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Lipase-mediated partial resolution of 1,2-diol and 2-alkanol derivatives: towards chiral building-blocks for pheromone synthesis

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Abstract

1,2-Propanediol **5**, 1-chloro-2-propanol **8** and its related 2-*O*-acetate **9** were partially resolved by chemoenzymatic acetylation and deacetylation, in the presence of *Pseudomonas fluorescens* lipase (Amano P.; PFL), to (*R*)-(–)-1-acetoxy-2-propanol **6**, (*R*)-(+)-2-acetoxy-1-chloropropane **9** and (*R*)-(–)-1-chloro-2-propanol **8**, respectively. On the other hand, treatment of (2*RS*)-**2** with vinyl acetate in ether and Chirazyme® L-2 gave 2-*O*-acetyl-1,3,4-trideoxy-5,6:7,8-di-*O*-isopropylidene-β-D-*manno*-non-5-ulo-5,9-pyranose **1** and 1,3,4-trideoxy-5,6:7,8-di-*O*-isopropylidene-β-D-*gluco*-non-5-ulo-5,9-pyranose **11**, respectively. Compound **10** was subsequently deacylated to **12**. Both alcohols **11** and **12** were treated with Me_2CO/H^+ to cause their rearrangement to (2*S*,5*R*,8*R*,9*R*,10*S*)-10-hydroxy-8,9-isopropylidenedioxy-2-methyl-1,6-dioxaspiro[4.5]decane **3** and its (2*R*)-epimer **4**, which closely matched the skeleton of the odour bouquet minor components of *Paravespula vulgaris* (L.).

1. Introduction

The *E*/*Z* mixture of 2-methyl-1,6-dioxaspiro[4.5]decane was identified by Francke et al.[1] as minor components of the odour bouquet of workers of the common wasp *Paravespula vulgaris* (L.), but no information about the absolute configuration of such compounds was given. In a previous paper,[2] the preparation from the 1,3,4-trideoxy-non-5-ulose derivative **2** of the epimeric 1,6-dioxaspiro compounds **3** and **4**, key intermediates for the synthesis of all possible stereoisomers of the pheromone minor components (see Scheme 1), has been reported by our group. Nevertheless, the synthesis was poor in stereoselectivity during the formation of a stereogenic centre at C-2 in **2**, it being necessary to use tedious chromatographical separations and recrystallizations for the resolution of **3** and **4**. Thus, the need to explore new synthetic methodologies leading to both epimers of **2** and allow their preparation in a highly stereoselective manner was apparent. Scheme 1 clearly shows that there are two means of achieving the above synthesis:

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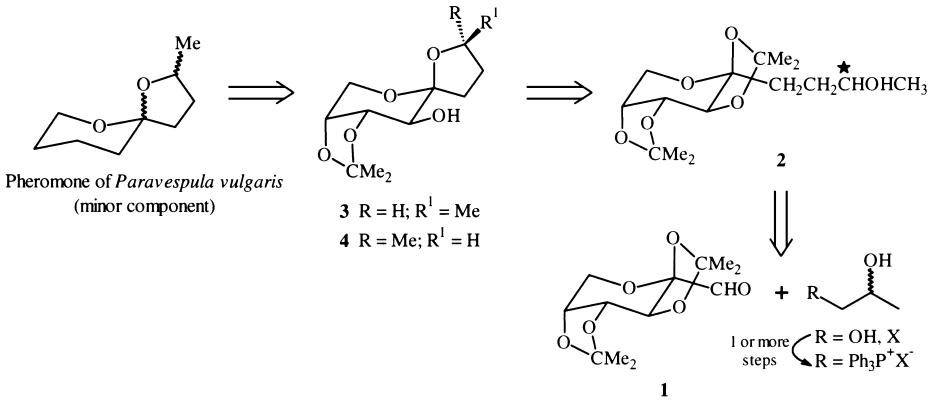
known Wittig methodology, but using the suitably protected aldulose **1**, derived from D-fructose, and the appropriate chiral phosphonium salts, readily available in one or more steps from 1,2-propanediol derivatives, or the resolution of both epimers of **2** prior to their transformation into the dioxaspiro compounds **3** and **4**.



