

Synthesis of Three 3-C-Hydroxymethylpentoses with the D-ribo-, D-xylo- and L-lyxo-Configurations. Identification of the Latter with a Monosaccharide Isolated from Phase I *Coxiella burnetii* Lipopolysaccharide

Olof Dahlman,^{a,b} Per J. Garegg,^{a,c*} Hubert Mayer^d and Stefan Schramek^e

^aDepartment of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden, ^bPresent address: Swedish Tobacco Company, Box 17007, S-104 62 Stockholm, Sweden, ^cPresent address: Department of Organic Pharmaceutical Chemistry, Biomedical Center, Box 574, S-751 23 Uppsala, Sweden, ^dMax-Planck-Institut für Immunbiologie, Postfach 1169, D-7800 Freiburg-Zähringen, West Germany and ^eInstitute of Virology, Slovak Academy of Sciences, CS-81703 Bratislava, Czechoslovakia

Dahlman, Olof, Garegg, Per J., Mayer, Hubert and Schramek, Stefan, 1986. Synthesis of Three 3-C-Hydroxymethylpentoses with the D-ribo-, D-xylo- and L-lyxo-Configurations. Identification of the Latter with a Monosaccharide Isolated from Phase I *Coxiella burnetii* Lipopolysaccharide. – Acta Chem. Scand. B 40: 15–20.

Three 3-C-hydroxymethylpentoses with the D-ribo-, D-xylo and L-lyxo-configurations, were synthesised *via* nitromethane addition for the first two and 1,3-dithiane addition for the last one, to appropriate 3-ulose derivatives. 3-C-Hydroxymethyl-L-lyxose is identical with a monosaccharide component previously isolated from hydrolysates of the phase I *Coxiella burnetii* lipopolysaccharide.

