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CARBOHYDRATE RESEARCH

Synthesis of a mixture of (2*S*,5*R*)- and (2*S*,5*S*)-2-methyl-1,6-dioxaspiro[4.5]decane, the odor bouquet minor components of *Paravespula vulgaris* (L.), from L-sorbose ☆

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Abstract

The synthesis of (2*S*,5*RS*)-2-methyl-1,6-dioxaspiro[4.5]decane (**1**) from (2*S*,4*S*,5*R*)- (**26**) and (2*S*,4*S*,5*S*)-4-hydroxy-2-methyl-1,6-dioxaspiro[4.5]decane (**27**), obtained in thirteen and fourteen steps from L-sorbose by two convergent syntheses, has been accomplished using Wittig methodology, Barton deoxygenation, reduction, and spiroketalation of the appropriately protected derivatives.

Keywords: Pheromones; *Paravespula vulgaris* (L.); Spiroacetals; Stereoselective synthesis; L-Sorbose

1. Introduction

Recently [2], our group has reported on the enantiospecific synthesis from D-fructose of the (2*S*,5*R*) and (2*R*,5*R*) isomers of **1**, minor components of the odor bouquet of the common wasp *Paravespula vulgaris* (L.), identified by Francke et al. [3] in 1978. Several racemic [3,4], diastereomeric [5] and enantiospecific syntheses [6] of **1** have been reported.

Retrosynthesis of **1** (see Scheme 1) showed that 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose [7] (**2**), readily available from L-sorbose, contains the required γ-hydroxy-

☆ Enantiospecific Synthesis of Spiroacetals, Part VII. For Part VI, see [1].

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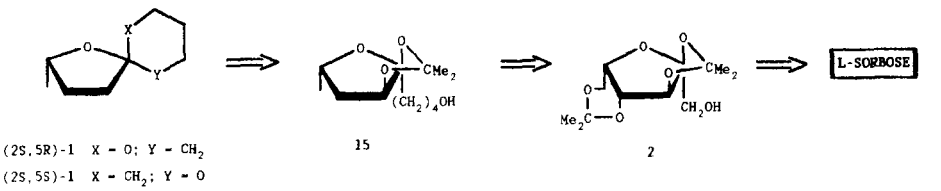


Scheme 1.

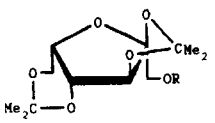
ketone fragment, precursor of the tetrahydrofuran ring in **1**. It also has adequate functionalisation at C-1, that will allow lengthening of the carbon chain (Wittig methodology) to produce the tetrahydropyran ring in **1**, and, finally, it has the appropriate configuration at C-5 (C-2 in **1**).

The synthesis of the key intermediate (**15**) was achieved by two convergent synthetic routes. The first involved the necessary transformations in the sugar moiety prior to the carbon chain elongation at C-1.

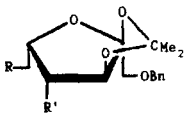
2. Results and discussion

1-*O*-Benzyl-2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose (**3**), obtained from **2** by a modified Klemer procedure [8], could be partially deacetonated to afford 1-*O*-benzyl-2,3-*O*-isopropylidene-α-L-sorbofuranose (**4**) because of the different stability [9] exhibited by the two isopropylidene groups present in **3**. Attempts to achieve the 4,6-dideoxygenation by the Barton method [10] of the corrresponding 4,6-dixanthate **5** were unsuccessful, as a complex mixture was obtained in the reduction step. However, selective protection of the primary hydroxyl group in **4**, via the *tert*-butyldiphenylsilyl ether (**6**), allowed the deoxygenation at C-4 by the above mentioned procedure to yield 1-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-deoxy-2,3-*O*-isopropylidene-α-L-*erythro*-hexulofuranose (**8**). Treatment of **8** with tetrabutylammonium fluoride caused desilylation at C-6 to produce **9**, which was transformed into the corresponding 6-*O*-*p*-toluenesulfonyl derivative (**10**). The reduction of **10** with lithium aluminium hydride yielded the required 1-*O*-benzyl-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-*erythro*-hexulofuranose (**11**).

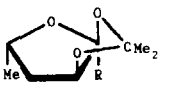
Elongation by three carbon atoms at C-1 to yield 2,3,4,7,9-pentadeoxy-5,6-*O*-isopropylidene-α-L-*erythro*-non-5-ulofuranose (**15**), was carried out by hydrogenolysis of the benzyl group at C-1 in **11** to give **12**. Oxidation with pyridinium chlorochromate (PCC) to the not fully characterised aldehyde **13** and subsequent Wittig reaction with (3-benzyloxypropyl)triphenylphosphorane, generated in situ from the related phosphonium bromide [11], gave the corresponding (*Z*)-alkene (**14**), which was finally hydrogenated to **15**. The configuration at C-3,4 in **14** was shown to be *Z*, as the coupling pattern of the olefinic protons was identical to that showed by an analogous compound previously described [11]. Because of the low yield of the Wittig reaction and the instability of **14** we investigated an alternative synthetic route.



2 R = H
3 R = Bn



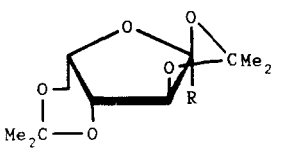
4 R = R' = OH
5 R = R' = MeSCSO
6 R = TBDPSO; R' = OH
7 R = TBDPSO; R' = MeSCSO
8 R = TBDPSO; R' = H
9 R = OH; R' = H
10 R = TsO; R' = H



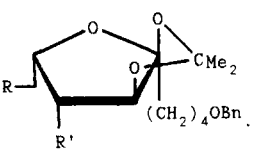
11 R = OBn
12 R = OH
13 R = CHO
14 R = HC=CH(CH$_2$)$_2$OBn
15 R = (CH$_2$)$_4$OH

TBDPS = *tert*-butyldiphenylsilyl

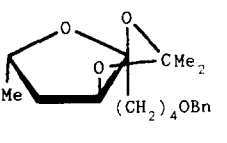
The synthesis of an unresolvable ≈ 3:1 mixture (^{1}H NMR evidence) of (*Z*)- and (*E*)-1-*O*-benzyl-2,3,4-trideoxy-5,6:7,9-di-*O*-isopropylidene-α-L-*xylo*-non-3-ene-5-ulofuranose (**17**) was achieved by treatment of the aldehyde **16** [1] with the ylide used above. In spite of the complexity of the ^{1}H and ^{13}C NMR spectra, some of the resonance signals for protons and carbons could be assigned (see Experimental). Hydrogenation of **17** over Pd–C gave **18** in quantitative yield. Conversion of **18** to **15** was performed using the same synthetic route as that in **3** → **15**.



16 R = CHO
17 R = HC=CH(CH$_2$)$_2$OBn
18 R = (CH$_2$)$_4$OBn



19 R = R' = OH
20 R = TBDPSO; R' = OH
21 R = TBDPSO; R' = MeSCSO
22 R = TBDPSO; R' = H
23 R = OH, R' = H
24 R = TsO; R' = H



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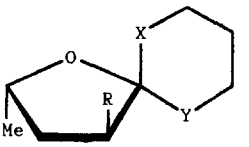
Treatment of **15** with trifluoroacetic acid hydrolysed the isopropylidene group and promoted intramolecular glycosidation to give a mixture of (2*S*,4*S*,5*R*)-4-hydroxy-2-methyl-1,6-dioxaspiro[4.5]decane (**26**) and its 5-epimer (**27**) in a 2.6:1 ratio, as shown by GLC analysis (see Experimental). Compounds **26** and **27** undergo facile epimerisation at the spiroketal linkage. Nevertheless, it was possible to measure their specific rotations and record their spectra. Structural elucidation of **26** and **27** could be made on the basis of their ^{1}H, ^{13}C, and two-dimensional ^{13}C–^{1}H heteronuclear shift-correlation spectra. Thus, the configurations at C-5 for both compounds were established from the chemical shift values of the methyl group at C-2, which shows a shielding effect in **26** (1.01 ppm) relative to that in **27** (1.22 ppm), because of its *E* configuration. These results were in accordance with those previously reported [2,12] for analogous compounds.