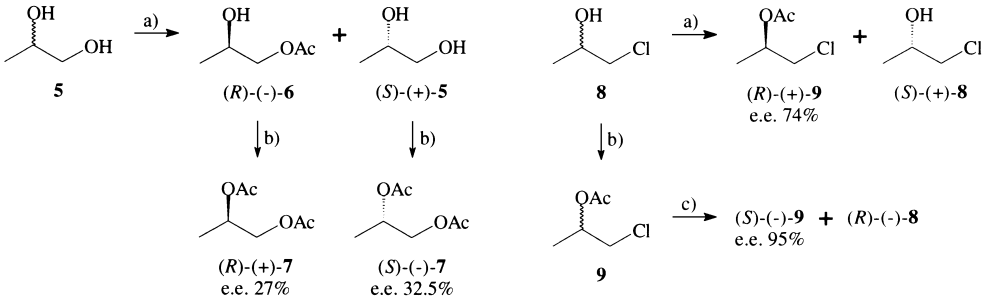
Scheme 1.

Both strategies have been applied using a chemoenzymatic approach and the results are reported herein.

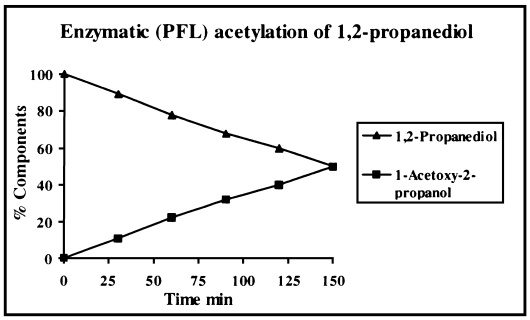
2. Results and discussion

Since 1,2-propanediol **5** is a cheap commercial product, it was used as starting material. Thus, treatment of **5** with vinyl acetate in CH_2Cl_2, in the presence of lipase from *Pseudomonas fluorescens* (Amano P.; PFL) at room temperature (see Scheme 2), caused its partial resolution to afford (*R*)-(–)-1-acetoxy-2-propanol **6**, isolated in 50.3% yield with 27% *ee*, determined after its transformation into (*R*)-(+)-1,2-diacetoxypropane **7**[3] by GLC (*E*) on a β-DEX™ column, together with (*S*)-(+)-**5**[4] in a 48% yield with a 32.5 *ee*, determined through its 1,2-diacetate (*S*)-(–)-**7** (see Fig. 1). The enantiomer of **6** has previously been synthesized by chemoenzymatic reduction with baker's yeast of 1-acetoxipropanone.[5] Transformation of (*R*)-(–)-**6** and (*S*)-(+)-**5** into their corresponding mentioned diacetoxy derivatives was justified as a consequence of the higher resolution found in the GLC analysis as peracetylated compounds on the β-DEX™ column. Due to the low *ee* found in this resolution process, the chemoenzymatic hydrolysis of (±)-**7** with PFL was investigated, but unfortunately the reaction proceeded without regio- or enantioselectivity and a new strategy, consisting of the use of (±)-1-chloro-2-propanol **8** as the substrate, was envisaged.

Since pure **8** is not commercially available, it was straightforwardly prepared in an 85% yield from chloroacetone by reduction with sodium borohydride. Treatment of **8** as mentioned above for **5** (see Scheme 2) for 3 days produced the corresponding (*R*)-(+)-2-acetoxy-1-chloropropane **9** (15% yield) with 74% *ee*, together with (*S*)-(+)-**8**[6] (19% yield) with 43% *ee*, both isolated after chromatography. The *ee*s for (*R*)-(+)-**9** and (*S*)-(+)-**8** were established by GLC (*D*) as above, after acetylation of the latter compound (see Fig. 2). A systematic study of the enzymatic trans-esterification of **8** with vinyl butyrate and Novozym® made by Norin et al.[7] afforded similar results, but neither the isolation nor practical yield of the products was given.