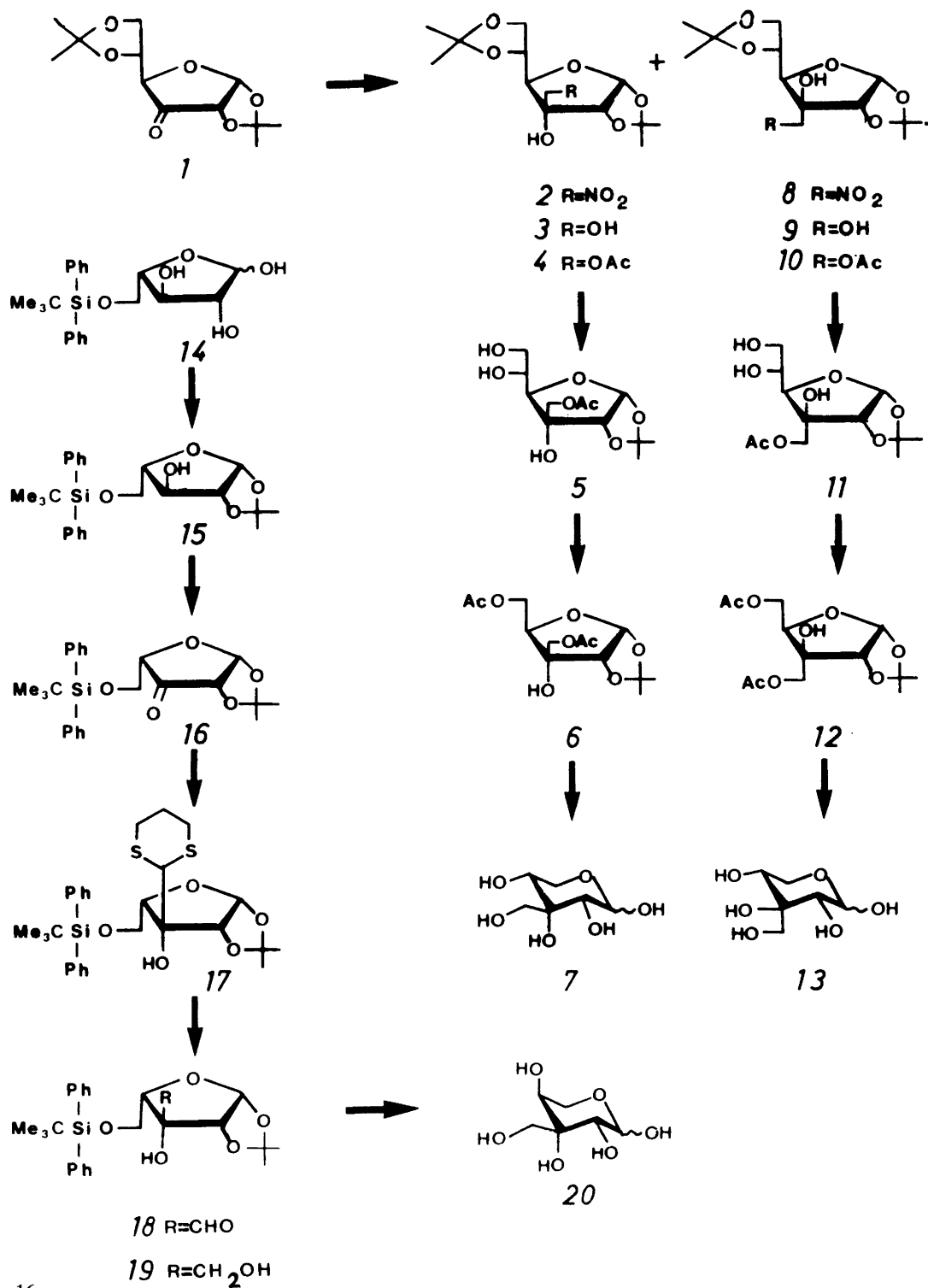
A novel branched-chain monosaccharide, isolated from hydrolysates of the phase I *Coxiella burnetii* lipopolysaccharide, has been assigned the structure of a 3-C-hydroxymethylpentose, based on GLC/MS evidence.¹ In the polysaccharide the new sugar is furanosidically linked.¹ In order to determine the correct configuration of this component we have now synthesised three 3-C-hydroxymethylpentoses with the D-ribo-, D-xylo- and L-lyxo-configurations, respectively. The latter compound proved to be identical with the natural sugar.

Two commonly used procedures for the synthesis of branched C-hydroxymethyl sugars are base-catalysed reactions of uloses with nitromethane² or dithiane³ followed by the appropriate synthetic manipulations. Using a previously published sequence,⁴ 1,2:5,6-di-*O*-isopropylidene- α -D-ribo-hexofuranosyl-3-ulose (**1**) was reacted with nitromethane to give the two epimeric 3-C-nitromethyl derivatives with the D-*allo*- (**2**) and D-*gluco*-configuration (**8**), respectively.

*To whom correspondence should be addressed.

Each of these was treated with alkaline permanganate followed by sodium borohydride reduction and then acetylation,² thus converting the nitromethyl group into an acetoxymethyl group (**4** and **10**). Subsequent removal of the 5,6-*O*-isopropylidene group by acid hydrolysis (**5** and **11**), periodate cleavage, sodium borohydride reduction and acetylation gave **6** and **12**. Deprotection of these derivatives then afforded the title compounds **7** and **13** with the D-ribo- and D-xylo-configurations, respectively.

Treatment of L-arabinose with *tert*-butyldiphenylchlorosilane and imidazole in *N,N*-dimethylformamide yielded 5-*O*-*tert*-butyldiphenylsilyl-L-arabinofuranose (**14**) in 55 % yield. Conversion of **14** into the isopropylidene derivative **15** was followed by oxidation⁵ to yield the 3-ulose **16** in 33 % total yield from L-arabinose. Reaction of **16** with 2-dithianyllithium in tetrahydrofuran afforded **17** in 85 % yield. The standard methods for conversion of a dithianyl group such as that in **17** into an aldehyde group (**18**) are treatments with mercury(II) chloride and mercury(II) oxide,⁶ *N*-bromosuccinimide⁶ or cerium(IV) ammo-



nium nitrate.⁷ These methods did not convert **17** into **18** in a useful yield. When, however, **17** was treated with iodomethane and calcium carbonate in 80 % aqueous acetonitrile **18** was produced in 88 % yield. Compound **18** was then reduced to the hydroxymethyl compound **19** and the latter was converted into the target compound **20** by acid hydrolysis.