26 X = O; Y = CH_2; R = OH
27 X = CH_2; Y = O; R = OH
28 X = O; Y = CH_2; R = MeSCSO
29 X = CH_2; Y = O; R = MeSCSO

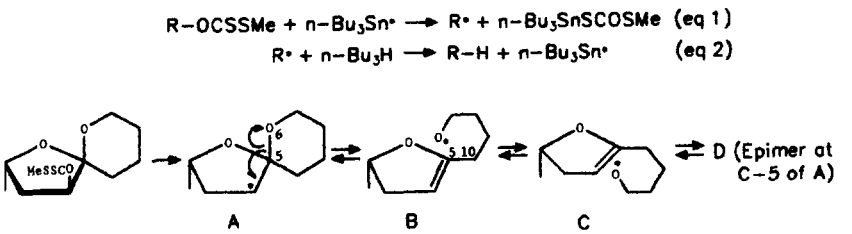
Compounds **26** and **27** were transformed into the corresponding 4-xanthates **28** and **29**, respectively. The optical rotation values of **26**, **27**, **28**, and **29** were also in agreement with the assigned configuration at C-5, since compounds with a *R* configuration at the spiro centre were levo- [2,6], whereas those with *S* configuration were dextro-rotatory [6].

Finally, treatment of **28** and **29** with tributyltin hydride gave a mixture of (2*S*,5*R*)- and (2*S*,5*S*)-**1** unresolvable by column chromatography. GLC–MS analysis of the mixture allowed the recording of the mass spectra for each compound, and these identical to those found in the literature [13]. Epimerisation at C-5 may have taken place during the deoxygenation reaction, since **28** and **29** were pure and stable diastereomers.

Scheme 2 shows the accepted mechanism for the Barton deoxygenation (Eqs. 1 and 2) and a possible explanation for the epimerisation at C-5 during the reduction step. Thus, the intermediate radical **A** could suffer a ring opening at C-5–O-6 to generate **B** that would either cyclise again to **A** or be transformed into **D** by rotation of the C-5–C-10 bond and subsequent ring closure of the conformer **C**. Reaction of radicals **A** and **D** with the hydride yielded (2*S*,5*R*)- and (2*S*,5*S*)-**1**, respectively [14]. It can be concluded that the procedure described above assured the chirality at C-2 but not at C-5 in the target molecule.

3. Experimental

General methods.—Melting points were determined with a Gallenkamp apparatus and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under



Scheme 2.

reduced pressure. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-300, and WP-80 WC spectrometers for solutions in $CDCl_3$ (internal Me_4Si). IR spectra were recorded with a Perkin–Elmer 782 instrument and mass spectra with a Hewlett–Packard HP-5988-A mass spectrometer. Optical rotations were measured for solutions in $CHCl_3$ (1-dm tube) with a Jasco DIP-370 polarimeter. GLC was performed on a Perkin–Elmer 8410 gas chromatograph equipped with a flame-ionisation detector and a steel column (2 m × 0.125 in. i.d.) packed with 5% OV-17 on Chromosorb W (100–120 mesh): (*A*) 120°C; (*B*) 220°C; (*C*) 230°C; (*D*) 180°C; and (*E*) 115°C. The N_2 flow rate was 30 mL/min, the injection port and zone-detector temperatures were (*A*) 170°C; (*B*) 270°C; (*C*) 290°C; (*D*) 230°C; and (*E*) 200°C. TLC was performed on Silica Gel (E. Merck) with detection by charring with H_2SO_4. Column chromatography was performed on Silica Gel (E. Merck, 7734).

1-O-Benzyl-2,3:4,6-di-O-isopropylidene-α-L-sorbofuranose (**3**).—To a stirred solution of NaH (80% oil dispersion) (1.2 g, 40 mmol) in dry Me_2SO (15 mL) and imidazole (100 mg) under Ar, 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose **2** [7] (7.8 g, 30 mmol) in dry THF (50 mL) was added at room temperature. After 30 min, the mixture was heated at 80°C for 15 min, then cooled and benzyl chloride (5.2 mL, 45 mmol) was added and the mixture was refluxed for 1 h. TLC (3:2 ether–hexane) then showed the absence of **2** and the presence of a new product of higher mobility. The mixture was cooled, poured into ice–water, and extracted with ether. The combined extracts were washed with brine, water, and concentrated. Column chromatography (1:3 ether–hexane) of the residue gave **3** (9.7 g, 92%) as a thick syrup; $[\alpha]_D^{25}$ −16° (*c* 1), [lit. [8] $[\alpha]_D$ −16.9° (*c* 1, $CHCl_3$)]; ν_{max}^{film} 1455 (benzyl), 1384 and 1374 (CMe_2), 739 and 698 cm^{-1} (aromatic); ^{13}C NMR data: δ 114.08 and 112.19 (C-2 and *C*Me_2 of 1,3-dioxolane ring), 97.19 (*C*Me_2, 1,3-dioxane ring), 84.26 (C-5), 73.53 (C-1), 73.20, and 72.08 (C-3,4), 69.89 (*C*H_2Ph), 60.27 (C-6), 28.86 and 18.58 (C*Me*$_2$, 1,3-dioxane ring), 27.56 and 26.50 (C*Me*$_2$, 1,3-dioxolane ring).

1-O-Benzyl-2,3-O-isopropylidene-α-L-sorbofuranose (**4**).—A solution of **3** (9.5 g, 27.14 mmol) in aq 50% AcOH (50 mL) was heated at 50°C for 30 min. TLC (ether) then showed the absence of **3** and the presence of a new compound of lower mobility. The mixture was concentrated and the residue dissolved in abs EtOH, neutralised with solid K_2CO_3, filtered, and concentrated. Column chromatography (ether) of the residue yielded crystalline **4** (6.5 g, 77%); mp 83–85°C (from ether); $[\alpha]_D^{25}$ + 36° (*c* 1); ν_{max}^{KBr} 3445 (OH), 1455 (benzyl), 1384 and 1375 (CMe_2), 747 and 699 cm^{-1} (aromatic). NMR data: ^{1}H, δ 7.40–7.26 (m, 5 H, CH_2*Ph*), 4.67 and 4.58 (2 d, 2 H, *J* 11.7 Hz, *C*H_2Ph), 4.42 (s, 1 H, H-3), 4.34 (dt, 1 H, $J_{4,5}$ 2.8, $J_{5,6}$ 5.2 Hz, H-5), 4.16 (d, 1 H, H-4), 3.91 (d, 2 H, H-6,6), 3.83 and 3.63 (2 d, 2 H, *J* 10 Hz, H-1,1′), 1.49 and 1.29 (2 s, 6 H, CMe_2); ^{13}C, δ 112.64 and 112.48 (C-2 and *C*Me_2), 86.94 (C-5), 81.83 (C-3), 75.50 (C-4), 74.10 (C-1), 71.50 (*C*H_2Ph), 61.32 (C-6), 27.25 and 26.18 (C*Me*$_2$). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.14. Found: C, 62.21; H; 7.12.

1-O-Benzyl-2,3-O-isopropylidene-4,6-di-O-[(methylthio)-thiocarbonyl]-α-L-sorbofuranose (**5**).—A solution of **4** (6.5 g, 20 mmol) in dry THF (40 mL) was added to a stirred solution of NaH (80% oil dispersion) (1.8 g, 60 mmol) and imidazole (100 mg) in dry Me_2SO (20 mL) under Ar at room temperature. The mixture was refluxed for 30 min, cooled, and CS_2 (5 mL, 80 mmol) was added dropwise. The mixture was refluxed

again for 15 min, cooled, and MeI (5 mL, 80 mmol) was added slowly, and the mixture was heated under reflux for 30 min. TLC (ether) then revealed the presence of a new product of higher mobility. The mixture was cooled and cautiously poured into ice–water and extracted with ether. The extracts were washed with brine, water, and concentrated. Column chromatography (1:4 ether–hexane) of the residue afforded **5** (9.5 g, 100%) as a syrup; $[\alpha]_D^{23}$ −46° (*c* 1.2); ν_{max}^{film} 1455 (benzyl), 1384 and 1375 (CMe_2), 1215 (C = S), 737 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 7.38–7.24 (m, 5 H, CH_2Ph), 6.03 (d, 1 H, $J_{4,5}$ 3 Hz, H-4), 4.88–4.72 (m, 3 H, H-5,6,6′), 4.68 (s, 1 H, H-3), 4.66 and 4.59 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 3.74 and 3.64 (2 d, 2 H, $J_{1,1'}$ 11 Hz, H-1,1′) 2.54 and 2.49 (2 s, 6 H, 2 SMe), 1.56 and 1.39 (2 s, 6 H, CMe_2); ^{13}C, δ 215.65 and 214.62 (C = S), 114.11 and 113.27 (C-2 and CMe_2), 84.14 (C-5), 83.11 (C-4), 77.10 (C-3), 73.86 (C-1), 70.02 and 69.92 (C-6 and CH_2Ph), 27.60 and 26.65 (CMe_2), 19.35 and 19.27 (SMe). EIMS: *m/z* 491 (59%, $M^+ + 1$) and 383 (100, $M^+ + 1 - SCO - MeSH$).

