Synthesis of Medium and Large Rings, XLVI[◇]

# Synthesis and Reactions of Optically Active Bridged Deoxyfuranose Derivatives

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Received December 12, 1997

**Keywords:** Bridged furanose derivatives / Resolution / Dimerization

Treatment of the bridged methyl furanosides **1**, **3** and **5** with dilute acid furnishes the corresponding deoxyfuranose derivatives **2**, **4** and **6**. The *trans*-substitution pattern of the tetrahydrofuran ring was established by X-ray structural analysis of **2** and by comparison of the $^1$H-NMR spectra. A new resolution procedure for *rac*-**3** via the dicamphanoates (+)-**7** and (−)-**7** is reported. The hemiacetals (+)-**6** and (−)-**6** dimerize readily under elimination of water in chloroform to give the bridged disaccharides (+)-**8** and (−)-**8**, respectively.

The synthesis of unnatural or modified carbohydrate derivatives has gained great attention for various reasons[1]. Many contributions in this field are also concerned with furanosides[2]. In previous publications[3][4] of this series we described the synthesis of optically active bridged methyl furanosides **1** and **3** and the assignment of their absolute configurations. We now report on the stereoselective hydrolysis of the furanosides to the corresponding hemiacetals and on their conversion to compounds with a disaccharide structure.

First experiments with racemic compounds showed that the hydrolysis could be performed by heating the acetals with 0.1 N $H_2SO_4$ in tetrahydrofuran. The 5-methoxy ester *rac*-**1**[3][4] furnished the 5-hydroxy derivative *rac*-**2** in 69% yield as the only isolated product. In this case an additional treatment with diazomethane was necessary to convert the free acid, formed by partial hydrolysis, to the methyl ester **2**. The $^1$H-NMR spectrum of **2** showed no $^3J$ coupling between 4-H and 5-H, thus indicating the same all-*trans* configuration in the tetrahydrofuran ring of **1**[3][4] and **2** as well.

This assignment was finally established by an X-ray structural analysis of suitable crystals of **2** by starting with a sample of **1** that was enriched in (+)-**1** obtained by our reported resolution procedure[4]. Figure 1 shows that the hydroxy group at C-5 is located on the site opposite to the heptano bridge.

It should be noted that we have no indications so far for equilibria mixtures of anomers in the case of **2** and of the related compounds **4** and **6** described later in this work. Apparently, the 5-hydroxy group occupies the sterically less

Scheme 1

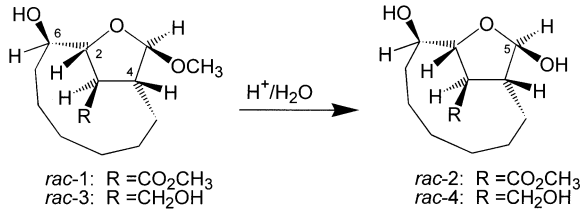
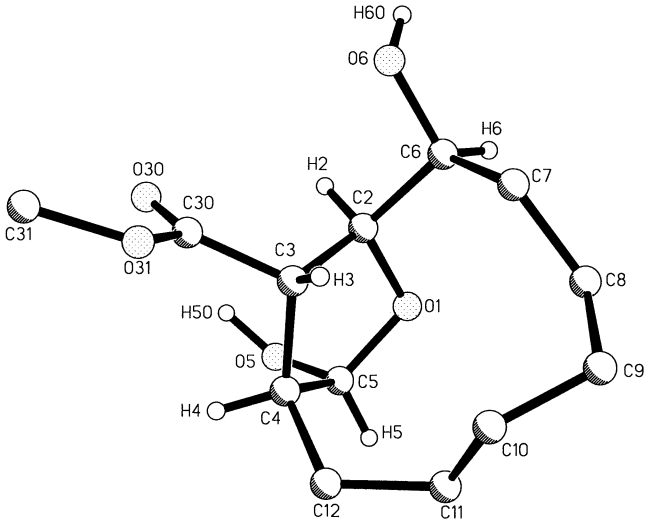



Figure 1. A molecule of **2** in the crystal[11]




[◇] Part XLV: W. Tochtermann, T. Panitzsch, C. Wolff, E.-M. Peters, K. Peters, H. G. von Schnering, submitted to *Eur. J. Org. Chem.*

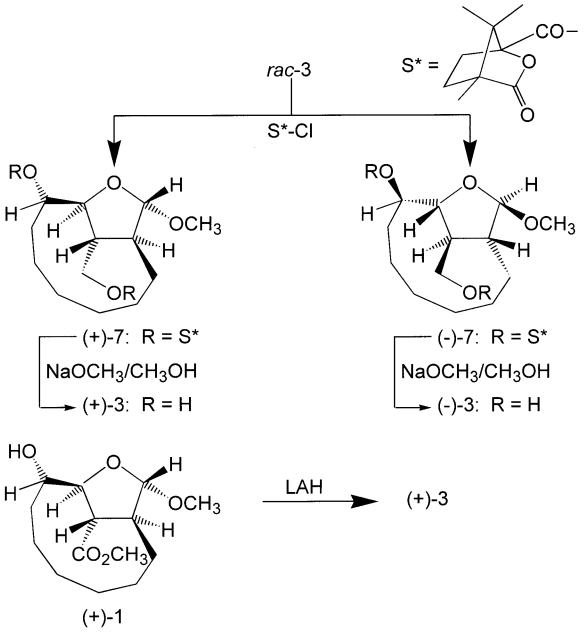
  1434−193X/98/0404−0683 $ 17.50+.50/0 

hindered position in this medium-sized ring system (see Figure 1).