Of the three final compounds, the *L*-lyxo isomer **20** was shown to be identical with the natural product (NMR, optical rotation, MS and retention time on GLC of its alditol acetate).

Experimental

General methods were the same as those described before.⁸ Mass spectra were recorded on a Kratos MS 50/DS 55 instrument operating at 70 eV, the sample being introduced *via* a direct inlet probe. High resolution mass spectra were recorded at a resolution of about 10000.

3-C-Acetoxyethyl-5-O-acetyl-1,2-O-isopropylidene- α -D-ribofuranose (6). A solution of sodium metaperiodate (750 mg, 3.5 mmol) in water (20 ml) was added to **3-C-acetoxyethyl-1,2-O-isopropylidene- α -D-allofuranose**² (**5**) (755 mg, 2.6 mmol) in methanol (20 ml). After 10 min at room temperature, the product was filtered and the filtrate was treated with excess sodium borohydride for 20 min. The solution was neutralised with Dowex 50 (H⁺) resin, filtered, and the filtrate was passed through a column of Amberlite IR-45 (HCO₃⁻). The combined eluate and washings (50 % aqueous methanol) were concentrated to dryness. The residue was treated with acetic anhydride (5 ml) and pyridine (10 ml) for 1 h at room temperature. After concentration and repeated co-concentrations with toluene, the product was purified by flash chromatography⁹ (SiO₂, toluene-ethyl acetate 4:1). Crystallisation from ethyl acetate-2,2,4-trimethylpentane furnished **6** (637 mg, 81 %), m.p. 101.5–103 °C, $[\alpha]_D^{+34}$ (c 1.0, CHCl₃); ¹H NMR (100 MHz, CDCl₃): δ 1.39 (3 H, s, CH₃), 1.60 (3 H, s, CH₃), 2.09 (3 H, s, OAc), 2.13 (3 H, s, OAc), 2.99 (1 H, s, OH), 4.01–4.46 (6 H, m), 5.84 (1 H, d, *J*_{1,2} 3.9 Hz, H-1); ¹³C NMR (25 MHz, CDCl₃): δ 20.7, 26.5, 61.6, 63.2, 78.4, 79.4, 79.9, 103.8, 112.8, 170.6. HR-MS (*m/z*): 289.0946 (M-CH₃)⁺, Calc. for C₁₂H₁₇O₈: 289.0923, MS (*m/z*, intensity in %): 289 (7), 244 (1), 211 (4), 201 (4), 169 (3), 103 (26), 86 (22), 71 (27), 59 (24), 43 (100).