1-O-Benzyl-6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-α-L-sorbofuranose (**6**). —To a stirred solution of **4** (930 mg, 3 mmol) in dry CH_2Cl_2 (10 mL), 4-dimethylaminopyridine (25 mg), Et_3N (0.5 mL), and *tert*-butyldiphenylchlorosilane (825 mg, 3 mmol) were added under Ar, and the mixture was left at room temperature for 24 h. TLC (1:3 ether–hexane) then revealed that **4** had disappeared and that a faster-running product was present. The mixture was washed with aq 10% HCl, water, satd aq $NaHCO_3$, water, and concentrated. Column chromatography (1:3 ether–hexane) of the residue gave **6** (1.14 g, 70%) as a colourless syrup; $[\alpha]_D^{23}$ +21.5° (*c* 1.4); ν_{max}^{film} 3457 (OH), 1455 (benzyl), 1384 and 1374 (CMe_2), 739 and 702 cm^{-1} (aromatic); NMR data: ^1H, δ 7.74–7.67 and 7.45–7.26 (2 m, 15 H, relative intensity 1:3, 3Ph), 4.60 and 4.55 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 4.45 (s, 1 H, H-3), 4.33 (ddd, 1 H, $J_{4,5}$ 2.6 Hz, H-5), 4.22 (bd, 1 H, H-4), 4.02 (dd, 1 H, $J_{5,6}$ 6.2, $J_{6,6'}$ 10.7 Hz, H-6), 3.92 (dd, 1 H, $J_{5,6'}$ 5 Hz, H-6′), 3.77 and 3.65 (2 d, 2 H, J 10 Hz, H-1,1′), 3.73–3.64 (bd, 1 H, OH-4), 1.50 and 1.33 (2 s, 6 H, CMe_2) and 1.05 (s, 9 H, CMe_3); ^{13}C, δ 112.85 and 112.23 (C-2 and CMe_2), 86.34 (C-5), 81.68 (C-3), 75.18 (C-4), 74.03 (C-1), 71.34 (CH_2Ph), 61.85 (C-6), 27.33 and 26.26 (CMe_2), 26.86 (CMe_3) and 19.25 (CMe_3). CIMS (CH_4): *m/z* 549 (80%, $M^+ + 1$) and 91 (100, $C_7H_7^+$).

1-O-Benzyl-6-O-tert-butyldiphenylsilyl-2,3-O-isopropylidene-4-O-[(methylthio)thiocarbonyl]-α-L-sorbofuranose (**7**).— To an ice–water-cooled and stirred solution of NaH (80% oil dispersion) (160 mg, 5.3 mmol) and imidazole (50 mg) in anhyd Me_2SO (5 mL) was added a solution of **6** (1.13 g, 2.1 mmol) in the same solvent (5 mL), CS_2 (0.5 mL) and MeI (0.5 mL), under Ar. The stirring was continued for 12 h at room temperature. TLC (1:2 ether–hexane) revealed the absence of **6** and the presence of a faster-running compound. The mixture was cautiously poured into ice–water and extracted with ether. The extracts were washed with brine, water, and concentrated. Column chromatography (1:6 ether–hexane) of the residue yielded crystalline **7** (1.1 g, 83%); mp 110–111°C (from hexane); $[\alpha]_D^{22}$ +7° (*c* 1); ν_{max}^{KBr} 1455 (benzyl), 1384 and 1374 (CMe_2), 1201 (C = S), 740 and 702 cm^{-1} (aromatic); NMR data: ^1H, δ 7.67–7.60 and 7.45–7.20 (2 m, 15 H, relative intensity 1:3, 3Ph), 6.08 (d, 1 H, $J_{4,5}$ 3 Hz, H-4), 4.64 (s, 1 H, H-3), 4.63 and 4.54 (2 d, 2 H, *J* 10 Hz, CH_2Ph), 4.61 (m, 1 H, H-5), 3.90 (dd, 1 H, $J_{5,6}$ 5.8, $J_{6,6'}$ 10 Hz, H-6), 3.85 (dd, 1 H, $J_{5,6'}$ 8.3 Hz, H-6′), 3.66 and 3.55 (2

d, 2 H, *J* 11 Hz, H-1,1'), 2.41 (s, 3 H, SMe), 1.57 and 1.39 (2 s, 6 H, CMe_2) and 1.02 (s, 9 H, CMe_3); ^{13}C, δ 214.42 (C = S), 113.63 and 113.00 (C-2 and CMe_2), 84.01 (C-5), 82.93 (C-4), 79.74 (C-3), 73.74 (C-1), 70.10 (CH_2Ph), 60.29 (C-6), 27.56 and 26.68 (CMe_2), 26.80 (CMe_3), 19.19 (CMe_3) and 18.94 (SMe). Anal. Calcd for $C_{34}H_{42}O_6S_2Si$: C, 63.91; H, 6.62. Found: C, 63.15; H, 6.53.

1-O-Benzyl-6-O-tert-butyldiphenylsilyl-4-deoxy-2,3-O-isopropylidene-α-L-erythro-hexulofuranose (**8**).—To a stirred boiling solution of **7** (1 g, 1.6 mmol) in dry toluene (10 mL), a solution of tributyltin hydride (0.8 mL, 3 mmol), and azobis(isobutyronitrile) (30 mg) in the same solvent (4 mL) was added dropwise, under Ar. Refluxing was continued for 16 h. TLC (1:2 ether–hexane) then revealed no **7** but a new compound of slightly lower mobility. The mixture was concentrated and the residue was chromatographed (1:6 ether–hexane) to afford **8** (690 mg, 81%) as a syrup; $[\alpha]_D^{22}$ −1.3°, $[\alpha]_{405}^{22}$ −4° (*c* 2); ν_{max}^{film} 1455 (benzyl), 1392 and 1372 (CMe_2), 740 and 702 cm^{-1} (aromatic); NMR data: ^1H, δ 7.70–7.64 and 7.47–7.20 (2 m, 15 H, relative intensity 1:3, 3 Ph), 4.72 (d, 1 H, $J_{3,4exo}$ 4.2 Hz, H-3), 4.64 and 4.54 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 4.43 (dq, 1 H, H-5), 3.81 (dd, 1 H, $J_{5,6}$ 4.3, $J_{6,6'}$ 11 Hz, H-6), 3.73 (dd, 1 H, $J_{5,6'}$ 4 Hz, H-6'), 3.67 and 3.59 (2 d, 2 H, *J* 11 Hz, H-1,1'), 2.09 (dd, 1 H, $J_{4endo,5}$ 4.7, $J_{4endo,4exo}$ 13.3 Hz, H-4*endo*), 1.94 (ddd, 1 H, $J_{4exo,5}$ 10.6 Hz, H-4*exo*), 1.54 and 1.39 (2 s, 6 H, CMe_2) and 1.04 (s, 9 H, CMe_3); ^{13}C, δ 113.93 and 111.52 (C-2 and CMe_2), 81.72 (C-5), 79.18 (C-3), 73.74 (C-1), 70.65 (CH_2Ph), 64.82 (C-6), 34.81 (C-4), 27.55 and 26.44 (CMe_2), 26.90 (CMe_3) and 19.33 (CMe_3). EIMS: *m/z* 517 (0.4, $M^{+\cdot}$ − Me) and 91 (100, $C_7H_7^+$).

1-O-Benzyl-4-deoxy-2,3-O-isopropylidene-α-L-erythro-hexulofuranose (**9**).—To a stirred solution of **8** (650 mg, 1.22 mmol) in dry THF (5 mL) was added tetrabutylammonium fluoride trihydrate (440 mg, 1.4 mmol) under Ar. The mixture was stirred at room temperature for 16 h. TLC (3:2 ether–hexane) then revealed no **8** but a new compound of lower mobility. The solvent was evaporated, and a solution of the residue in ether was washed with brine and water, and then concentrated. Column chromatography (1:1 → 3:1 ether–hexane) of the residue yielded **9** (290 mg, 81%) as a syrup; $[\alpha]_D^{23}$ +14° (*c* 1); ν_{max}^{film} 3489 (OH), 1455 (benzyl), 1383 and 1373 (CMe_2), 739 and 699 cm^{-1} (aromatic); NMR data: ^1H, δ 7.38–7.23 (m, 5 H, Ph), 4.64 (d, 1 H, $J_{3,4exo}$ 4.3 Hz, H-3), 4.59 and 4.55 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 4.49 (m, 1 H, H-5), 3.87 (dd, 1 H, $J_{5,6}$ 2.6, $J_{6,6'}$ 12 Hz, H-6), 3.71 and 3.57 (2 d, 2 H, *J* 10 Hz, H-1,1'), 3.48 (dd, 1 H, $J_{5,6'}$ 3.2 Hz, H-6'), 2.10 (ddd, 1 H, $J_{4exo,5}$ 10.4, $J_{4exo,4endo}$ 13.5 Hz, H-4*exo*), 1.98 (dd, 1 H, $J_{4endo,5}$ 5.2 Hz, H-4*endo*), 1.51 and 1.31 (2 s, 6 H, CMe_2); ^{13}C, δ 113.13 and 111.61 (C-2 and CMe_2) 83.25 (C-5), 79.82 (C-3), 73.60 (C-1), 71.55 (CH_2Ph), 63.09 (C-6), 33.28 (C-4), 27.44 and 26.30 (CMe_2). EIMS: *m/z* 279 (3%, $M^{+\cdot}$ − Me) and 91 (100, $C_7H_7^+$).