Further experiments were performed using the 5-methoxy compound *rac*-**3** as starting material. *rac*-**3** is readily available by lithium aluminium hydride reduction of the corresponding 6-oxo-3-carboxylic acid[3][4] (see Experimental Section). The hydrolysis of *rac*-**3** furnished the unnatural furanose *rac*-**4** in high yield. According to its $^1$H-NMR spectrum **4** has the same stereochemistry at C-5 as **2**.

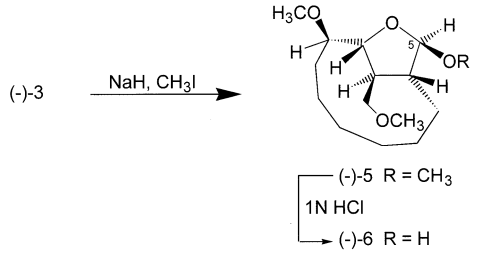
*rac*-**3** could be resolved into its enantiomers (+)-**3** and (−)-**3** by column chromatography of the diastereomeric dicamphanoates (+)-**7** (46% yield) and (−)-**7** (48% yield) and subsequent removal of the chiral auxiliary with sodium methoxide in methanol. (+)-**3** was also obtained by lithium aluminium hydride reduction of (2*S*,3*S*,4*S*,5*S*,6*S*)-(+)-**1**[4] and is consequently the (2*S*,3*R*,4*S*,5*S*,6*S*)-(+) enantiomer.

Scheme 2



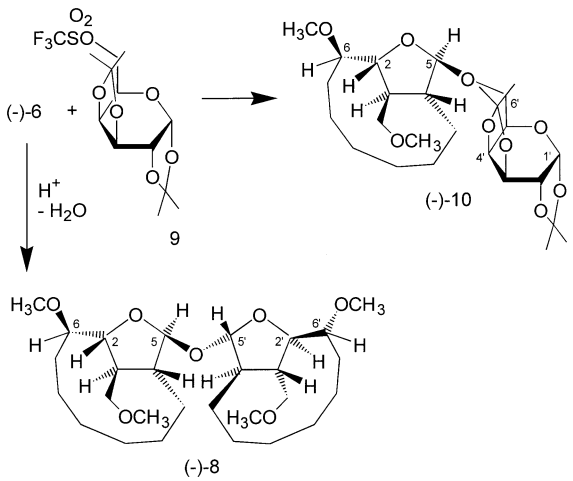

With the aim to prepare compounds having an unnatural disaccharide structure *rac*-**3**, (+)-**3** and (−)-**3** were methylated with sodium hydride/methyl iodide to give *rac*-**5**, (+)-**5** and (−)-**5**, respectively. Treatment of these permethylated compounds with 1 N HCl at room temp. led to the furanose derivatives *rac*-**6**, (+)-**6** and (−)-**6** in high yield (see Experimental Section).

Scheme 3




The $^1$H-NMR spectrum of **6** showed no $^3J$ coupling between 4-H and 5-H indicating the same stereochemistry as in **2**. (+)-**6** and (−)-**6** were isolated as colourless oils and could be characterized by their NMR and mass spectra. However, these hemiacetals showed a great tendency to dimerize under elimination of water. When (+)-**6** or (−)-**6** were dissolved in commercial, not purified chloroform the crystalline dimers (+)-**8** and (−)-**8** were isolated as the only products after evaporation of the solvent. The symmetric arrangement of the ring systems is derived from the $^1$H- and $^{13}$C-NMR spectra which show only half of the number of signals to be expected for a dimer. The formation of **8** can be explained by protonation of **6** with traces of acid present in the solvent, formation of the corresponding oxonium ion or the enol ether and subsequent addition of a second molecule of **6** from the sterically least hindered direction. In other reactions of our compounds we also observed the easy formation of the corresponding glycal[5].

Scheme 4




It is noteworthy that in going from (−)-**5** ($[\alpha]_D^{26}$ = −67.3, $CHCl_3$) and (−)-**6** ($[\alpha]_D^{22}$ = -36.8, $CHCl_3$) to (−)-**8** ($[\alpha]_D^{23}$ = −134.5, $CH_2Cl_2$) a significant increase of the specific rotation is observed. 2,2′-Tetrahydrofuran derivatives linked by an oxygen are described in the literature[6]. Most of them are prepared from the corresponding hemiacetals. The direct connection of anomeric centers that we observed in **8** is well known from the disaccharide trehalose[7]. Recently, Mulzer et al.[8] synthesized a bis(deoxyfuranoside) of this structural type by domino transformations via cationic intermediates.

In a preliminary experiment we could finally show that the monomers **6** can also be used for the synthesis of disaccharides with different monomeric units. The reaction of deprotonated (−)-**6** with diisopropylidene-D-galactose triflate[9] furnished (−)-**10**, however only in 16% yield[10].