3-C-Hydroxymethyl-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (9). The nitro alcohol **8**⁴ (1.20 g, 3.8 mmol) was dissolved in 0.1 M potassium hydroxide (46 ml, 4.6 mmol). Sodium chloride was added to give a saturated solution. To the resulting solution was added saturated aqueous sodium chloride (64 ml), 2 M magnesium sulfate (18 ml) and chloroform (32 ml). The mixture was cooled to -10 °C. Potassium permanganate (0.60 g) in saturated aqueous sodium chloride (62 ml) was added with vigorous stirring. After 15 min, excess sodium borohydride was added and the stirred mixture was allowed to attain room temperature. Sodium sulfite (1 g) was added, followed by the dropwise addition of 2 M hydrochloric acid to give a clear mixture. The organic phase was separated and the aqueous phase was extracted with chloroform (3×60 ml). The combined chloroform solutions were washed with water (30 ml), dried (MgSO₄), filtered and concentrated. The residue was purified by flash chromatography (SiO₂, toluene-ethyl acetate 1:1). Compound **9** (0.66 g, 61 %) had m.p. 86–87 °C, $[\alpha]_D^{+25}$ (c 0.9, CHCl₃); ¹H NMR (100 MHz, CDCl₃): δ 1.31, 1.37, 1.45, 1.51 (each 3 H, each s, CH₃), 3.08–3.22 (2 H, m), 3.80 (1 H, d, *J* 2.4 Hz), 3.87 (1 H, s), 4.03–4.32 (4 H, m), 4.40 (1 H, d, *J* 3.9 Hz, H-2), 5.88 (1 H, d, *J* 3.9 Hz, H-1); ¹³C NMR (25 MHz, CDCl₃): δ 25.2, 26.4, 26.8, 27.1, 62.5, 67.7, 72.1, 81.2, 82.7, 86.5, 104.7, 109.8, 112.7.

3-C-Acetoxyethyl-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (10). Compound **9** (0.57 g) was acetylated and the product was worked up to yield **10** as an oil which crystallised (0.65 g, 100 %), m.p. 80–83 °C, $[\alpha]_D^{+51}$ (c 1.4, CHCl₃); ¹H NMR (100 MHz, CDCl₃): δ 1.34 (6 H, s, CH₃), 1.42 and 1.52 (each 3 H, each s, CH₃), 2.14 (3 H, s, OAc), 2.78 (1 H, s, OH), 3.8–4.7 (7 H, m), 5.88 (1 H, d, *J* 3.4 Hz, H-1); ¹³C NMR (25 MHz, CDCl₃): δ 20.8, 25.2, 26.6, 26.8, 27.1, 64.8, 67.5, 72.4, 81.2, 81.3, 85.3, 104.8, 109.5, 112.7, 171.3.

3-C-Acetoxyethyl-5-O-acetyl-1,2-O-isopropylidene- α -D-xylofuranose (12). Hydrochloric acid (0.1 M, 14 ml) was added with stirring to a solution of **10** (0.45 g, 1.35 mmol) in methanol (25 ml) and water (15 ml). After 22 h at room temperature, the solution was poured through a column of Amberlite IR-45 (HCO₃⁻) resin which was eluted with methanol-water 1:1. The combined eluate and washings were concentrated to

dryness. Drying in a vacuum over phosphorus(V) oxide produced a foam containing **11** (0.379, ca 90%), contaminated with about 5% of the corresponding 3-*C*-hydroxymethyl compound; ^1H NMR (100 MHz, CDCl_3): δ 1.33 and 1.50 (each 3 H, each s, CH_3), 2.13 (3 H, s, OAc), 3.4–4.8 (10 H, m), 5.88 (1 H, d, J 3.9 Hz, H-1); ^{13}C NMR (25 MHz, CDCl_3): δ 21.0, 26.6, 27.0, 64.7, 65.1, 69.4, 80.2, 81.7, 85.2, 104.5, 112.7, 172.0.

Compound **11** (0.34 g) was sequentially subjected to oxidation with sodium metaperiodate, sodium borohydride reduction and acetylation as described above for the synthesis of **6**. The product **12** was obtained as an oil (0.24 g, 68%), $[\alpha]_{\text{D}}^{+50}$ (c 0.9, CHCl_3); ^1H NMR (100 MHz): 1.34 and 1.52 (each 3 H, each s, CH_3), 2.10 and 2.15 (each 3 H, each s, OAc), 2.84 (1 H, s, OH), 4.1–4.5 (6 H, m), 5.95 (1 H, d, J 3.4 Hz, H-1); ^{13}C NMR (25 MHz, CDCl_3): δ 20.8, 26.5, 27.0, 62.6, 64.5, 79.0, 80.8, 85.4, 104.8, 112.8, 171.0, 171.3. HR-MS (m/z): 289.0934 ($\text{M}-\text{CH}_3$) $^+$. Calc. for $\text{C}_{11}\text{H}_{17}\text{O}_8$: 289.0923, MS (m/z , intensity in %): 289 (7), 211 (3), 201 (5), 169 (7), 103 (21), 100 (24), 86 (11), 85 (13), 71 (21), 59 (22), 43 (100).