1-O-Benzyl-4-deoxy-2,3-O-isopropylidene-6-O-(p-toluenesulfonyl)-α-L-erythro-hexulofuranose (**10**).—To an ice-cooled and stirred solution of **9** (2.07 g, 7 mmol) in dry pyridine (14 mL), *p*-toluenesulfonyl chloride (1.78 g, 9.34 mmol) was added stepwise and the mixture was left at room temperature for 30 min. TLC (2:1 ether–hexane) showed the absence of **9** and the presence of a new compound of higher mobility. Usual work-up of the mixture gave a residue that yielded **10** (2 g, 64%) as a syrup after chromatography (1:4 ether–hexane); $[\alpha]_D^{25}$ −2° (*c* 1); ν_{max}^{film} 1455 (benzyl),

1383 and 1367 (CMe_2), 740 and 699 cm^{-1} (aromatic); NMR data: ^1H, δ 7.76 and 7.37–7.24 (d and m, 9 H, CH_2*Ph* and CH_3-C_6H_4-SO_2), 4.65 (d, 1 H, $J_{3,4exo}$ 4.3 Hz, H-3), 4.53 (s, 2 H, *CH*$_2$Ph), 4.45 (m, 1 H, H-5), 4.14 (dd, 1 H, $J_{5,6}$ 3.8, $J_{6,6'}$ 10.7 Hz, H-6), 4.05 (dd, 1 H, $J_{5,6'}$ 5 Hz, H-6'), 3.56 and 3.51 (2 d, 2 H, *J* 11 Hz, H-1,1'), 2.40 (s, 3 H, *CH*$_3$-C_6H_4-SO_2), 2.06 (dd, 1 H, $J_{4endo,5}$ 4.7, $J_{4endo,4exo}$ 13.5 Hz, H-4*endo*), 1.77 (ddd, 1 H, $J_{4exo,5}$ 10.8 Hz, H-4*exo*), 1.46 and 1.32 (2 s, 6 H, CMe_2); ^{13}C, δ 113.95 and 111.85 (C-2 and *C*Me_2), 81.59 (C-5), 75.65 (C-3), 73.74 (C-1), 70.72 (*C*H_2Ph), 70.22 (C-6), 34.83 (C-4), 27.56 and 26.22 (C*Me*$_2$) and 21.66 (*Me*-C_6H_4-SO_2). EIMS: *m/z* 433 (0.6%, $M^{+\cdot}$ – Me) and 91 (100, $C_7H_7^+$).

*1-O-Benzyl-4,6-dideoxy-2,3-O-isopropylidene-α-*L-erythro-*hexulofuranose* (**11**).—To an ice-cooled and stirred solution of **10** (2 g, 4.46 mmol) in anhyd ether (15 mL), $LiAlH_4$ (200 mg, 5.2 mmol) was added. Stirring was continued at room temperature for 16 h followed by reflux for 6 h. TLC (1:1 ether–hexane) then revealed the absence of **10** and the presence of a new compound of higher mobility. The excess of reagent was decomposed by cautious addition of ether saturated with water and water. The aqueous phase was extracted with ether and the combined extracts washed with aq 10% HCl, water, satd aq $NaHCO_3$, water, and concentrated. Flash chromatography (1:3 ether–hexane) of the residue afforded **11** (1 g, 81%) as a coluorless syrup; $[\alpha]_D^{26}$ +19,4° (*c* 1.4). ν_{max}^{film} 1455 (benzyl), 1383 and 1372 (CMe_2), 737 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 7.32 (m, 5 H, CH_2*Ph*), 4.67 (d, 1 H, $J_{3,4exo}$ 4.5 Hz, H-3), 4.64 and 4.59 (2 d, 2 H, *J* 12 Hz, *CH*$_2$Ph), 4.42 (m, 1 H, H-5), 3.66 and 3.60 (2 d, 2 H, *J* 11 Hz, H-1,1'), 2.10 (dd, 1 H, $J_{4endo,5}$ 4, $J_{4endo,4exo}$ 13.2 Hz, H-4*endo*), 1.51 (ddd, 1 H, $J_{4exo,5}$ 10.8 Hz, H-4*exo*), 1.52 and 1.34 (2 s, 6 H, CMe_2) and 1.28 (d, 3 H, $J_{5,6}$ 6 Hz, H-6,6,6); ^{13}C, δ 113.54 and 111.13 (C-2 and *C*Me_2), 82.47 (C-5), 74.72 (C-3), 73.70 (C-1), 71.36 (*C*H_2Ph), 40.67 (C-4), 27.35 and 26.36 (C*Me*$_2$) and 19.73 (C-6). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.32; H, 7.71.

*4,6-Dideoxy-2,3-*O*-isopropylidene-α-*L-erythro-*hexulofuranose* (**12**).—A solution of **11** (1 g, 3.6 mmol) in anhyd MeOH (20 mL) was hydrogenated at 4 atm over palladium hydroxide on carbon (150 mg) for 12 h. TLC (1:1 ether–hexane) then revealed no **11** but a new compound of lower mobility. The catalyst was collected and washed with MeOH and the combined filtrate concentrated. Column chromatography (2:1 ether–hexane) of the residue yielded **12** (600 mg, 89%) as a colourless syrup; $[\alpha]_D^{23}$ +22° (*c* 1); ν_{max}^{film} 3492 (OH), 1385 and 1374 cm^{-1} (CMe_2); NMR data: ^1H, δ 4.64 (d, 1 H, $J_{3,4exo}$ 4.3 Hz, H-3), 4.43 (m, 1 H, H-5), 3.65 (s, 2 H, H-1,1), 2.12 (dd, 1 H, $J_{4endo,5}$ 4.1, $J_{4endo,4exo}$ 13.3 Hz, H-4*endo*), 1.88 (bs, 1 H, OH), 1.51 and 1.34 (2 s, 6 H, CMe_2), 1.47 (ddd, 1 H, $J_{4exo,5}$ 10.8 Hz, H-4*exo*) and 1.27 (d, 3 H, $J_{5,6}$ 6 Hz, H-6,6,6); ^{13}C, δ 113.87 and 111.11 (C-2 and *C*Me_2), 82.49 (C-5), 74.92 (C-3), 63.94 (C-1), 41.09 (C-4), 27.28 and 26.59 (C*Me*$_2$) and 19.69 (C-6). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.88; H, 8.75.

*(Z)-1-*O*-Benzyl-2,3,4,7,9-pentadeoxy-5,6-*O*-isopropylidene-α-*L-erythro-*non-3-ene-5-ulofuranose* (**14**).—To a stirred solution of **12** (600 mg, 3.2 mmol) in dry CH_2Cl_2 (15 mL) were added pyridinium chlorochromate (2 g, 9.3 mmol) and 4A molecular sieves (2 g). Stirring was continued at room temperature for 30 min. GLC (*A*) then showed that **12** (t_R 4.44 min) had disappeared and that a new product (t_R 2.68 min) was present. The mixture was diluted with ether (100 mL), stirred for 30 min, filtered through a

Cellite–Silica Gel G pad, and concentrated to afford 4,6-dideoxy-2,3-*O*-isopropylidene-α-L-*erythro*-hexos-2-ulo-2,5-furanose (**13**; 355 mg, 59%) and its hydrated form; ν_{max}^{film} 3466 (hydrate) and 1747 cm^{-1} (C = O).