The optically active furanosides **3** which are now available in desirable amounts can also be used for the synthesis of nucleosides. These results will be reported in a subsequent paper.

Financial support by the *Stiftung Volkswagenwerk* and the *Fonds der Chemischen Industrie* is acknowledged with gratitude. We are indebted to Dr. *C. Wolff*, Universität Kiel, for his kind assistance in NMR-assignment problems.

## Experimental Section

*General:* IR: Perkin-Elmer 1600 FTIR. − $^1$H NMR: TMS int.; Bruker AC 200 P, AM 300. − $^{13}$C NMR: TMS int.; Bruker AC 200 P, AM 300. − MS: Finnigan-MAT 8230; direct inlet (EI: 70 eV; CI: isobutane). − CC: Macherey-Nagel Silica gel MN 60 (0.04−0.063 mm). − TLC: Macherey-Nagel SIL G/UV$_{254}$. − Melting points: uncorrected; Büchi 510 . − Optical rotations: Perkin-Elmer polarimeter 241. − All reactions were carried out in purified and, if necessary, dried solvents. Reactions with hydrides were performed under nitrogen.

**A) *Syntheses with Racemic Compounds***

1. *Methyl (±)-2,3,4,5-Tetrahydro-5,6-dihydroxy-2,4-heptanofuran-3-carboxylate* (*rac*-**2**): A solution of *rac*-**1**[3][4] (511 mg, 1.88 mmol) in THF (20 ml) and 0.1 N $H_2SO_4$ (20 ml) was refluxed for 5 h. After cooling to room temp., the solution was extracted with $CH_2Cl_2$. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. The crude residue was dissolved in anhydrous $Et_2O$ and an ethereal solution of $CH_2N_2$ was added until the mixture turned yellow. After stirring for 30 min, the excess of $CH_2N_2$ was destroyed by addition of silica gel. The mixture was filtered, the solvent was removed in vacuo and the resulting residue was purified by CC (eluent: $Et_2O$) to afford 335 mg (69%) of *rac*-**2** ($R_f$ = 0.30) as colourless crystals; m.p. 82°C ($Et_2O$/*n*-pentane). − IR (KBr): $\tilde{\nu}$ = 3497 cm$^{-1}$ (OH), 1733 (ester C=O). − $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.27−2.00 (m, 12 H, C*H*$_2$), 2.36 (s, br., exchangeable, 1 H, 6-O*H*), 2.71 (ddd, $^3J_{4,12}$ = 5.3 Hz, $^3J_{4,12}$ = 3.4 Hz, $^3J_{4,3}$ = 3.4 Hz, 1 H, 4-*H*), 3.36 (dd, $^3J_{3,2}$ = 7.2 Hz, $^3J_{3,4}$ = 3.4 Hz, 1 H, 3-*H*), 3.67 (s, br., exchangeable, 1 H, 5-O*H*), 3.77 (s, 3 H, 3-COOC*H*$_3$), 4.13 (ddd, $^3J_{6,7}$ = 10.8 Hz, $^3J_{6,7}$ = 3.3 Hz, $^3J_{6,2}$ = 3.3 Hz, 1 H, 6-*H*), 4.65 (dd, $^3J_{2,3}$ = 7.2 Hz, $^3J_{2,6}$ = 3.3 Hz, 1 H, 2-*H*), 5.22 (s, 1 H, 5-*H*). − $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 17.08/19.15/25.43/26.62/29.25/29.97 (t, *C*-7, -8, -9, -10, -11, -12), 45.42 (d, *C*-3), 50.48 (d, *C*-4), 52.75 (q, 3-COO*C*H$_3$), 70.06 (d, *C*-6), 85.32 (d, *C*-2), 102.59 (d, *C*-5), 176.65 (s, 3-*C*OOCH$_3$). − MS (EI); *m*/*z* (%): 240 ($M^+$ − $H_2O$, 24), 181 ($M^+$ − $CO_2CH_3$ − $H_2O$, 100). − MS (CI); *m*/*z* (%): 259 ($M^+$ + H, 2), 241 ($M^+$ + H − $H_2O$, 100). − $C_{13}H_{22}O_5$ (258.3): calcd. C 60.45, H 8.58; found C 60.50, H 8.66. − Suitable crystals of **2** for the X-ray structure analysis were obtained in the following way: The resolution of the corresponding oxo acid [*rac*-**1**, C=O instead of CHOH at C-6, COOH instead of $COOCH_3$] and the reduction of its levorotatory methyl ester with $NaBH_4$ is described in ref.[4]. In the same way a sample of **1** enriched with (+)-**1** was obtained from the mother liquor of the above resolution. A solution of enriched (+)-**1** (206 mg, 0.76 mmol) in THF (10 ml) and 0.1 N $H_2SO_4$ (10 ml) was refluxed for 4.5 h. An analogous procedure yielded 121 mg (61%) enriched in (+)-**2** as colourless crystals; $[\alpha]_D^{18}$ = + 0.23 (*c* = 0.22, $CHCl_3$). Recrystallization ($Et_2O$) at room temp. furnished crystals suitable for the X-ray structure analysis.