Scheme 2. (a) *Pseudomonas fluorescens* lipase (PFL)/vinyl acetate/Cl_2CH_2/rt; (b) Ac_2O/Py; (c) PFL/buffer (pH 7)/rt



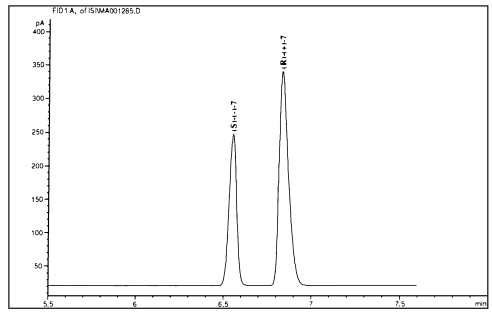
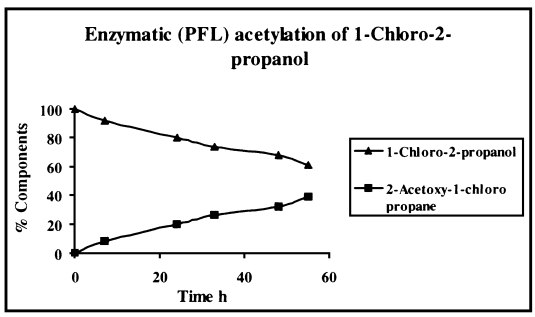
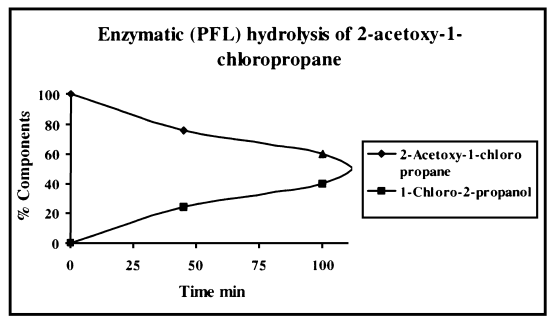
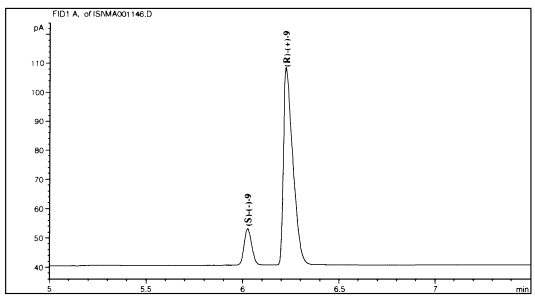


Figure 1. Kinetics for enzymatically (PFL) catalyzed monoacetylation of **5** and GLC analysis (*ee*) on β-DEX™ column data of acetate of (*R*)-(–)-**6**







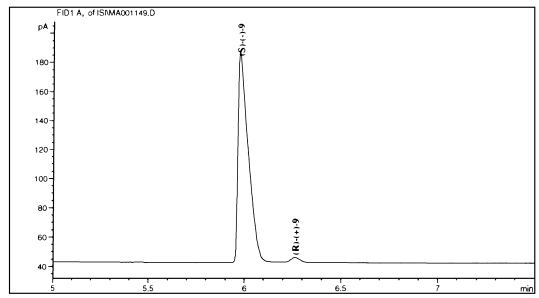


Figure 2. Kinetics for enzymatically (PFL) catalyzed acetylation of **8** and hydrolysis of **9** and GLC analysis (*ee*) on β-DEX™ column data

Due to the low rate found in the acetylation of **8**, the chemoenzymatic hydrolysis (PFL) of (±)-**9** was explored. Monitoring of the reaction by GLC (*A*) showed that after 110 min the 50% conversion of (±)-**9** was reached. Work-up of the reaction mixture allowed the isolation of (*S*)-(–)-**9** (7% yield) with 95% *ee* as well as (*R*)-(–)-**8** (15% yield) with 36% *ee*, after its acetylation (see Fig. 2). The low practical yield obtained in both processes made it necessary to plan a new strategy.