To a stirred solution potassium *tert*-butoxide (280 mg, 2.5 mmol) in anhyd THF (10 mL) under Ar, (3-benzyloxypropyl)triphenylphosphonium bromide [11] (1.2 g, 2.4 mmol) was added at room temperature. The mixture was stirred for 30 min to yield an orange solution of the ylide. A solution of **13** (350 mg, 1.9 mmol) in the same solvent (5 mL) was added dropwise. The reaction was left at room temperature for 16 h. TLC (3:2 ether–hexane) revealed the absence of **13** and the presence of a new product of higher mobility. The mixture was poured into ice–water, extracted with ether (4 × 15 mL), and the combined extracts washed with brine, water, and concentrated. Column chromatography (1:3 ether–hexane) of the residue gave **14** (260 mg, 43%) as a colourless syrup; $[\alpha]_D^{22}$ +17.5° (*c* 1.2); t_R (*B*) 8.65 min; ν_{max}^{film} 1455 (benzyl), 1383 and 1373 (CMe_2), 737 and 698 cm^{-1} (aromatic); NMR data: ^1H (80 Mz), δ 7.30 (bs, 5 H, CH_2*Ph*), 5.80–5.42 (m, 2 H, H-3,4), 4.45 (s, 2 H, *CH*$_2$Ph), 4.47 (d, 1 H, $J_{6,7exo}$ 4.5 Hz, H-6), 4.50–4.10 (m, 1 H, H-8), 3.47 (t, 2 H, $J_{1,2}$ 6.5 Hz, H-1,1), 2.80–2.50 (m, 2 H, H-2,2), 2.00 (dd, 1 H, $J_{7endo,7exo}$ 13.5, $J_{7endo,8}$ 4 Hz, H-7*endo*), 1.65–1.30 (m, 1 H, H-7*exo*), 1.44 and 1.27 (2 s, 6 H, CMe_2) and 1.23 (d, 3 H, $J_{8,9}$ 6 Hz, H-9,9,9).

*2,3,4,7,9-Pentadeoxy-5,6-*O*-isopropylidene-α-*L-erythro-*non-5-ulofuranose* (**15**).—A solution of **14** (230 mg, 0.71 mmol) in anhyd MeOH (3 mL) was hydrogenated at 4 atm over palladium hydroxide on carbon (50 mg) for 5 h. GLC (*B*) then indicated that **14** had disappeared and that a new compound (t_R 1.53 min) was present. The catalyst was filtered off, washed with MeOH and the filtrate concentrated. Column chromatography (1:2 ether–hexane → ether) of the residue gave **15** (107 mg, 66%) as a colourless syrup; $[\alpha]_D^{22}$ +20° (*c* 1.8); ν_{max}^{film} 3444 (OH), 1383 and 1372 cm^{-1} (CMe_2); NMR data: ^1H, δ 4.42 (d, 1 H, $J_{6,7exo}$ 4.3 Hz, H-6), 4.34 (ddq, 1 H, H-8), 3.63 (t, 2 H, $J_{1,2}$ 6.2 Hz, H-1,1), 2.05 (dd, 1 H, $J_{7endo,8}$ 4, $J_{7endo,7exo}$ 13.2 Hz, H-7*endo*), 1.93–1.46 (m, 7 H, H-2,2,3,3′,4,4′,OH), 1.47 and 1.30 (2 s, 6 H, CMe_2), 1.40 (ddd, 1 H, $J_{7exo,8}$ 11 Hz, H-7*exo*), and 1.23 (d, 3 H, $J_{8,9}$ 6 Hz, H-9,9,9); ^{13}C, δ 115.08 (C-5), 110.11 (*C*Me_2), 83.44 (C-8), 74.14 (C-6), 62.63 (C-1), 41.32 (C-4), 37.95 (C-7), 32.60 (C-2), 27.33 and 26.59 (*C*Me_2), 20.50 (C-3) and 19.60 (C-9). EIMS: *m/z* 215 (16%, $M^{+\cdot}$ − Me) and (100, Ac^+).

*(Z)- and (*E*)-1-*O*-Benzyl-2,3,4-trideoxy-5,6:7,9-di-*O*-isopropylidene-α-*L-xylo-*non-3-ene-5-ulofuranose* (**17**).—To a stirred solution of potassium *tert*-butoxide (1.5 g, 13.4 mmol) in anhyd THF (15 mL) under Ar (3-benzyloxypropyl)triphenylphosphonium bromide (5.5 g, 11.2 mmol) was added at room temperature. The mixture was stirred for 30 min to yield an orange solution of the ylide. A solution of 2,3:4,6-di-*O*-isopropylidene-α-L-*xylo*-hexos-2-ulo-2,5-furanose [1] (**16**, 2.45 g, 9.5 mmol), in the same solvent (10 mL) was added dropwise. The mixture was left at room temperature for 75 min. TLC (3:2 ether–hexane) revealed the absence of **16** and the presence of a new product of higher mobility. The mixture was poured into ice–water, extracted with ether, and the extracts washed with brine, water, and concentrated. Column chromatography (1:3 ether–hexane) of the residue yielded **17** (2.2 g, 59%) as a colourless syrup; $[\alpha]_D^{23}$ +19° (*c* 1); t_R (*C*) 18.02 min; ν_{max}^{film} 1455 (benzyl), 1384 and 1374 (CMe_2), 738 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 6.15 (dt, *J* 7, J 15 Hz) and 5.79–5.62 (m) olefinic

protons; ^{13}C, (*Z*)-**17** δ 113.60 (C-5), 111.36 (CMe$_2$, 1,3-dioxolane ring), 97.47 (CMe$_2$, 1,3-dioxane ring), 89.14 (C-8), 74.06 (C-6), 72.77 (CH$_2$Ph), 72.24 (C-7), 70.13 (C-1), 60.25 (C-9), 28.61 (C-2), 28.89 and 18.77 (C*Me*$_2$, 1,3-dioxane ring), 27.12 and 26.26 (C*Me*$_2$, 1,3-dioxolane ring); (*E*)-**17** δ 112.94 (C-5), 111.32 (CMe$_2$, 1,3-dioxolane ring), 97.37 (CMe$_2$, 1,3-dioxane ring), 87.89 (C-8), 73.73 (C-6), 73.02 (CH$_2$Ph), 72.25 (C-7), 69,62 (C-1), 60.33 (C-9), 32.54 (C-2), 29.03 and 18.71 (C*Me*$_2$, 1,3-dioxane ring), 27.12 and 26.26 (C*Me*$_2$, 1,3-dioxolane ring). CIMS (CH_4): *m/z* 391 (100%, $M^{+\cdot}+1$).

*1-O-Benzyl-2,3,4-trideoxy-5,6:7,9-di-O-isopropylidene-α-*L-xylo-*non-5-ulofuranose* (**18**).—A solution of **17** (6 g, 15.4 mmol) in anhyd MeOH (100 mL), was hydrogenated at 4 atm over 10% Pd–C (1 g) for 15 min. GLC (*C*) then indicated that **17** had disappeared and that a new product (t_R 16.9 min) was present. The catalyst was filtered off, washed with MeOH, and the filtrate concentrated. Column chromatography (1:1 ether–hexane) of the residue gave **18** (6 g, 100%) as a colourless syrup; $[\alpha]_D^{24}$ +1.5° (*c* 1); ν_{max}^{film} 1455 (benzyl), 1384 and 1374 (CMe$_2$), 736 and 698 cm^{-1} (aromatic); NMR data: ^{1}H, δ 7.31 (m, 5 H, CH$_2$*Ph*), 4.48 (s, 2 H, *CH*$_2$Ph), 4.24 (s, 1 H, H-6), 4.23 (d, 1 H, $J_{7,8}$ 1 Hz, H-7), 4.02 (m, 3 H, H-8,9,9′), 3.48 (m, 2 H, H-1,1′), 2.00–1.91 and 1.73–1.57 (2 m, 6 H), 1.46, 1.40, 1.34, and 1.32 (4 s, 12 H, 2CMe$_2$); ^{13}C, δ 115.71 (C-5), 110.81 (CMe$_2$, 1,3-dioxolane ring), 97.26 (CMe$_2$, 1,3-dioxane ring), 86.19 (C-8), 73.74 and 71.79 (C-6,7), 73.00 (CH$_2$Ph), 70.42 (C-1), 60.46 (C-9), 37.61 (C-4), 30.02 (C-2), 28.87 and 18.87 (C*Me*$_2$, 1,3-dioxane ring), 27.54 and 26.77 (C*Me*$_2$, 1,3-dioxolane ring) and 21.00 (C-3). Anal. Calcd for $C_{22}H_{32}O_6$: C, 67.32; H, 8.22. Found: C, 67.00; H, 7.97.