*X-ray Structure Analysis of* **2**[11]: The data of an enantiomerically pure crystal of **2** with the approximate dimensions 0.35 × 1.25 × 0.2 mm were obtained with a Siemens R3m/V diffractometer (Mo-$K_\alpha$ radiation, graphite monochromator). Cell dimensions were refined from 22 reflections *hkl*: *a* = 815.2(4), *b* = 2070(2), *c* = 794.4(2) pm, *V* = 1340(2)·10$^6$ pm$^3$, orthorhombic, space group $P2_12_12_1$, *Z* = 4, $\rho_{calcd.}$ = 1.280 g·cm$^{-3}$, 2039 unique intensities, in the Θ range 1.75−27.5° of which 1794 [$F_o > 3\sigma(F_o)$] were observed, measured in ω-scan technique. The structure was solved using Direct Methods and refined on *F* using SHELXTL PLUS. Parameters, anisotropic displacement parameters for all atoms except hydrogen atoms, groupwise isotropic displacement parameters for all hydrogen atoms, treated as rigid groups. $R$ = 0.064, $R_w$ = 0.051, $w = 1/\sigma^2(F)$.

2. *(±)-2,3,4,5-Tetrahydro-6-hydroxy-3-hydroxymethyl-5-methoxy-2,4-heptanofuran* (*rac*-**3**): Lithium aluminium hydride (600 mg, 15.83 mmol) was suspended in anhydrous THF (10 ml) under nitrogen. A solution of (±)-2,3,4,5-tetrahydro-5-methoxy-6-oxo-2,4-heptanofuran-3-carboxylic acid[3][4] (1.50 g, 5.86 mmol) in anhydrous THF (30 ml) was added and the mixture was refluxed for 2.5 h. After cooling with an ice bath, the mixture was slowly hydrolyzed with 3% NaOH. The residue was filtered off, the filtrate was dried ($MgSO_4$) and concentrated in vacuo to yield 1.23 g (87%) of *rac*-**3** after recrystallization as colourless needles; m.p. 95°C ($Et_2O$/*n*-pentane). − IR (KBr): $\tilde{\nu}$ = 3224 cm$^{-1}$ (br., OH). − $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.21−2.07 (m, 13 H, C*H*$_2$, therein 4-*H* at δ = 1.95), 2.66 (dddd, $^3J_{3,13}$ = 10.8 Hz, $^3J_{3,2}$ = 7.0 Hz, $^3J_{3,13}$ = 3.9 Hz, $^3J_{3,4}$ = 3.9 Hz, 1 H, 3-*H*), 3.30 (s, 3 H, OC*H*$_3$), 3.50 (ddd, $^3J_{13,3}$ = 10.8 Hz, $^2J_{13,13}$ = 9.1 Hz, $^3J_{13,13\text{-OH}}$ = 0.8 Hz, 1 H, 13-*H*), 3.75 (m, 1 H, 13-*H*), 3.77 (s, br., exchangeable, 2 H, 6-O*H*, 13-O*H*), 4.07 (m, 1 H, 6-*H*), 4.12 (ddd, $^3J_{2,3}$ = 7.0 Hz, $^3J_{2,6}$ = 3.8 Hz, $^4J_{2,5}$ = 0.8 Hz, 1 H, 2-*H*), 4.70 (s, 1 H, 5-*H*). − $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 16.58/19.07/25.55/27.31/30.06/30.18 (t, *C*-7, -8, -9, -10, -11, -12), 43.10 (d, *C*-3), 48.17 (d, *C*-4), 54.02 (q, 5-OCH$_3$), 66.14 (t, *C*-13), 69.19 (d, *C*-6), 87.68 (d, *C*-2), 108.21 (d, *C*-5). − MS (CI); *m*/*z* (%): 213 ($M^+$ + H − $CH_3OH$, 100), 195 ($M^+$ + H − $CH_3OH$ − $H_2O$, 25). − $C_{13}H_{24}O_4$ (244.33): calcd. C 63.91, H 9.90; found C 63.85, H 9.84.