Since not entirely satisfactory results were achieved in the above resolutions, we investigated the diastereomeric resolution of (2*R*,*S*)-**2** through its partial esterification using an immobilized enzyme as catalyst (Fig. 3). Thus, reaction of (2*R*,*S*)-**2** in ether with vinyl acetate in the presence of Chirazyme® L-2 gave the corresponding (2*R*)-2-*O*-acetyl derivatives of **2** (**10**) and (2*S*)-**2** (**11**), both in the pure state. The configurations for **10** and **11** were established after previous deacetylation of **10** to (2*R*)-**2** (**12**), followed by treatment of both alcohols **11** and **12** with Me_2CO/H^+ that caused an internal glycosidation to afford the corresponding (2*S*,5*R*,8*R*,9*R*,10*S*)- **3** and (2*R*,5*R*,8*R*,9*R*,10*S*)-10-hydroxy-8,9-isopropylidenedioxy-2-methyl-1,6-dioxaspiro[4.5]decane **4**, respectively (Scheme 3). The physical and spectroscopic data for **10**, **11** and **12**, not previously reported, as well as the ^{13}C NMR signal assignments (^{13}C–^{1}H heteronuclear shift correlation), are included herein.

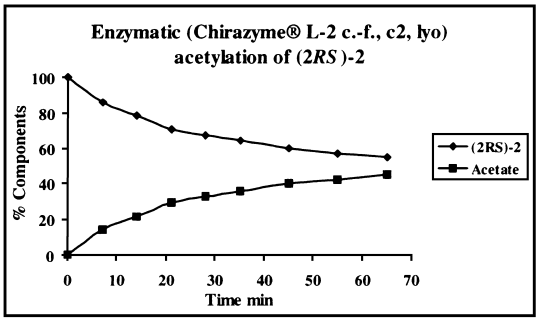
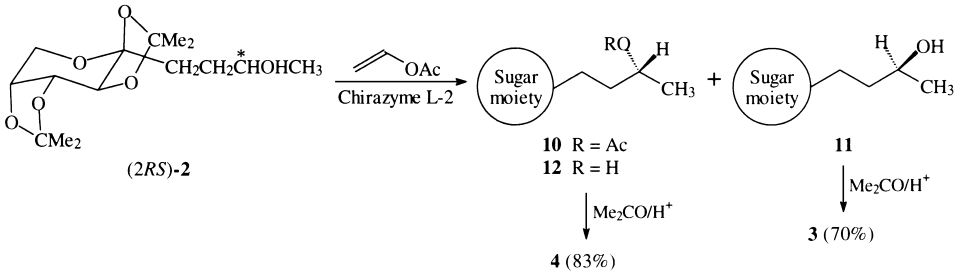


Figure 3. Kinetics for enzymatically (Chirazyme® L-2 c.-f., c2, lyo) catalyzed partial acetylation of (2*RS*)-**2**



Scheme 3.

3. Conclusions

The results described above indicate that the use of the chiral pool (carbohydrates) combined with chiral catalysts (enzymes), both from natural sources, could be an excellent methodology in order to overcome many problems in the stereoselective synthesis of complex biologically active natural products.

