (0.1 mL) was stirred for 24 h at room temperature with anhydrous copper sulfate (2 g). T.l.c. then revealed the presence of a compound with R_F 0.5. Treatment of the reaction mixture as described above gave, after column chromatography (ether–hexane, 1:2), syrupy 3,7-anhydro-1,2-dideoxy-4,5-*O*-isopropylidene-β-D-*ribo*-3-heptulo-3,6-furanose (**14**; 280 mg, 77%), $[\alpha]_D$ −67° (*c* 1.32); ν_{max}^{film} 2983, 2945, and 2896 (C–H), 1383 and 1374 (CMe_2), 1261, 1212, 1165, 1093, 1059, 1029, 915, and 866 cm^{-1} (1,3-dioxolane ring). ^{1}H-N.m.r. data: δ (CCl_4) 4.44 (d, 1 H, $J_{5,6} = J_{6,7endo} = 0$, $J_{6,7exo}$ 3.5 Hz, H-6), 4.24 (d, 1 H, $J_{4,5}$ 5.5 Hz, H-5), 4.03 (d, 1 H, H-4), 3.39 (dd, 1 H, $J_{7endo,7exo}$ 7 Hz, H-7*exo*), 3.22 (d, 1 H, H-7*endo*), 1.88 (bq, 2 H, H-2,2′), 1.35 and 1.20 (2 s, 6 H, CMe_2), and 0.99 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1). Mass spectrum: *m/z* 186 ($M^{+\cdot}$ + 1 − Me), 185 ($M^{+\cdot}$ − Me), 143 ($M^{+\cdot}$ − EtCO), 142 ($M^{+\cdot}$ − Me_2CO), 126, 125, 113, 112, 111, 100, 99, 98, 97, 95, 86, 85, 84, 83, 81, 71, 70, 69, 68, 59 (Me_2COH^+), 58, 57 ($EtCO^+$, base peak), 55, and 43 (Ac^+).

Acetonation of **9** *and* **11**. — A solution of a mixture of **9** and **11** (436 mg) in dry acetone (20 mL) and conc. sulfuric acid (0.1 mL) was stirred at room temperature with anhydrous copper sulfate (2 g). After 3 h, t.l.c. revealed two components (R_F 0.68 and 0.58). The mixture was neutralised (K_2CO_3), filtered, and concentrated. Column chromatography (ether–hexane, 1:3) of the residue gave, first, a ~1:1 (based on ^{1}H-n.m.r. data) mixture (455 mg) of 1,2-dideoxy-3,4:5,6-di-*O*-isopropylidene-β-D-*arabino*-3-heptulo-3,7-pyranose (**15**) and 1,2-dideoxy-4,5:6,7-di-*O*-isopropylidene-*keto*-D-*arabino*-3-heptulose (**16**).

Eluted second was syrup 1,2-dideoxy-3,4:5,7-di-*O*-isopropylidene-α-D-*xylo*-3-heptulo-3,6-furanose (**17**, 70 mg), $[\alpha]_D$ −3°, $[\alpha]_{365}$ −19° (*c* 1.3); ν_{max}^{film} 2992, 2941, and 2888 (C–H), 1385 and 1374 (CMe_2), 1240, 1197, 1164, 1126, 1098, 1083, 994, and 834 cm^{-1} (1,3-dioxolane ring). ^{1}H-N.m.r. data: δ 4.23 and 4.03 (2 s, 5 H, relative intensities 2:3, H-4,5,6,7,7′), 1.98 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 1.46, 1.40, and 1.35 (3 s, 12 H, relative intensities 1:1:2, 2 CMe_2), and 1.05 (t, 3 H, H-1,1,1). Mass spectrum: *m/z* 245 ($M^{+\cdot}$ + 2 − Me), 244 ($M^{+\cdot}$ + 1 − Me), 243 ($M^{+\cdot}$ − Me), 185 ($M^{+\cdot}$ − Me − Me_2CO), 183 ($M^{+\cdot}$ − Me − AcOH), 171 ($M^{+\cdot}$ − Et − Me_2CO), 167 ($M^{+\cdot}$ − Me − Me_2CO − H_2O), 158, 157 ($C_8H_{13}O_3^+$), 155, 143, 142, 141, 129, 128, 127, 126, 125 ($M^{+\cdot}$ − Me − AcOH − Me_2CO), 115, 113 ($C_6H_9O_2^+$), 114, 111, 109, 107, 101, 100 ($C_5H_8O_2^+$), 99, 97, 95, 85 ($C_4H_5O_2^+$), 83, 73, 69, 59 (Me_2COH^+), 57

($EtCO^+$, base peak), 55, and 43 (Ac^+, base peak).