3. *(±)-2,3,4,5-Tetrahydro-5,6-dihydroxy-3-hydroxymethyl-2,4-heptanofuran* (*rac*-**4**): A solution of *rac*-**3** (321 mg, 1.31 mmol) in THF (20 ml) and 1 N $H_2SO_4$ (20 ml) was refluxed for 1 h. After cooling to room temp., the solution was diluted with water (10 ml) and extracted with $CH_2Cl_2$ (4 × 30 ml). The combined organic extracts were dried ($MgSO_4$). By concentrating in vacuo *rac*-**4** precipitated quantitatively as colourless amorphous solid. Recrystallization provided crystals; m. p. 152°C (EtOH/acetone/$Et_2O$). − IR (KBr): $\tilde{\nu}$ = 3300 cm$^{-1}$ (br., OH). − $^1$H NMR (300 MHz, [D$_6$]DMSO): δ = 1.02−1.96 (m, 12 H, C*H*$_2$), 2.05 (m, 1 H, 4-*H*), 2.42 (dtd, $^3J_{3,2}$ = 7.4 Hz, $^3J_{3,13}$ = 7.2 Hz, $^3J_{3,4}$ = 3.0 Hz, 1 H, 3-*H*), 3.40 (m, 2 H, 13-*H*), 3.80 (ddd, br., $^3J_{6,7}$ = 11.2 Hz, $^3J_{6,7}$ = 3.2 Hz, $^3J_{6,2}$ = 3.0 Hz, 1 H, 6-*H*), 3.96 (dd, br., $^3J_{2,3}$ = 7.4 Hz, $^3J_{2,6}$ = 3.0 Hz, 1 H, 2-*H*), 4.82 (s, br., exchangeable, 2 H, 6-O*H*, 13-O*H*), 5.01 (s, br., 1 H, 5-*H*), 5.74 (s, br., exchangeable, 1 H, 5-O*H*). − $^1$H NMR (200 MHz, [D$_6$]DMSO, selected data): δ = 4.81 (d, exchangeable, $^3J$ = 5.0 Hz, 1 H, 6-O*H* or 13-O*H*), 4.83 (d, exchangeable, $^3J$ = 5.8 Hz, 1 H, 6-O*H* or 13-O*H*), 5.01 (d, $^3J_{5,5\text{-OH}}$ = 3.8 Hz, 1 H, 5-*H*), 5.74 (d, exchangeable, $^3J_{5\text{-OH},5}$ = 3.8 Hz, 1 H, 5-O*H*). − $^{13}$C NMR (75 MHz, [D$_6$]DMSO): δ = 16.35/18.73/24.93/27.04/29.24/30.15 (t, *C*-7, -8, -9, -10, -11, -12), 42.99 (d, *C*-3), 49.22 (d, *C*-4), 65.13 (t, *C*-13), 68.36 (d, *C*-6), 85.27 (d, *C*-2), 100.88 (d, *C*-5). − MS (EI); *m*/*z* (%): 212 ($M^+$ − $H_2O$, 21), 181 ($M^+$ − $H_2O$ − $OCH_3$, 100), 163 ($M^+$ − 2 $H_2O$ − $OCH_3$, 6). − MS (CI): *m*/*z* (%) = 213 ($M^+$ + H − $H_2O$, 100). − $C_{12}H_{22}O_4$ (230.3): calcd. C 62.58, H 9.63; found C 62.55, H 9.50.

4. *(±)-2,3,4,5-Tetrahydro-5,6-dimethoxy-3-methoxymethyl-2,4-heptanofuran* (*rac*-**5**): 60% NaH/mineral oil suspension (100 mg, 2.5 mmol) was washed with *n*-pentane (2 ml) under nitrogen. Under cooling with an ice bath a solution of *rac*-**3** (264 mg, 1.08 mmol) in anhydrous THF (4 ml) was slowly added. After 20 min, MeI (1.0 ml, 16.0 mmol) was added and the mixture was stirred at room temp. for 14 h. After hydrolysis with 2 N aq. $NH_3$ solution (5 ml), the mixture was diluted with $H_2O$ (20 ml) and extracted with $CH_2Cl_2$ (3 × 30 ml). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to yield 270 mg (92%) of *rac*-

**5** ($R_f$ = 0.54) after CC on silica gel [eluent: $Et_2O$/*n*-pentane (1:1)] as colourless oil. − IR (film): $\tilde{\nu}$ = 1108 $cm^{-1}$ (ether CO). − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.20−1.95 (m, 12 H, C*H*$_2$), 2.35 (ddd, $^3J_{4,12}$ = 5.0 Hz, $^3J_{4,12}$ = 3.4 Hz, $^3J_{4,3}$ = 3.3 Hz, 1 H, 4-*H*), 2.67 (dddd, $^3J_{3,13}$ = 10.1 Hz, $^3J_{3,2}$ = 7.8 Hz, $^3J_{3,13}$ = 4.8 Hz, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3-*H*), 3.24 (dd, $^3J_{13,3}$ = 10.1 Hz, $^2J_{13,13}$ = 8.6 Hz, 1 H, 13-*H*), 3.30 (s, 3 H, 5-OC*H*$_3$), 3.33 (s, 3 H, OC*H*$_3$), 3.37 (s, 3 H, OC*H*$_3$), 3.45 (dd, $^2J_{13,13}$ = 8.6 Hz, $^3J_{13,3}$ = 4.8 Hz, 1 H, 13-*H*), 3.56 (ddd, $^3J_{6,7}$ = 11.2 Hz, $^3J_{6,2}$ = 3.0 Hz, $^3J_{6,7}$ = 3.0 Hz, 1 H, 6-*H*), 3.94 (dd, $^3J_{2,3}$ = 7.8 Hz, $^3J_{2,6}$ = 3.0 Hz, 1 H, 2-*H*), 4.71 (s, 1 H, 5-*H*). − $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.15/19.68/25.32/25.79/27.35/30.66 (t, *C*-7, -8, -9, -10, -11, -12), 40.92 (d, *C*-3), 50.11 (d, *C*-4), 54.19 (q, 5-OC*H*$_3$), 57.28/58.75 (q, 6-, 13-OC*H*$_3$), 77.25 (t, *C*-13), 79.88 (d, *C*-6), 81.83 (d, *C*-2), 109.63 (d, *C*-5). − MS (EI); *m/z* (%): 272 ($M^+$, 1) 240 ($M^+$ − $CH_3OH$, 32). − MS (CI); *m/z* (%): = 273 ($M^+$ + H, 1) 241 ($M^+$ + H − $CH_3OH$, 100), 209 ($M^+$ + H − 2 $CH_3OH$, 29). − $C_{15}H_{28}O_4$ (272.39) calcd. C 66.14, H 10.36; found C 66.16, H 10.35.