5-O-tert-Butyldiphenylsilyl-L-arabinofuranose (**14**). L-Arabinose (15 g, 0.1 mol) was added with stirring to a solution of *tert*-butyldiphenylchlorosilane (27.5 g, 0.1 mol) and imidazole (13.6 g, 0.2 mol) in *N,N*-dimethylformamide (200 ml). After 2 h at 60°C the reaction mixture was poured into hydrochloric acid (1 M, 250 ml). The solution was extracted with dichloromethane (3×150 ml), the organic phase was washed with water (100 ml), saturated aqueous sodium hydrogencarbonate (100 ml), dried (MgSO_4), filtered and concentrated. The product was purified by flash chromatography (SiO_2 , 2,2,4-trimethylpentane – ethyl acetate 1:4) to yield **14** as an oil (21.4 g, 55%), $[\alpha]_{\text{D}}^{-22}$ (c 1.0, CHCl_3); ^1H NMR (100 MHz, CDCl_3): δ 5.27 (1 H, d, J 3.9 Hz, H-1, α -anomer), 5.43 (1 H, d, J 4.4 Hz, H-1, β -anomer); ^{13}C NMR (25 MHz, CDCl_3): δ 19.0, 19.1, 26.7, 26.8, 64.2 (C-5, β -anomer), 64.9 (C-5, α -anomer), 77.1 (C-3, α -anomer), 77.7 (C-4, α -anomer), 77.8 (C-3, β -anomer), 79.6 (C-4, β -anomer), 82.7 (C-2, α -anomer), 86.4 (C-2, β -anomer), 96.4, C-1, α -anomer), 103.2 (C-1, β -anomer), 127.9, 130.0, 132.0, 132.2, 132.6, 132.9, 134.6, 135.8.

5-O-tert-Butyldiphenylsilyl-1,2-O-isopropylidene- β -L-arabinofuranose (**15**). Anhydrous copper (II) sulfate (11 g, 69 mmol) and sulfuric acid

(sp.gr. 1.84, 0.5 ml, 2.5 mmol) were added to a stirred solution of **14** (9.7 g, 25 mmol) in anhydrous acetone (110 ml). After stirring for 17 h at room temperature, the mixture was filtered and then neutralised with calcium hydroxide. The mixture was filtered and the filtrate was concentrated to dryness. The product was purified by flash chromatography (SiO_2 , 2,2,4-trimethylpentane – ethyl acetate 4:1) to yield **15** as an oil (7.4 g, 69%), $[\alpha]_{\text{D}}^{-5}$ (c 1.2, CHCl_3); ^1H NMR (100 MHz, CDCl_3): δ 1.06 [9 H, s, $\text{C}(\text{CH}_3)_3$], 1.28 and 1.32 (each 3 H, each s, CH_3), 2.00 (1 H, d, J 4.3 Hz, OH), 3.78 (1 H, d, J 1.5 Hz), 3.85 (1 H, s), 4.0 (1 H, m), 4.42 (1 H, m), 4.54 (1 H, d, J 4.4 Hz, H-2), 5.87 (1 H, d, J 4.4 Hz, H-1), 7.3–7.4 (6 H, m), 7.6–7.7 (4 H, m); ^{13}C NMR (25 MHz, CDCl_3): δ 19.3, 26.1, 26.8, 63.8, 76.0, 87.2, 87.8, 105.7, 112.4, 127.8, 129.8, 133.3, 133.4, 135.7.