Borohydride reduction of **15** *and* **16**. — To a stirred solution of **15** and **16** (380 mg) in anhydrous methanol (10 mL) was added portionwise sodium borohydride (150 mg). The mixture was left for 1 h at room temperature. T.l.c. then revealed the presence of **15** and two products of lower mobility. The mixture was neutralised with acetic acid and concentrated, the residue was extracted with chloroform (3 × 10 mL), and the combined extracts were concentrated. Column chromatography (ether–hexane, 1:3) of the residue gave, first, syrupy **15** (125 mg), R_F 0.69, $[\alpha]_D$ −9° (*c* 1.1); ν_{max}^{film} 2990, 2941, and 2903 (C–H), 1383 and 1373 (CMe_2), 1252, 1212, 1183, 1113, 1076, 1041, 939, and 897 cm^{-1} (1,3-dioxolane ring). ^{1}H-N.m.r. data: δ 4.56 (dd, 1 H, $J_{4,5}$ 2.3, $J_{5,6}$ 8 Hz, H-5), 4.19 (ddd, 1 H, $J_{6,7}$ 1.7, $J_{6,7'}$ 0.7 Hz, H-6), 4.09 (d, 1 H, H-4), 3.89 (dd, 1 H, $J_{7,7'}$ 12.7 Hz, H-7), 3.68 (dd, 1 H, H-7′), 2.03–1.67 (m, 2 H, H-2,2′), 1.49, 1.45, and 1.33 (3 s, 12 H, relative intensities 1:1:2, 2 CMe_2), and 1.03 (t, 3 H, $J_{1,2}$ 7 Hz, H-1,1,1). Mass spectrum: *m/z* 245 ($M^{+\cdot}$ + 2 − Me), 244 ($M^{+\cdot}$ + 1 − Me), 185 ($M^{+\cdot}$ − Me − Me_2CO), 184, 183 ($M^{+\cdot}$ − Me − AcOH), 172, 171, 169, 143, 142, 141, 129, 128, 127, 126, 125 ($M^{+\cdot}$ − Me − Me_2CO − AcOH), 114, 113 ($C_6H_9O_2^+$), 111, 109, 101, 100 ($C_5H_8O_2^+$), 99, 98, 97, 85, ($C_4H_5O_2^+$), 84, 83, 71, 69, 68, 59 (Me_2COH^+), 58, 57 ($EtCO^+$), and 43 (Ac^+, base peak).

The products (140 mg) of lower mobility were oxidised as follows. To a vigorously stirred solution of the mixture (100 mg) in chloroform (10 mL) were added saturated aqueous sodium hydrogen carbonate (5 mL) and ruthenium dioxide (100 mg) followed, dropwise, by aqueous 5% sodium periodate (6 mL) at room temperature until the starting products had disappeared (t.l.c.) and no further reduction of the tetraoxide occurred. The residual tetraoxide was reduced with 2-propanol (3 mL), the organic phase was separated, the aqueous phase was extracted with chloroform (3 × 5 mL), and the combined extracts were concentrated. Column chromatography (ether–hexane, 1:3) of the residue yielded **16** (80 mg), isolated as a mobile oil, R_F 0.68, $[\alpha]_D$ −2°, $[\alpha]_{365}$ −39° (*c* 1.3); ν_{max}^{film} 2990, 2942, and 2884 (C–H), 1725 (ketone, C=O), 1384 and 1374 (CMe_2), 1255, 1214, 1152, 1074, and 843 cm^{-1} (1,3-dioxolane ring). ^{1}H-N.m.r. data: δ 4.45–3.73 (m, 5 H, H-4,5,6,7,7′), 2.68 (q, 2 H, $J_{1,2}$ 7 Hz, H-2,2), 1.45, 1.41, and 1.38 (3 s, 12 H, relative intensities 1:1:2, 2 CMe_2), and 1.08 (t, 3 H, H-1,1,1). Mass spectrum: *m/z* 245 ($M^{+\cdot}$ + 2 − Me), 244 ($M^{+\cdot}$ + 1 − Me), 243 ($M^{+\cdot}$ − Me), 202 ($M^{+\cdot}$ + 1 − EtCO), 201 ($M^{+\cdot}$ − EtCO), 185 ($M^{+\cdot}$ − Me − Me_2CO), 183 ($M^{+\cdot}$ − Me − AcOH), 171, 157 ($M^{+\cdot}$ − $C_5H_9O_2$), 144 ($M^{+\cdot}$ + 1 − EtCO − Me_2CO), 143 ($M^{+\cdot}$ − EtCO − Me_2CO), 125 ($M^{+\cdot}$ − Me − Me_2CO − AcOH), 113, 111, 102, 101 ($C_5H_9O_2^+$), 97, 85, 83, 73, 72, 71, 69, 68, 59 (Me_2COH^+), 58, 57 ($EtCO^+$), 55, and 43 (Ac^+, base peak).