5. *(±)-2,3,4,5-Tetrahydro-5-hydroxy-6-methoxy-3-methoxymethyl-2,4-heptanofuran* (*rac*-**6**): A solution of *rac*-**5** (1.66 g, 6.10 mmol) in THF (45 ml) and 1 N HCl (150 ml) was stirred at room temp. for 2 h. The mixture was extracted with $CH_2Cl_2$ (3 × 50 ml). The combined organic extracts were deacidified (satd. aq. $NaHCO_3$), dried ($MgSO_4$) and the solvent was removed in vacuo. The resulting colourless residue was purified by CC [eluent: $Et_2O$/*n*-pentane (1:1)] to afford 1.33 g (85%) of (±)-**6** ($R_f$ = 0.24) as colourless crystals; m.p. 64−65°C ($Et_2O$/*n*-pentane). − IR (KBr): $\tilde{\nu}$ = 3398 $cm^{-1}$ (OH), 1100 (ether CO). − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 1.20−2.00 (m, 12 H, C*H*$_2$), 2.31 (ddd, $^3J_{4,12}$ = 5.4 Hz, $^3J_{4,3}$ = 3.0 Hz, $^3J_{4,12}$ = 3.0 Hz, 1 H, 4-*H*), 2.57 (dddd, $^3J_{3,2}$ = 7.2 Hz, $^3J_{3,13}$ = 2.8 Hz, $^3J_{3,13}$ = 2.8 Hz, $^3J_{3,4}$ = 2.8 Hz, 1 H, 3-*H*), 3.36 (dd, $^2J_{13,13}$ = 8.6 Hz, $^3J_{13,3}$ = 2.8 Hz, 1 H, 13-*H*), 3.38 (s, 3 H, OC*H*$_3$), 3.43 (s, 3 H, OC*H*$_3$), 3.47 (dd, $^2J_{13,13}$ = 8.6 Hz, $^3J_{13,3}$ = 2.8 Hz, 1 H, 13-*H*), 3.61 (ddd, $^3J_{6,7}$ = 11.3 Hz, $^3J_{6,2}$ = 3.1 Hz, $^3J_{6,7}$ = 3.1 Hz, 1 H, 6-*H*), 4.37 (dd, $^3J_{2,3}$ = 7.2 Hz, $^3J_{2,6}$ = 3.1 Hz, 1 H, 2-*H*), 4.65 (d, exchangeable, $^3J_{5\text{-OH},5}$ = 10.6 Hz, 1 H, 5-O*H*), 5.02 (d, $^3J_{5,5\text{-OH}}$ = 10.6 Hz, 1 H, 5-*H*). − $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 17.12/19.09/25.60/25.68/27.15/30.61 (t, *C*-7, -8, -9, -10, -11, -12), 40.78 (d, *C*-3), 50.20 (d, *C*-4), 57.40/59.12 (q, 6-, 13-OC*H*$_3$), 74.00 (t, *C*-13), 79.63 (d, *C*-6), 80.00 (d, *C*-2), 101.77 (d, *C*-5). − MS (EI); *m/z* (%): 240 ($M^+$ − $H_2O$, 32), 208 ($M^+$ − $CH_3OH$ − $H_2O$, 10). − MS (CI); *m/z* (%): 257 (2), 241 ($M^+$ + H − $H_2O$, 92), 209 ($M^+$ + H − $CH_3OH$ − $H_2O$, 100). − $C_{14}H_{26}O_4$ (258.36) calcd. C 65.09, H 10.14; found C 65.19, H 10.16.