4. Experimental

4.1. General

Melting points were determined with a Gallenkamp apparatus and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under reduced pressure. The ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-300 and ARX-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si). IR spectra were recorded with a Perkin–Elmer 782 instrument and mass spectra with Hewlett–Packard HP-5988-A and Fisons mod. Platform II and VG Autospec-Q mass spectrometers. Optical rotations were measured for solutions in $CHCl_3$ (1 dm tube) with a Jasco DIP-370 polarimeter. GLC was performed on a Hewlett–Packard 6890 gas chromatograph equipped with split/splitless injector, a flame-ionization detector and a capillary HP-5 column (30 m×0.25 mm i.d.×0.25 μm film thickness) at: (*A*) 70°C; (*B*) 80°C; (*C*) 3 min at 180°C, program to 250°C, 10°C/min; or a β-DEX™ 325 (Supelco™) capillary column (30 m×0.25 mm i.d.×0.25 μm film thickness) at: (*D*) 90°C: (*E*) 110°C; (*F*) 2 min at 50°C, program to 100°C, 2°C/min. The He flow rate was 1.1 mL/min, the injection port and the zone-detector temperatures were 275°C. TLC was performed on precoated silica gel 60 F_{254} aluminium sheets and detection by charring with H_2SO_4. Column chromatography was performed on silica gel (Merck, 7734). The non-crystalline compounds were shown to be homogeneous by chromatography and characterized by NMR and HRMS.

4.2. Partial enzymatic (PFL) acetylation of 1,2-propanediol **5**

To a gently stirred solution of **5** (2.76 g, 36.4 mmol) in dry CH_2Cl_2 (75 mL) and vinyl acetate (7.5 mL, 81 mmol) was added PFL (Amano P., 1.82 g), and the mixture was kept at room temperature for 2.5 h. The reaction was monitored by GLC analysis (*B*). The reaction was quenched by filtering off the enzyme that was thoroughly washed with dichloromethane. The combined filtrate and washings were concentrated to a residue that was chromatographed (ether:hexane = 1:1→ether→ether:methanol = 10:1) to afford first (*R*)-(–)-1-acetoxy-2-propanol (**6**, 2.16 g, 50.3%), T_R 3.99 min (*B*), $[\alpha]_D^{27}$ –6, $[\alpha]_{405}^{27}$ –14 (*c* 1.4) [lit.[5] $[\alpha]_D$ +20 (*c* 1.65, chloroform) for (*S*)-(+)-**6**]. The second fraction was (*S*)-(+)-**5** (1.34 g, 48%), T_R 2.58 min (*B*), $[\alpha]_D^{27}$ +6, $[\alpha]_{405}^{27}$ +14 (*c* 7.57, water) [lit.[4a] $[\alpha]_D$ +20.1 (*c* 7.5, water); lit.[4b] $[\alpha]_D^{23}$ +21.9 (*c* 0.74, water)].

Conventional acetylation of (*R*)-(–)-**6** (137 mg, 1.16 mmol) in dry pyridine (1 mL) and acetic anhydride (0.5 mL) gave, after work-up and column chromatography (ether:hexane = 1:2), (*R*)-(+)-1,2-diacetoxypropane (**7**, 143 mg, 77%), T_R 6.83 min (*E*), *ee* 27% (*E* = 2.2) (see Fig. 1), $[\alpha]_{405}^{26}$ +3 (*c* 1.6) [lit.[3] $[\alpha]_D^{28}$ +2 (*c* 6.5, chloroform)].

Conventional acetylation of (*S*)-(+)-**5** (130 mg, 1.71 mmol) in dry pyridine (1 mL) and acetic anhydride (0.5 mL), as above, gave (*S*)-(–)-**7** (164 mg, 60%), T_R 6.56 min (*E*), *ee* 32.5% (*E* = 2.6) (see Fig. 1), $[\alpha]_{405}^{25}$ –3 (*c* 1.9).

4.3. Partial enzymatic (PFL) acetylation of 1-chloro-2-propanol **8**

Compound **8** (1.65 g, 17.5 mmol) in CH_2Cl_2 (30 mL) was treated with vinyl acetate (6.5 mL, 70 mmol) and PFL (Amano P., 900 mg) for 3 days, as above. The reaction was monitored by GLC analysis (*A*). Work-up of the reaction mixture and column chromatograhy (ether:hexane = 1:10→ether) afforded first (*R*)-(+)-2-acetoxy-1-chloropropane (**9**, 360 mg, 15%), T_R 4.60 min (*A*),

$[\alpha]_D^{27}$ +9.3, $[\alpha]_{405}^{26}$ +22 (*c* 1.9), T_R 6.22 min (*D*), *ee* 74% (*E* = 14.7) (see Fig. 2). The second fraction was (*S*)-(+)-**8** (315 mg, 19%), T_R 2.42 min (*A*), $[\alpha]_D^{26}$ +7, $[\alpha]_{405}^{26}$ +18 (*c* 1.5) [lit.[6a] $[\alpha]_D$ +22.1 (*c* 1.06, chloroform); lit.[6b] $[\alpha]_D$ +15.5 (*c* 3.5, chloroform)].