*1-O-Benzyl-2,3,4-trideoxy-5,6-O-isopropylidene-α-*L-xylo-*non-5-ulofuranose* (**19**).—A solution of **18** (5.83 g, 14.87 mmol) in aq 50% AcOH (16 mL) was heated at 50°C for 1 h. TLC (ether) then showed no **18** and the presence of a new product of lower mobility. The solution was concentrated and the residue dissolved in abs EtOH, neutralised with solid K_2CO_3, filtered, and concentrated again. Column chromatography (5:1 ether–hexane) of the residue afforded crystalline **19** (5 g, 100%); mp 62–63°C (from hexane); $[\alpha]_D^{24}$ +7° (*c* 1); ν_{max}^{KBr} 3426 (OH), 1455 (benzyl), 1383 and 1373 (CMe$_2$), and 698 cm^{-1} (aromatic); NMR data: ^{1}H, δ 7.31 (m, 5 H, CH$_2$*Ph*), 4.48 (s, 2 H, *CH*$_2$Ph), 4.25 (d, 1 H, $J_{7,8}$ 3 Hz, H-7), 4.22 (s, 1 H, H-6), 4.16 (m, 1 H, H-8), 4.05 (dd, 1 H, $J_{8,9}$ 4, $J_{9,9'}$ 12.5 Hz, H-9), 3.95 (dd, 1 H, $J_{8,9'}$ 3 Hz, H-9′), 3.48 (bt, 2 H, H-1,1), 3.36 (bs, 2 H, OH-7,9), 2.00–1.87 and 1.73–1.54 (2 m, 6 H), 1.45 and 1.31 (2 s, 6 H, CMe$_2$); ^{13}C, δ 115.25 (C-5), 110.88 (CMe$_2$), 87.39 (C-8), 78.86 (C-7), 72.98 (CH$_2$Ph), 70.19 (C-1), 61.42 (C-9), 37.69 (C-4), 29.84 (C-2), 27.51 and 26.67 (C*Me*$_2$) and 20.83 (C-3). Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.00. Found: C, 64.94; H, 8.19.

*1-O-Benzyl-9-O-*tert*-butyldiphenylsilyl-2,3,4-trideoxy-5,6-O-isopropylidene-α-*L-xylo-*non-5-ulofuranose* (**20**).—Compound **19** (2.14 g, 6.08 mmol) in dry CH_2Cl_2 (20 mL) was treated with 4-dimethylaminopyridine (40 mg), Et_3N (0.9 mL) and *tert*-butyldiphenylchlorosilane (2.03 g, 7.4 mmol) as for compound **4** for 16 h. TLC (ether) then showed the absence of **19** and the presence of a new compound of higher mobility. Work-up of the mixture followed by column chromatography (1:5 ether–hexane) afforded **20** (2.9 g, 81%) as a colourless syrup; $[\alpha]_D^{26}$ −10° (*c* 0.7); ν_{max}^{film} 3461 (OH), 1455 (benzyl), 1382 and 1372 (CMe$_2$), 737 and 702 cm^{-1} (aromatic); NMR data: ^{1}H, δ

7.75–7.65 and 7.44–7.25 (2 m, 15 H, relative intensity 4:11, 2Ph and CH_2*Ph*), 4.48 (s, 2 H, *CH*$_2$Ph), 4.35 (d, 1 H, $J_{7,8}$ 2.6 Hz, H-7), 4.29 (s, 1 H, H-6), 4.18–4.05 (m, 3 H, H-8,9,9′), 3.48 (bt, 2 H, H-1,1′), 2.10–1.65 (m, 7 H), 1.45 and 1.34 (2 s, 6 H, CMe_2), and 1.04 (s, 9 H, CMe_3); ^{13}C, δ 115.31 (C-5), 110.70 (*C*Me$_2$), 87.42 (C-8), 78.46 and 77.93 (C-6,7), 73.00 (*C*H$_2$Ph), 70.45 (C-1), 63.35 (C-9), 38.28 (C-4), 30.10 (C-2), 27.54 and 26.71 (C*Me*$_2$), 26.71 (C*Me*$_3$), 20.85 (C-3) and 19.08 (*C*Me$_3$). Anal. Calcd for $C_{35}H_{46}O_6Si$: C, 71.15; H, 7.85. Found: C, 70.83; H, 7.91.

1-O-*Benzyl-9*-O-tert-*butyldiphenylsilyl-2,3,4-trideoxy-5,6*-O-*isopropylidene-7*-O-*[(methylthio)thiocarbonyl]*-α-L-xylo-*non-5-ulofuranose* (**21**).—To an ice–water-cooled and stirred suspension of NaH (80% oil dispersion) (250 mg, 8.16 mmol) and imidazole (20 mg) in anhyd THF (10 mL), a solution of **20** (2.83 g, 4.8 mmol) in the same solvent (15 mL) was added. After 10 min CS_2 (1 mL, 16 mmol) and MeI (1 mL, 16 mmol) were added. The stirring was continued for 15 min, and then for 75 min at room temperature. TLC (1:2 ether–hexane) then showed that **20** had disappeared and that a new faster-running compound was present. The mixture was neutralised with AcOH (0.1 mL) and concentrated. The residue was dissolved in ether, washed with brine, water, and concentrated. Column chromatography (1:6 ether–hexane) of the residue yielded **21** (3.1 g, quantitative) as a pale yellow syrup; $[\alpha]_D^{22}$ +29° (*c* 1.3); ν_{max}^{film} 1455 (benzyl), 1383 and 1374 (CMe_2), 740 and 702 cm^{-1} (aromatic); NMR data: ^{1}H, δ 7.75–7.65 and 7.44–7.26 (2 m, 15 H, Ph), 6.04 (d, 1 H, $J_{7,8}$ 3 Hz, H-7), 4.57 (ddd, 1 H, $J_{8,9}$ 6, $J_{8,9'}$ 8.2 Hz, H-8), 4.48 (s, 2 H, *CH*$_2$Ph), 4.40 (s, 1 H, H-6), 3.92 (dd, 1 H, $J_{9,9'}$ 10 Hz, H-9), 3.87 (dd, 1 H, H-9′), 3.46 (t, 2 H, $J_{1,2}$ 6.5 Hz, H-1,1), 2.48 (s, 3 H, SMe), 1.95–1.76 and 1.69–1.47 (2 m, 6 H), 1.54 and 1.34 (2 s, 6 H, CMe_2), and 1.02 (s, 9 H, CMe_3); ^{13}C, δ 214.64 (C = S), 115.39 (C-5), 111.71 (*C*Me$_2$), 84.58 and 84.50 (C-7,8), 79.39 (C-6), 73.05 (*C*H$_2$Ph), 70.30 (C-1), 60.32 (C-9), 37.91 (C-4), 29.95 (C-2), 27.50 and 26.64 (C*Me*$_2$), 26.81 (C*Me*$_3$), 20.83 (C-3), 19.20 (*C*Me$_3$) and 19.10 (SMe). Anal. Calcd for $C_{37}H_{48}O_6S_2Si$: C, 65.26; H, 7.10. Found: C, 65.08; H, 6.86.

1-O-*Benzyl-9*-O-tert-*butyldiphenylsilyl-2,3,4,7-tetradeoxy-5,6*-O-*isopropylidene*-α-L-erythro-*non-5-ulofuranose* (**22**).—Compound **21** (3.04 g, 4.48 mmol) in dry toluene (35 mL) was treated with tributyltin hydride (1.3 g, 4.5 mmol) and azobis(isobutyronitrile) (50 mg) in the same solvent (15 mL), as for compound **7**, for 16 h. TLC (1:4 ether–hexane) then revealed the absence of **21** and the presence of a new compond of slightly lower mobility. Column chromatography (1:6 ether–hexane) gave **22** (2.53 g, 100%) as a colourless syrup; $[\alpha]_D^{25}$ +4° (*c* 1); ν_{max}^{film} 1455 (benzyl), 1381 and 1371 (CMe_2), 740 and 702 cm^{-1} (aromatic); NMR data: ^{1}H, δ 7.76–7.63 and 7.50–7.25 (2 m, 15 H, Ph), 4.50 (d, 1 H, $J_{6,7exo}$ 4 Hz, H-6), 4.48 (s, 2 H, *CH*$_2$Ph), 4.43–4.32 (m, 1 H, H-8), 3.87 (dd, 1 H, $J_{8,9}$ 4, $J_{9,9'}$ 11 Hz, H-9), 3.71 (dd, 1 H, $J_{8,9'}$ 3.4 Hz, H-9′), 3.44 (bt, 2 H, $J_{1,2}$ 6.5 Hz, H-1,1), 2.06–1.28 (m, 8 H), 1.51 and 1.35 (2 s, 6 H, CMe_2) and 1.05 (s, 9 H, CMe_3); ^{13}C, δ 115.37 (C-5), 110.35 (*C*Me$_2$), 82.97 (C-8), 78.68 (C-6), 72.98 (*C*H$_2$Ph), 70.24 (C-1), 64.33 (C-9), 37.84 (C-4), 34.84 (C-7), 29.99 (C-2), 27.50 and 26.63 (C*Me*$_2$), 26.87 (C*Me*$_3$), 20.98 (C-3) and 19.31 (*C*Me$_3$). Anal. Calcd for $C_{35}H_{46}O_5Si$: C, 73.13; H, 8.07. Found: C, 72.66; H, 7.83.