**B) *Syntheses with Optically Active Compounds***

1. *(1′S,1″S,2S,3R,4S,5S,6S)-(+)-6-Camphanoyloxy-3-camphanoyloxymethyl-2,3,4,5-tetrahydro-5-methoxy-2,4-heptanofuran* [(+)-**7**] *and (1′S,1″S,2R,3S,4R,5R,6R)-(−)-6-Camphanoyloxy-3-camphanoyloxymethyl-2,3,4,5-tetrahydro-5-methoxy-2,4-heptanofuran* [(−)-**7**]: Under cooling with an ice bath (1*S*)-(−)-camphanoyl chloride (3.56 g, 16.43 mmol) was added to a solution of *rac*-**3** (1.69 g, 6.92 mmol) in anhydrous pyridine (47 ml). After stirring at room temp. for 4 d, the mixture was hydrolyzed with water (50 ml). The organic layer was separated and the aqueous one was extracted with $CH_2Cl_2$. The combined organic extracts were washed with 2 N HCl, dried ($MgSO_4$) and the solvent was removed in vacuo. The residue of both diastereomers (+)-**7**/(−)-**7** was separated by repeated CC [eluent: $Et_2O$/*n*-pentane (2:1)] to provide 1.91 g (46%) of (+)-**7** ($R_f$ = 0.34) as colourless needles and 1.99 g (48%) of (−)-**7** ($R_f$ = 0.28) as colourless needles. − (+)-**7**: M.p. 185.5−186°C ($CH_2Cl_2$/$Et_2O$/*n*-pentane). − $[\alpha]_D^{22}$ = + 47.4 (*c* = 0.54, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1782 $cm^{-1}$ (ester C=O), 1749 (ester C=O). − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 3 H, C*H*$_3$), 0.99 (s, 3 H, C*H*$_3$), 1.06 (s, 3 H, C*H*$_3$), 1.07 (s, 3 H, C*H*$_3$), 1.11 (s, 3 H, C*H*$_3$), 1.12 (s, 3 H, C*H*$_3$), 1.28−2.11 (m, 18 H, C*H*$_2$), 2.33−2.50 (m, 3 H, 4-*H*, 5′-*H*, 5″-*H*), 2.94 (dddd, $^3J_{3,13}$ = 9.4 Hz, $^3J_{3,2}$ = 7.4 Hz, $^3J_{3,13}$ = 4.2 Hz, $^3J_{3,4}$ = 3.4 Hz, 1 H, 3-*H*), 3.29 (s, 3 H, 5-OC*H*$_3$), 3.93 (dd, $^3J_{2,3}$ = 7.4 Hz, $^3J_{2,6}$ = 3.4 Hz, 1-H, 2-*H*), 4.09 (dd, $^2J_{13,13}$ = 10.6 Hz, $^3J_{13,3}$ = 9.4 Hz, 1 H, 13-*H*), 4.45 (dd, $^2J_{13,13}$ = 10.6 Hz, $^3J_{13,3}$ = 4.2 Hz, 1 H, 13-*H*), 4.75 (s, 1 H, 5-*H*), 5.39 (ddd, $^3J_{6,7}$ = 11.0 Hz, $^3J_{6,7}$ = 3.5 Hz, $^3J_{6,2}$ = 3.4 Hz, 1 H, 6-*H*). − $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 9.68 (2 q, 4′-*C*H$_3$, 4″-*C*H$_3$), 16.77 (t, 4 q, *C*-8, 2 7′-*C*H$_3$, 2 7″-*C*H$_3$), 19.27/25.26/26.12/26.61 (t, *C*-9, -10, -11, -12), 28.80/28.96 (t, *C*-5′,-5″), 30.11 (t, *C*-7), 30.53/30.67 (t, *C*-6′,-6″), 40.05 (d, *C*-3), 49.55 (d, *C*-4), 54.03/54.18/54.76 (s, *C*-4′, -4″, -7′,-7″), 54.34 (q, 5-OC*H*$_3$), 68.14 (t, *C*-13), 73.55 (d, *C*-6), 81.16 (d, *C*-2), 90.88/91.13 (s, *C*-1′,-1″), 109.28 (d, *C*-5), 166.34/167.25 (s, 1′-, 1″-*C*=O) 177.95/178.09 (s, *C*-3′, -3″). − MS (EI); *m/z* (%): 572 ($M^+$ − $CH_3OH$, 12). − MS (CI); *m/z* (%): 605 ($M^+$ + H, 5), 573 ($M^+$ + H − $CH_3OH$, 100). − $C_{33}H_{48}O_{10}$ (604.74): calcd. C 65.54, H 8.00; found C 65.42, H 8.00. − (−)-**7**: M.p. 163.5−165°C ($CH_2Cl_2$/$Et_2O$/*n*-pentane). − $[\alpha]_D^{22}$ = −55.6 (*c* = 0.50, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1790 $cm^{-1}$ (ester C=O), 1743 (ester C=O). − $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 3 H, C*H*$_3$), 0.98 (s, 3 H, C*H*$_3$), 1.07 (s, 3 H, C*H*$_3$), 1.07 (s, 3 H, C*H*$_3$), 1.11 (s, 3 H, C*H*$_3$), 1.12 (s, 3 H, C*H*$_3$), 1.22−2.21 (m, 18 H, C*H*$_2$), 2.36−2.48 (m, 3 H, 4-*H*, 5′-*H*, 5″-*H*), 2.92 (dddd, $^3J_{3,13}$ = 10.0 Hz, $^3J_{3,2}$ = 7.5 Hz, $^3J_{3,13}$ = 4.0 Hz, $^3J_{3,4}$ = 3.5 Hz, 1 H, 3-*H*), 3.29 (s, 3 H, 5-OC*H*$_3$), 3.89 (dd, $^3J_{2,3}$ = 7.5 Hz, $^3J_{2,6}$ = 3.3 Hz, 1 H, 2-*H*), 4.07 (dd, $^2J_{13,13}$ = 10.3 Hz, $^3J_{13,3}$ = 10.0 Hz, 1 H, 13-*H*), 4.37 (dd, $^2J_{13,13}$ = 10.3 Hz, $^3J_{13,3}$ = 4.0 Hz, 1 H, 13-*H*), 4.75 (s, 1 H, 5-*H*), 5.44 (ddd, $^3J_{6,7}$ = 11.1 Hz, $^3J_{6,7}$ = 3.4 Hz, $^3J_{6,2}$ = 3.3 Hz, 1 H, 6-*H*). − $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 9.61/9.66 (q, 4′-, 4″-*C*H$_3$), 16.72/16.75 (q, 7′-, 7″-*C*H$_3$), 16.79 (t, *C*-8), 16.85/16.87 (q, 7′-, 7″-*C*H$_3$), 19.26/25.34/26.27/26.65 (t, *C*-9, -10, -11, -12), 28.94/28.99 (t, *C*-5′, -5″), 30.16 (t, *C*-7), 30.64/30.67 (t, *C*-6′, -6″), 40.13 (d, *C*-3), 49.76 (d, *C*-4), 54.00/54.06/54.76 (s, *C*-4′, -4″, -7′, -7″), 54.29 (q, 5-OC*H*$_3$), 68.12 (t, *C*-13), 73.39 (d, *C*-6), 81.12 (d, *C*-2), 90.83/91.05 (s, *C*-1′, -1″), 109.12 (d, *C*-5), 165.98/167.24 (s, 1′-, 1″-*C*=O), 173.64/177.90 (s, *C*-3′, -3″). − MS (EI); *m/z* (%): 572 ($M^+$ − $CH_3OH$, 8). − MS (CI); *m/z* (%): 605 ($M^+$ + H, 13), 573 ($M^+$ + H − $CH_3OH$, 100). − $C_{33}H_{48}O_{10}$ (604.74): calcd. C 65.54, H 8.00; found C 65.42, H 7.98.