5-O-tert-Butyldiphenylsilyl-1,2-O-isopropylidene- β -L-threo-pentofuranose-3-ulose (**16**). Chromium(VI) oxide (5.0 g, 50 mmol) was added to pyridine (8.1 ml, 100 mmol) in dichloromethane (100 ml) and the resulting solution was stirred at room temperature for 15 min. A solution of **15** (5.4 g, 12.6 mol) in dichloromethane (20 ml) was added, immediately followed by the addition of acetic anhydride (4.9 ml, 50 mmol). After 10 min at room temperature, ethyl acetate (50 ml) and toluene (50 ml) were added. The solution was decanted and then passed through a short column of silica gel (toluene – ethyl acetate 1:2). Concentration and repeated co-concentration with toluene gave **16** as an oil (4.5 g, 84%), $[\alpha]_{\text{D}}^{-12}$ (c 1.0, CHCl_3); ^1H NMR (100 MHz, CDCl_3): δ 1.05 [9 H, s, $\text{C}(\text{CH}_3)_3$], 1.36 (6 H, s), 3.90 (1 H, d, J 1.5 Hz), 3.96 (1 H, s), 4.2–4.4 (2 H, m), 6.03 (1 H, d, J 4.4 Hz, H-1), 7.3–7.4 (6 H, m), 7.6–7.8 (4 H, m); ^{13}C NMR (25 MHz, CDCl_3): 19.2, 26.7, 27.4, 64.5, 76.7, 82.2, 102.6, 114.6, 127.6, 129.6, 132.8, 133.0, 135.6, 135.7, 206.9.

5-O-tert-Butyldiphenylsilyl-3-C-formyl-1,2-O-isopropylidene- β -L-lyxofuranose trimethylenedithioacetal (**17**). Butyllithium in hexane (11.5 ml, 15.0 mmol) was added to a solution of dithiane (1.80 g, 15.0 mmol) in tetrahydrofuran (20 ml) in an atmosphere of N_2 at –30°C. The resulting solution was stirred for 2 h and then cooled to –78°C. A solution of **16** (4.37 g, 10.2 mmol) in tetrahydrofuran (25 ml) was added at this temperature and the mixture was allowed to attain room temperature during 2 h. The reaction mixture was poured into water (150 ml) and the re-

sulting mixture was extracted with dichloromethane (3×75 ml). The combined extract was washed with water (2×50 ml), dried (K_2CO_3), filtered and concentrated. The product was purified by flash chromatography (SiO_2 , 2,2,4-trimethylpentane – ethyl acetate 4:1 containing 0.1% pyridine) to give **17** as an oil, (4.71 g, 85%), $[\alpha]_D -6^\circ$ (c 1.1, $CHCl_3$); 1H NMR (100 MHz, $CDCl_3$): δ 1.07 [9 H, s, $C(CH_3)_3$], 1.39 and 1.46 (each 3 H, each s), 1.9–2.1 (2 H, m), 2.8–3.0 (4 H, m), 3.66 (1 H, s, OH), 3.82 and 4.14 (2 H, AB part of ABX spectrum, J_{AB} 10.4 Hz and J_{AX} 5.8 Hz, H-5), 4.22 (1 H, s, formyl H), 4.46 (1 H, t, J 5.8 Hz, H-4), 4.82 (1 H, d, J 4.4 Hz, H-2), 5.71 (1 H, d, J 4.4 Hz, H-1), 7.3–7.4 (6 H, m), 7.7–7.8 (4 H, m); ^{13}C NMR (25 MHz, $CDCl_3$): δ 19.3, 25.6, 26.8, 27.0, 29.7, 29.8, 53.6, 63.5, 81.0, 82.3, 82.9, 104.7, 114.6, 127.7, 129.7, 133.2, 133.4, 135.7.