Isomerisation of **16**. — To a solution of **16** (80 mg, 0.3 mmol) in dry acetone (5 mL) was added conc. sulfuric acid (0.02 mL). The mixture was left for 24 h at room temperature, then neutralised (K_2CO_3), filtered, and concentrated. The ^{1}H-n.m.r. spectrum showed the residue to be a ~1:1 mixture of **15** and **16**.

*1,2-Dideoxy-*D-lyxo*-3-heptulose* (**18**). — A solution of **5** (25 mg, 0.1 mmol) in aqueous 30% acetic acid (1.5 mL) was left overnight at room temperature. T.l.c.

then revealed that **5** had disappeared and that a non-mobile substance was present. The mixture was concentrated and residual acetic acid was removed by co-distillation with water to afford **18** (18 mg, quantitative) that was homogeneous by p.c. [R_F 0.55 (solvent *A*), 0.52 (solvent *B*), and 0.73 (solvent *C*)], and had m.p. 124–125° (from ethanol), $[\alpha]_D$ −15° (*c* 1.1, water); ν_{max}^{KBr} 3504, 3421, 3366, and 3320 (OH), 2999, 2963, and 2923 (C–H), 1467, 1388, 1373, 1273, 1252, 1198, 1135, 1089, 1067, 1051, 1008, 985, 961, and 795 cm^{-1}. For the ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C, 46.93; H, 8.10.

*1,2-Dideoxy-*D-ribo*-3-heptulose* (**19**). — Hydrolysis of **7** (50 mg, 0.23 mmol) in aqueous 30% acetic acid (3 mL), as described above, yielded syrupy **19** (35 mg, 85%) that was homogeneous by p.c. [R_F 0.61 (solvent *A*), 0.60 (solvent *B*), and 0.88 (solvent *C*)] and had $[\alpha]_D$ −36° (*c* 1.34, water). For the ^{13}C-n.m.r. data, see Table III.

*1,2-Dideoxy-*D-arabino*-3-heptulose* (**20**). — Hydrolysis of **9** (45 mg, 0.2 mmol) in aqueous 30% acetic acid (2 mL), as described above, yielded syrupy **20** (35 mg, quantitative) that was homogeneous by p.c. [R_F 0.53 (solvent *A*), 0.50 (solvent *B*), and 0.60 (solvent *C*)] and had $[\alpha]_D$ −39° (*c* 2.1, water). For the ^{13}C-n.m.r. data, see Table IV.

*1,2-Dideoxy-*D-xylo*-3-heptulose* (**21**). — Hydrolysis of **11** (50 mg, 0.23 mmol) in aqueous 30% acetic acid (3 mL), as described above, yielded syrupy **21** (35 mg, 85%) that was homogeneous by p.c. [R_F 0.57 (solvent *A*), 0.52 (solvent *B*), and 0.85 (solvent *C*)] and had $[\alpha]_D$ +59° (*c* 0.7, water). For the ^{13}C-n.m.r. data, see Table V.

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