1-O-*Benzyl-2,3,4,7-tetradeoxy-5,6*-O-*isopropylidene*-α-L-erythro-*non-5-ulofuranose* (**23**).—Compound **22** (2.35 g, 4.1 mmol) in dry THF (20 mL) was treated with tetrabutylammonium fluoride trihydrate (1.6 g, 5.1 mmol), as for compound **8**, for 16 h.

Column chromatography (3:2 ether–hexane) gave **23** (1.1 g, 88%) as a colourless syrup; $[\alpha]_D^{24}$ +4° (*c* 1.3); ν_{max}^{film} 1455 (benzyl), 1382 and 1372 (CMe_2), 738 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 7.31 (m, 5 H, CH_2*Ph*), 4.48 (s, 2 H, CH_2Ph), 4.46 (d, 1 H, $J_{6,7exo}$ 4.5 Hz, H-6), 4.36 (ddt, 1 H, $J_{8,9}$ 3, $J_{7endo,8} = J_{8,9'} = 4.5$, $J_{7exo,8}$ 11 Hz, H-8), 3.83 (dd, 1 H, $J_{9,9'}$ 12 Hz, H-9), 3.52 (dd, 1 H, H-9′), 3.46 (t, 2 H, $J_{1,2}$ 6.3 Hz, H-1,1), 1.96 (dd, 1 H, $J_{7endo,7exo}$ 13.3 Hz, H-7*endo*), 1.90–1.48 (m, 7 H), 1.49 and 1.32 (2 s, 6 H, CMe_2); ^{13}C, δ 115.33 (C-5), 110.58 (CMe_2), 83.01 (C-8), 78.67 (C-6), 72.98 (CH_2Ph), 69.99 (C-1), 63.42 (C-9), 37.50 (C-4), 34.30 (C-7), 29.85 (C-2), 27.41 and 26.58 (CMe_2) and 21.06 (C-3). EIMS: *m/z* 336 (7%, $M^{+\cdot}$) and 91 (100, $C_7H_7^+$).

*1-O-Benzyl-2,3,4,7-tetradeoxy-5,6-O-isopropylidene-9-O-(p-toluenesulfonyl)-α-*L-erythro-*non-5-ulofuranose* (**24**).—Compound **23** (1 g, 3 mmol) in cooled dry pyridine (5 mL) was treated with *p*-toluenesulfonyl chloride (670 mg, 3.5 mmol) for 16 h. Usual work-up of the mixture, followed by column chromatography (1:2 ether–hexane) afforded **24** (1.3 g, 88%) as a colourless syrup; $[\alpha]_D^{26}$ −1.5° (*c* 1.5); ν_{max}^{film} 1455 (benzyl), 1368 (CMe_2), 738 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 7.76 and 7.37–7.24 (d and m, 9 H, CH_2*Ph* and CH_3-C_6H_4-SO_2), 4.49 (s, 2 H, CH_2Ph), 4.41 (d, 1 H, $J_{6,7exo}$ 4.2 Hz, H-6), 4.37 (bdq, 1 H, $J_{8,9} = J_{8,9'} = J_{7endo,8} = 4.3$, $J_{7exo,8}$ 11 Hz, H-8), 4.13 (dd, 1 H, $J_{9,9'}$ 11 Hz, H-9), 4,04 (dd, 1 H, H-9′), 3.45 (t, 2 H, $J_{1,2}$ 6.4 Hz, H-1,1), 2.40 (s, 3 H, CH_3-C_6H_4-SO_2), 2.03 (dd, 1 H, $J_{7endo,7exo}$ 13.3 Hz, H-7*endo*), 1.82–1.35 (m, 7 H), 1.43 and 1.29 (2 s, 6 H, CMe_2); ^{13}C, δ 115.50 (C-5), 110.77 (CMe_2), 82.43 (C-8), 75.23 (C-6), 73.00 (CH_2Ph), 70.10 (C-1), 69.96 (C-9), 37.29 (C-4), 34.99 (C-7), 29.85 (C-2), 27.37 and 26.48 (CMe_2), 21.66 ($MeC_6H_4SO_2$) and 20.89 (C-3). Anal. Calcd for $C_{26}H_{34}O_7S$: C, 63.64; H, 6.99. Found: C, 63.16; H, 6.52.

*1-O-Benzyl-2,3,4,7,9-pentadeoxy-5,6-O-isopropylidene-α-*L-erythro-*non-5-ulofuranose* (**25**).—Compound **24** (1.3 g, 2.6 mmol) in anhyd ether (10 mL) was treated with $LiAlH_4$ (190 mg, 5 mmol), as for compound **10**, for 48 h at room temperature and then refluxed for 45 min. To the mixture a saturated solution of ammonium chloride (10 mL) was added; the mixture was filtered through a Celite pad and the organic phase washed with brine and concentrated. Column chromatography (1:2 ether–hexane) of the residue gave **25** (620 mg, 74,5%) as a colourless syrup; $[\alpha]_D^{23}$ +14° (*c* 1); ν_{max}^{film} 1455 (benzyl), 1382 and 1371 (CMe_2), 736 and 698 cm^{-1} (aromatic); NMR data: ^1H, δ 7.32 (m, 5 H, CH_2*Ph*), 4.49 (s, 2 H, CH_2Ph), 4.42 (d, 1 H, $J_{6,7exo}$ 4.3 Hz, H-6), 4.35 (ddq, 1 H, H-8), 3.47 (t, 2 H, $J_{1,2}$ 6.4 Hz, H-1,1), 2.06 (dd, 1 H, $J_{7endo,8}$ 4, $J_{7endo,7exo}$ 13.2 Hz, H-7*endo*), 1.93–1.43 (m, 6 H), 1.49 and 1.31 (2 s, 6 H, CMe_2), 1.40 (ddd, 1 H, $J_{7exo,8}$ 10.8 Hz, H-7*exo*) and 1.25 (d, 3 H, $J_{8,9}$ 6 Hz, H-9,9,9); ^{13}C, δ 115.12 (C-5), 110.05 (CMe_2), 83.35 (C-8), 74.08 (C-6), 72.98 (CH_2Ph), 70.19 (C-1), 41.34 (C-4), 38.04 (C-7), 29.94 (C-2), 27.36 and 26.58 (CMe_2), 21.07 (C-3) and 19.62 (C-9). EIMS: *m/z* 320 (9%, $M^{+\cdot}$), and 91 (100, $C_7H_7^+$).

Hydrogenation of **25** (600 mg, 1.87 mmol) in anhyd MeOH (7 mL) at 4 atm over 10% Pd–C (0.2 g) for 5 h, followed by column chromatography (5:1 ether–hexane) gave **15** (380 mg, 88%).

(2S,4S,5R)- (**26**) *and (2S,4S,5S)-4-Hydroxy-2-methyl-1,6-dioxaspiro[4.5]decane* (**27**).—A solution of **15** (480 mg, 2.1 mmol) in aq 75% CF_3CO_2H (4 mL) was left at room temperature for 4 h. GLC (*D*) then revealed the absence of **15** (t_R 4.75 min) and the presence of two new compounds (t_R 1.68 and 2.12 min) in a 2.6:1 ratio, respec-

tively, were present. The mixture was concentrated, and water and then CH_2Cl_2 were distilled repeatedly from the residue. Column chromatography (2:3 ether–hexane) gave first **26** (125 mg, 35%) as a colourless syrup; $[\alpha]_D^{26}$ −49° (*c* 0.6); ν_{max}^{film} 3472 cm^{-1} (OH); NMR data (C_6D_6): ^1H, δ 4.14 (ddq, 1 H, H-2), 3.85 (dt, 1 H, $J_{7a,7e} = J_{7a,8a} = 11$, $J_{7a,8e}$ 2.5 Hz, H-7a), 3.82 (dd, 1 H, H-4), 3.51 (dm, 1 H, H-7e), 1.99 (ddd, 1 H, $J_{2,3}$ 7.8, $J_{3,4}$ 6.7, $J_{3,3'}$ 12.5 Hz, H-3), 1.86–1.67 (m, 3 H, H-9a,10e,OH), 1.61 (ddd, 1 H, $J_{2,3'}$ 5.6, $J_{3',4}$ 8.4 Hz, H-3'), 1.48–1.28 (m, 3 H, H-8a,9e,10a), 1.19–1.11 (m, 1 H, H-8e), 1.01 (d, 3 H, $J_{2,Me}$ 6.3 Hz, Me-2); ^{13}C, δ 102.54 (C-5), 76.86 (C-4), 71.70 (C-2), 61.58 (C-7), 40.49 (C-3), 32.02 (C-10), 25.84 (C-8), 22.12 (Me-2) and 19.98 (C-9). EIMS: *m/z* 157 (0.1%, $M^{+\cdot} - Me$) and 101 (100, $C_5H_9O_2^+$).