5-O-tert-Butyldiphenylsilyl-3-C-formyl-1,2-O-isopropylidene- β -L-lyxofuranose (**18**). Iodomethane (2.5 ml, 40 mmol) was added to a stirred mixture of **17** (2.13 g, 3.9 mmol), acetonitrile (20 ml), water (5 ml), and calcium carbonate (4.4 g, 44 mmol). The mixture was stirred for 3 h at 55°C, and filtered; the filtrate was diluted with water (50 ml) and extracted with dichloromethane (3×50 ml). The combined organic phase was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), filtered and concentrated. The product was purified by flash chromatography (SiO_2 , toluene – ethyl acetate 4:1) to give **18** together with its hydrate. Drying the mixture over phosphorus(V) oxide at about 1 Pa for 16 h gave pure **18**, (1.57 g, 88%), $[\alpha]_D +20^\circ$ (c 1.0, $CHCl_3$); 1H NMR (100 MHz, $CDCl_3$): δ 1.02 [9 H, s, $C(CH_3)_3$], 1.43 and 1.57 (each 3 H, each s, CH_3), 3.47 (1 H, s, OH), 3.1–4.1 (3 H, m), 4.72 (1 H, d, J 4.4 Hz, H-2), 5.76 (1 H, d, J 4.4 Hz, H-1), 7.3–7.4 (6 H, m), 7.6–7.7 (4 H, m), 9.85 (1 H, s, CHO); ^{13}C NMR (25 MHz, $CDCl_3$): δ 19.1, 26.7, 27.3, 27.6, 60.4, 81.8, 84.0 (C-2 and C-4), 105.2, 116.5, 127.8, 129.8, 132.7, 132.8, 135.6, 204.1.

5-O-tert-Butyldiphenylsilyl-3-C-hydroxymethyl-1,2-O-isopropylidene- β -L-lyxofuranose (**19**). Excess sodium borohydride was added to a solution of **18** (1.10 g) in methanol (15 ml) and ethyl acetate (5 ml). After stirring at room temperature for 15 min, the solution was acidified with Dowex 50 (H^+) resin, filtered, concentrated and co-concentrated several times with methanol. Purification of the product by flash chromatography

(SiO_2 , toluene – ethyl acetate 4:1) gave **19** as an oil (1.04 g, 94%), $[\alpha]_D -17^\circ$ (c 1.2, $CHCl_3$); 1H NMR (100 MHz, $CDCl_3$): δ 1.05 [9 H, s, $C(CH_3)_3$], 1.35 and 1.43 (each 3 H, each s, CH_3), 2.27 (1 H, dd, OH), 3.58 (1 H, s, OH), 3.3–4.2 (5 H, m), 4.47 (1 H, d, J 4.44 Hz, H-2), 5.71 (1 H, d, J 4.4 Hz, H-1), 7.3–7.4 (6 H, m), 7.6–7.7 (4 H, m); ^{13}C NMR (25 MHz, $CDCl_3$): δ 19.1, 26.5, 26.8, 63.4, 66.1, 78.9, 81.4, 82.8, 104.5, 113.8, 127.7, 129.7, 132.8, 133.2, 135.6. HR-MS (m/z): 443.1907 ($M-CH_3$)⁺, Calc. for $C_{24}H_{31}SiO_6$: 443.1888, MS (m/z , intensity in %): 443 (2), 383 (1), 343 (3), 325 (11), 241 (31), 223 (37), 207 (19), 199 (100), 181 (28), 163 (39), 135 (21), 105 (12), 101 (11), 91 (18), 77 (16), 59 (16), 43 (24).

The acetyl derivative (**21**) of compound **19** was prepared by acetylation with acetic anhydride in pyridine. 1H NMR (100 MHz, $CDCl_3$): δ 1.06 [9 H, s, $C(CH_3)_3$], 1.36 and 1.45 (each 3 H, each s, CH_3), 2.09 (3 H, s, OAc), 3.51 (1 H, s, OH), 3.8–4.1 (5 H, m), 4.41 (1 H, d, J 4.0 Hz, H-2), 5.71 (1 H, d, J 4.0 Hz, H-1), 7.3–7.4 (6 H, m), 7.6–7.7 (4 H, m). ^{13}C NMR (25 MHz, $CDCl_3$): δ 19.1, 20.8, 26.8, 27.0, 63.0, 67.1, 77.1, 82.3, 82.6, 104.7, 114.4, 127.7, 129.8, 133.0, 133.1, 135.6, 170.6. HR-MS (m/z): 485.1980 ($M-CH_3$)⁺, Calc. for $C_{26}H_{33}SiO_6$: 485.1995. MS (m/z , intensity in %): 485 (3), 443 (2), 427 (2), 385 (5), 365 (1), 325 (17), 307 (7), 241 (45), 235 (25), 199 (57), 181 (15), 163 (27), 135 (17), 105 (11), 101 (23), 91 (12), 77 (15), 59 (19), 43 (100).