Conventional acetylation of (*S*)-(+)-**8** (120 mg, 1.27 mmol) in dry CH_2Cl_2 (3 mL) with triethylamine (0.2 mL) and acetic anhydride (0.2 mL) gave, after work-up and column chromatography, (*S*)-(–)-(**9**) (160 mg, 92%), T_R 6.03 min (*D*), *ee* 43% (*E* = 3.8) (see Fig. 2).

4.4. Partial enzymatic (PFL) hydrolysis of **9**

To a gently stirred suspension of **9** (1.45 g, 10.6 mmol) in 100 mL of a buffered (pH 7) aqueous 0.5 M phosphate solution (KH_2PO_4) was added PFL (500 mg) and the mixture was kept at room temperature for 2 h. The reaction was monitored by GLC analysis (*A*). The enzyme was filtered off and the filtrate saturated with sodium chloride and extracted with ethyl acetate. The combined extracts were concentrated to give a residue that was constituted [GLC (*A*)] by **8** (60%) and **9** (40%). Column chromatography (ether:hexane = 1:10→ether) of the residue gave first (*S*)-(–)-**9** (100 mg, 7%); $[\alpha]_D^{26}$ –11.3, $[\alpha]_{405}^{27}$ –27.5 (*c* 1.5), T_R 5.98 min (*D*), *ee* 95% (*E* = 146) (see Fig. 2). The second fraction was (*R*)-(–)-**8** (150 mg, 15%); $[\alpha]_D^{25}$ –5.5, $[\alpha]_{405}^{25}$ –14.5 (*c* 1.6). Conventional acetylation of (*R*)-(–)-**8** as above afforded (*R*)-(+)-**9**, *ee* 36% (*E* = 3) (see Fig. 2).

4.5. Partial enzymatic (Chirazyme® L-2) acetylation of 1,3,4-trideoxy-5,6:7,8-di-O-isopropylidene-β-D-manno- and gluco-non-5-ulo-5,9-pyranose **2**

Compound **2** (1.08 g, 3.5 mmol) in ether (25 mL) was treated with vinyl acetate (2.7 mL, 29.3 mmol) and Chirazyme® L-2 c.-f., c2, lyo (Roche Co., 270 mg) for 80 min as above. The reaction was monitored by GLC analysis (*C*). Work-up of the reaction mixture and column chromatography (ether:hexane = 1:2→ether) gave first 2-*O*-acetyl-1,3,4-trideoxy-5,6:7,8-di-*O*-isopropylidene-β-D-*manno*-non-5-ulo-5,9-pyranose (**10**, 580 mg, 47.4%), T_R 7.60 min (*C*), $[\alpha]_D^{27}$ –6.7 (*c* 1); ν_{max}^{film} 1740 (C=O, acetate), 1383 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.87 (m, 1H, H-2), 4.54 (dd, 1H, $J_{6,7} = 2.5$, $J_{7,8} = 8$ Hz, H-7), 4.20 (dd, 1H, H-8), 4.07 (d, 1H, H-6), 3.82 (dd, 1 H, $J_{8,9ax} = 1.8$, $J_{9ax,9eq} = 13$ Hz, H-9ax), 3.69 (d, 1H, H-9eq), 1.99 (s, 3H, Ac), 1.89–1.72 (m, 4H, H-3,3′,4,4′), 1.49, 1.46 and 1.32 (3 s, 12H, 2 CMe_2) and 1.20 (d, 3H, $J_{1,2} = 6.2$ Hz, H-1,1,1); ^{13}C, δ 170.86 (Me*C*O), 108.96 and 107.53 (2 *C*Me_2), 103.83 (C-5), 73.87 (C-6), 71.10 (C-2), 70.83 (C-8), 70.60 (C-7), 60.96 (C-9), 36.88 (C-4), 29.64 (C-3), 26.45, 25.83, 25.13 and 24.13 (2 C*Me*$_2$), 21.40 (*Me*CO) and 20.07 (C-1). Mass spectrum (LSIMS): *m*/*z* 367.17458 (M^++Na). For $C_{17}H_{28}O_7Na$ 367.17327 (deviation –3.6 ppm).