Eluted second was **27** (55 mg, 15%) as a colourless syrup; $[\alpha]_D^{27}$ +93° (*c* 0.5); ν_{max}^{film} 3446 cm^{-1} (OH); NMR data (C_6D_6): ^1H, δ 4.41 (m, 1 H, H-2), 3.96 (dt, 1 H, $J_{7a,8a} = J_{7a,7e} = 11$, $J_{7a,8e}$ 2.7 Hz, H-7a), 3.94 (m, 1 H, H-4), 3.51 (ddt, 1 H, $J_{7e,8e} = J_{7e,9e} = 2$, $J_{7e,8a}$ 5 Hz, H-7e), 1.98–1.78 (m, 3 H, H-3,9a,10e), 1.77–1.66 (m. 1 H, H-3'), 1.64–1.34 (m, 4 H, H-8a,9e,10a,OH), 1.28–1.18 (m, 1 H, H-8e), 1.22 (d, 3 H, $J_{2,Me}$ 6.2 Hz, Me-2); ^{13}C, δ 107.25 (C-5), 78.84 (C-4), 75.10 (C-2), 60.85 (C-7), 41.01 (C-3), 29.33 (C-10), 26.01 (C-8), 25.43 (Me-2) and 20.04 (C-9). EIMS: *m/z* 157 (0.1%, $M^{+\cdot} - Me$) and 101 (100, $C_5H_9O_2^+$).

(2S,4S,5R)-2-Methyl-4-[(methylthio)thiocarbonyloxy]-1,6-dioxaspiro[4.5]decane (**28**).—Compound **26** (50 mg, 0.29 mmol) in anhyd THF (4 mL) was treated with a suspension of NaH (80% oil dispersion) (17 mg, 0.7 mmol) and imidazole (20 mg) in the same solvent (3 mL). After 10 min, CS_2 (0.05 ml, 0.8 mmol) and MeI (0.05 ml, 0.8 mmol) were added and the mixture was stirred for 30 min. TLC (1:1 ether–hexane) then showed that only a new compound with higher mobility was present. Work-up of the mixture as above, followed by column chromatography (1:2 ether–hexane) afforded **28** (55 mg, 72%) as a pale yellow syrup; $[\alpha]_D^{27}$ −50° (*c* 1); ν_{max}^{film} 1209 cm^{-1} (C = S); NMR data: ^1H, δ 5.50 (t, 1 H, $J_{3,4}$ 8.2 Hz, H-4), 4.32 (sex, 1 H, $J_{2,Me} = J_{2,3} = 6.3$ Hz, H-2), 3.88 (dt, 1 H, $J_{7a,7e} = J_{7a,8a} = 11.3$, $J_{7a,8e}$ 3 Hz, H-7a), 3.72 (ddt, 1 H, $J_{7e,8e} = J_{7e,9e} = 2$, $J_{7e,8a}$ 6 Hz, H-7e), 2.56 (s, 3 H, SMe), 2.12 (dd, 2 H, H-3,3), 1.83–1.20 (m, 6 H) and 1.27 (d, 3 H, Me-2); ^{13}C, δ 216.22 (C = S), 102.64 (C-5), 84.71 (C-4), 71.43 (C-2), 61.44 (C-7), 35.69 (C-3), 31.77 (C-10), 25.04 (C-8), 21.90 (Me-2), 19.77 (C-9) and 19.26 (Me-S). CIMS (CH_4): *m/z* 263 (100%, $M^{+\cdot} + 1$).

(2S,4S,5S)-2-Methyl-4-[(methylthio)thiocarbonyloxy]-1,6-dioxaspiro[4.5]decane (**29**).—Compound **27** (340 mg, 1.97 mmol) in anhyd THF (10 mL) was subjected to the same treatment as **26** with NaH (118 mg, 5 mmol), imidazole (20 mg), CS_2 (0.25 mL, 4 mmol) and MeI (0.25 mL, 4 mmol). Column chromatography gave **29** (500 mg, 97%) as a pale yellow syrup; $[\alpha]_D^{27}$ +55° (*c* 0.7); ν_{max}^{film} 1204 cm^{-1} (C = S); NMR data: ^1H, δ 5.84 (bd, 1 H, $J_{3',4}$ 4.5 Hz, H-4), 4.43 (dquint, 1 H, $J_{2,Me} = J_{2,3} = 6.3$, $J_{2,3'}$ 8.7 Hz, H-2), 3.92 (dt, 1 H, $J_{7a,7e} = J_{7a,8a} = 11$, $J_{7a,8e}$ 3.4 Hz, H-7a), 3.60 (2 m, 1 H, H-7e), 2.53 (s, 3 H, S-Me), 2.21 (ddd, 1 H, $J_{3,4}$ 0.7, $J_{3,3'}$ 14 Hz, H-3), 2.10 (ddd, 1 H, H-3'), 1.85–1.43 (m, 6 H) and 1.31 (d, 3 H, Me-2); ^{13}C, δ 214.77 (C = S), 106.15 (C-5), 88.12 (C-4), 75.35 (C-2), 61.15 (C-7), 37.89 (C-3), 29.03 (C-10), 25.16 (C-8), 23.00 (Me-2), 19.40 (C-9) and 18.86 (S-Me). CIMS (CH_4): *m/z* 263 (100%, $M^{+\cdot} + 1$).

(2S,5RS)-2-Methyl-1,6-dioxaspiro[4.5]decane (**1**).—To a stirred, refluxing solution of **29** (450 mg, 1.72 mmol) in dry toluene (4 mL), tributyltin hydride (0.9 mL, 3.3

mmol) and azobis(isobutyronitrile) (5 mg) were added under Ar. Refluxing was continued for 30 min. TLC (1:3 ether–*n*-pentane) then revealed the absenceof **29** and the presence of a new product of slightly lower mobility. Column chromatography (*n*-pentane → 1:10 ether–*n*-pentane) of the mixture gave (2*S*,5*RS*)-**1** (200 mg, 74%) as an unresolvable mixture. GLC (*E*, t_R 2.93 and 3.03 min); $[\alpha]_D^{25}$ +52° (*c* 1, *n*-pentane), [For (2*S*,5*R*)-**1**: lit. [2] $[\alpha]_D$ −81.4° (*c* 0.4, *n*-pentane); lit. [6b] $[\alpha]_D$ −79.1° (*c* 0.392, *n*-pentane). For (2*S*,5*S*)-**1**: lit. [6b] +84.2° (*c* 0.101, *n*-pentane)]. EIMS: for (2*S*,5*R*)-**1**, *m/z* 156 (7.8%, $M^{+\cdot}$), 155 (1.4, $M^{+\cdot}-1$), 141 (5.7, $M^{+\cdot}-Me$), 128 (7.8, $C_7H_{12}O_2^+$), 126 (1.9, $C_8H_4O^+$), 112 (21.3, $C_7H_{12}O^+$), 111 (18.3, $C_7H_{11}O^+$), 101 (100, $C_5H_9O_2^+$), 100 (46.8, $C_5H_8O_2^+$), 99 (10.7, $C_5H_7O_2^+$), 98 (71.1, $C_6H_{10}O^+$), 97 (10.9, $C_6H_9O^+$), 85 (15.7, $C_4H_5O_2^+$), and 83 (55.5, $C_5H_7O^+$). For (2*S*,5*S*)-**1**, *m/z* 156 (8.1%, $M^{+\cdot}$), 155 (1.2, $M^{+\cdot}-1$), 141 (6.1, $M^{+\cdot}-Me$), 128 (7.8, $C_7H_{12}O_2^+$), 126 (1.6, $C_8H_{14}O^+$), 112 (16.7, $C_7H_{12}O^+$), 111 (16.4, $C_7H_{11}O^+$), 101 (100, $C_5H_9O_2^+$), 100 (43.0, $C_5H_8O_2^+$), 99 (10.0, $C_5H_7O_2^+$), 98 (65.3, $C_6H_{10}O^+$), 97 (9.3, $C_6H_9O^+$), 85 (17.1, $C_4H_5O_2^+$), and 83 (50.2, $C_5H_7O^+$).

Treatment of **28** (55 mg, 0.2 mmol) as **29** in dry toluene (1 mL) with tributyltin hydride (0.1 mL, 0.4 mmol) and azobis(isobutyronitrile) (2 mg) gave (2*S*,5*RS*)-**1** (25 mg, 80%) as above.

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