3-C-Hydroxymethyl-D-ribose (**7**), 3-C-hydroxymethyl-D-xylose (**13**), and 3-C-hydroxymethyl-L-lyxose (**20**). Compounds **6**, **12** and **19** were treated with aqueous trifluoroacetic acid (0.5 M) at 100°C for 13 h. The solutions were concentrated and then co-concentrated with water to give the monosaccharides **7**, **13** and **20** as anomeric mixtures, contaminated by presumed 1,5-anhydro derivatives. Each of these sugars was analysed by 1H (400 MHz) and ^{13}C (25 MHz) NMR and by GLC and MS on the derived alditol pentaacetates. Compound **20** and the natural sugar gave superimposable NMR spectra. 1H NMR (400 MHz, D_2O , 60°C, characteristic, major signals): δ 3.48 (1 H, d, $J_{1,2}$ 7.8 Hz H-2), 3.65, 3.74, 3.78, 3.80, 3.83, 4.00, 4.03, 4.80 (1 H, d, $J_{1,2}$ 7.8 Hz, H-1). After purification on a reversed-phase HPLC-ODS-column using methanol-water 85:15, **20** had $[\alpha]_D +18.7^\circ$ (c 1.4, H_2O) as compared to $[\alpha]_D +16^\circ$ for the natural sugar. Furthermore the GLC retention times for the de-

rived alditol acetates were identical and distinct from those of the corresponding isomeric compounds. The GLC retention times (min) on an OV-1701 fused silica capillary column fitted in a Hewlett-Packard 5880 instrument, using a carrier gas flow of 0.5 ml/min and a temperature gradient of 10°C/min from 150 to 250°C were 16.64 for 3-*C*-hydroxymethyl-*D*-xylitol pentaacetate, 16.80 for 3-*C*-hydroxymethyl-*D*-ribitol pentaacetate and 16.90 for 3-*C*-hydroxymethyl-*L*-lyxitol pentaacetate.

Acknowledgements. We are indebted to Professor Bengt Lindberg for his interest, to the Swedish Natural Science Research Council and the National Swedish Board for Technical Development for financial support.

References

1. Schramek, Š., Radziejewska-Lebrecht, J. and Mayer, H. *Eur. J. Biochem.* **148** (1985) 455.
2. Blackstock, W. P., Kuenzle, C. C. and Eugster, C. H. *Helv. Chim. Acta* **57** (1974) 1003.
3. Paulsen, H., Sinnwell, V. and Stadler, P. *Chem. Ber.* **105** (1972) 1978.
4. Albrecht, H. P. and Moffatt, J. G. *Tetrahedron Lett.* (1970) 1063.
5. Garegg, P. J. and Samuelsson, B. *Carbohydr. Res.* **67** (1978) 267.
6. Corey, E. J. and Erickson, B. W. *J. Org. Chem.* **36** (1971) 3553.
7. Ho, T.-L., Ho, H. C. and Wong, C. M. *J. Chem. Soc. Chem. Commun.* (1972) 791.
8. Garegg, P. J., Konradsson, P., Kvarnström, I., Norberg, T. and Wigilius, B. *Acta Chem. Scand. B* **39** (1985) 569.
9. Still, W. C., Kahn, M. and Mitra, A. *J. Org. Chem.* **43** (1978) 2923.

Received March 12, 1985.