The second fraction was syrupy 1,3,4-trideoxy-5,6:7,8-di-*O*-isopropylidene-β-D-*gluco*-non-5-ulo-5,9-pyranose (**11**, 550 mg, 51%); $[\alpha]_D^{24}$ –4.6 (*c* 1); ν_{max}^{film} 3465 (OH), 1381, 1378 and 1373 cm^{-1} (CMe_2). NMR data: ^1H, δ 4.57 (dd, 1H, $J_{6,7} = 2.5$, $J_{7,8} = 8$ Hz, H-7), 4.22 (bdd, 1H, H-8), 4.11 (d, 1H, H-6), 3.86 (dd, 1H, $J_{8,9ax} = 1.9$, $J_{9ax,9eq} = 13$ Hz, H-9ax), 3.85 (m, 1H, H-2), 3.73 (bd, 1H, H-9eq), 2.02–1.98 and 1.87–1.65 (2 m, 4H, H-3,3′,4,4′), 1.96 (bs, 1H, OH-2), 1.52, 1.49, 1.36 and 1.35 (4 s, 12H, 2 CMe_2) and 1.20 (d, 3H, $J_{1,2} = 6.2$ Hz, H-1,1,1); ^{13}C, δ 109.02 and 107.65 (2 *C*Me_2), 104.04 (C-5), 74.04 (C-6), 70.82 (C-8), 70.63 (C-7), 67.86 (C-2), 61.05 (C-9), 37.17 (C-4), 32.74 (C-3), 26.45, 25.88, 25.13 and 24.16 (2 C*Me*$_2$) and 23.50 (C-1). Mass spectrum (LSIMS): *m*/*z* 325.16294 (M^++Na). For $C_{15}H_{26}O_6Na$ 325.16271 (deviation –0.7 ppm).

4.6. (2S,5R,8R,9R,10S)-10-Hydroxy-8,9-isopropylidenedioxy-2-methyl-1,6-dioxaspiro[4.5]decane **3**

To a stirred solution of **11** (550 mg, 1.82 mmol) in a 2 M solution of sulfuric acid in dry acetone (5 mL) was added anhydrous copper sulfate (2 g) and the mixture was kept at room temperature for 3 h. GLC (*C*) then revealed the presence of **3**. The reaction mixture was neutralized (NH_3), filtered and concentrated. Column chromatography (ether:hexane = 1:1.5) of the residue gave crystalline **3** (310 mg, 70%) which had the same physical spectroscopic data as those previously reported.[2] ^{13}C NMR data: δ 109.16 (*C*Me$_2$), 107.43 (C-5), 78.09 (C-9), 75.91 (C-2), 73.86 (C-8), 72.15 (C-10), 59.73 (C-7), 33.99 (C-4), 31.62 (C-3), 28.19 and 26.19 (C*Me*$_2$) and 20.81 (Me-2).

4.7. 1,3,4-Trideoxy-5,6:7,8-di-O-isopropylidene-β-D-manno-non-5-ulo-5,9-pyranose **12**

To a solution of **10** (580 mg, 1.69 mmol) in dry methanol (20 mL) 0.5 M sodium methoxide (0.2 mL) was added and the mixture left at room temperature for 2 h. TLC (ether:hexane = 3:2) then revealed a slower-running compound. The mixture was neutralized (acetic acid) and concentrated. The residue was partitioned in ether–water and the organic phase was separated and the aqueous extracted with ether. Concentration of the combined extracts gave a residue that was chromatographed (ether:hexane = 1:1→ether) to give **12** (480 mg, 93%) as a colourless oil; $[\alpha]_D^{24}$ –19 (*c* 1); ν_{max}^{film} 3465 (OH), 1382 and 1373 cm^{-1} (CMe$_2$). NMR data: ^{1}H, δ 4.54 (dd, 1H, $J_{6,7}$ = 2.5, $J_{7,8}$ = 8 Hz, H-7), 4.20 (dd, 1H, H-8), 4.07 (d, 1H, H-6), 3.82 (dd, 1H, $J_{8,9ax}$ = 2, $J_{9ax,9eq}$ = 13 Hz, H-9ax), 3.80 (m, 1H, H-2), 3.70 (d, 1H, H-9eq), 2.03 (bs, 1H, OH-2), 1.99–1.91 and 1.84–1.62 (2 m, 4H, H-3,3′,4,4′), 1.49, 1.46, 1.33 and 1.32 (4 s, 12H, 2 CMe$_2$) and 1.17 (d, 3H, $J_{1,2}$ = 6.2 Hz, H-1,1,1); ^{13}C, δ 108.97 and 107.66 (2 *C*Me$_2$), 103.95 (C-5), 74.18 (C-6), 70.82 (C-8), 70.61 (C-7), 68.07 (C-2), 60.99 (C-9), 37.42 (C-4), 32.64 (C-3), 26.43, 25.89, 25.11 and 24.12 (2 C*Me*$_2$) and 23.53 (C-1). Mass spectrum (LSIMS): *m*/*z* 325.16294 (M$^+$+Na). For $C_{15}H_{26}O_6Na$ 325.16271 (deviation –0.7 ppm).

4.8. (2R,5R,8R,9R,10S)-10-Hydroxy-8,9-isopropylidenedioxy-2-methyl-1,6-dioxaspiro[4.5]decane **4**

Treatment of compound **12** (480 mg, 1.59 mmol) with a 2 M solution of sulfuric acid in dry acetone (5 mL) and anhydrous copper sulfate (2 g) for 3 h, as above, gave, after work-up and column chromatography (ether:hexane = 1:1.5), crystalline **4** (284 mg, 83%) which had the same physical spectroscopic data as those previously reported.[2] ^{13}C NMR data: δ 109.22 (*C*Me$_2$), 107.38 (C-5), 79.14 (C-2), 78.27 (C-9), 74.00 (C-8), 72.20 (C-10), 59.37 (C-7), 34.40 (C-4), 31.37 (C-3), 28.31 and 26.29 (C*Me*$_2$) and 22.67 (Me-2).

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References

1. Francke, W.; Hindorf, G.; Reith, W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 862.
2. Izquierdo, I.; Plaza, M.-T.; Richardson, A. C. *J. Chem. Ecol.* **1993**, *19*, 1265–1283.

3. Cope, A. C.; Bly, R. K.; Burrows, E. P.; Ceder, O. J.; Ciganek, E.; Gillis, B. T.; Porter, R. F.; Johnson, H. E. *J. Am. Chem. Soc.* **1962**, *84*, 2170–2178.
4. (a) Baer, E.; Fischer, H. O. L. *J. Am. Chem. Soc.* **1948**, *70*, 609–610; (b) Cotterill, A.-S.; Hill, M.; Milanovic, N.-M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1215–1222.
5. Ishihara, K.; Sakai, T.; Tsuboi, S.; Utaka, M. *Tetrahedron Lett.* **1994**, *35*, 4569–4570.
6. (a) Nájera, C.; Yus, M.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 289–300; (b) Sakai, T.; Wada, K.; Murakami, T.; Kohra, K.; Imajo, N.; Ooga, Y.; Tsuboi, S.; Takeda, A.; Utaka, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 631–638.
7. Rotticci, D.; Orrenius, C.; Hult, K.; Norin, T. *Tetrahedron: Asymmetry* **1997**, *8*, 359–362.