2a. (2*S*,3*R*,4*S*,5*S*,6*S*)-*(+)-2,3,4,5-Tetrahydro-6-hydroxy-3-hydroxymethyl-5-methoxy-2,4-heptanofuran* [(+)-**3**]: Under cooling with an ice bath a solution of (+)-**7** (2.27 g, 3.75 mmol) in anhydrous MeOH (200 ml) and anhydrous $CH_2Cl_2$ (70 ml) was treated with NaOMe (9.20 g, 170 mmol) and stirred first at 0°C for 30 min, then at room temp. for 2 h. The mixture was hydrolyzed with water (150 ml) and acidified with 2 N HCl (100 ml). The solution was extracted with $CH_2Cl_2$ and the combined organic layers were carefully dried ($MgSO_4$). After concentrating in vacuo, the remaining residue was prepurified by CC (eluent: $Et_2O$) to provide 866 mg of a mixture of (+)-**3** and (+)-**7** ($R_f$ = 0.32) which could not be separated by CC but by fractional crystallization ($Et_2O$/*n*-pentane). The first fraction furnished 350 mg of a mixture of (+)-**3** and (+)-**7** as colourless cotton-like needles. Recrystallization of the mother liquor yielded 470 mg (51%) of (+)-**3** as colourless crystals; m.p. 96°C ($Et_2O$/*n*-pentane). − $[\alpha]_D^{23}$ = + 76.3 (*c* = 0.52, $CHCl_3$). − $C_{13}H_{24}O_4$ (244.33) calcd. C 63.91, H 9.90; found C 63.99, H 9.83. − The spectral data are identical to those of *rac*-**3**.

2b. (2*S*,3*R*,4*S*,5*S*,6*S*)-*(+)-2,3,4,5-Tetrahydro-6-hydroxy-3-hydroxymethyl-5-methoxy-2,4-heptanofuran* [(+)-**3**]: Lithium aluminium hydride (17 mg, 0.45 mmol) was suspended in anhydrous THF (1 ml) under nitrogen. A solution of (+)-**1**[4] (150 mg, 0.55

mmol) in anhydrous THF (5 ml) was added and the mixture was refluxed for 1 h. After cooling to room temp., it was slowly hydrolyzed with $H_2O$. The residue was dissolved (5 N $H_2SO_4$) and extracted with $CH_2Cl_2$. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. The resulting colourless residue was purified by CC [eluent: $Et_2O$/*n*-pentane (2:1)] to afford 66 mg (49%) of (+)-**3** ($R_f$ = 0.33, $Et_2O$) as colourless crystals; m.p. 96°C ($Et_2O$/*n*-pentane). The spectral data ($^1H$ NMR) and optical rotation are identical to those of (+)-**3** described under 2a.

3. *(2R,3S,4R,5R,6R)-(−)-2,3,4,5-Tetrahydro-6-hydroxy-3-hydroxymethyl-5-methoxy-2,4-heptanofuran* [(−)-**3**]: A solution of (−)-**7** (3.00 g, 4.96 mmol) in anhydrous MeOH (200 ml) and anhydrous $CH_2Cl_2$ (50 ml) was treated with NaOMe (12.6 g, 233 mmol) as described for (+)-**3**. After work-up, CC (eluent: $Et_2O$) afforded 1.17 g (97%) of (−)-**3** ($R_f$ = 0.31) as colourless crystals; m.p. 96°C ($Et_2O$/*n*-pentane). − $[\alpha]_D^{19}$ = −76.5 (*c* = 0.43, $CHCl_3$). − $C_{13}H_{24}O_4$ (244.33): calcd. C 63.91, H 9.90; found C 63.88, H 9.98. − The spectral data are identical to those of *rac*-**3**.

4. *(2S,3R,4S,5S,6S)-(+)-2,3,4,5-Tetrahydro-5,6-dimethoxy-3-methoxymethyl-2,4-heptanofuran* [(+)-**5**]: A solution of (+)-**3** (335 mg, 1.37 mmol) in anhydrous THF (5 ml) was slowly added to washed 60% NaH/mineral oil suspension (130 mg, 3.25 mmol); after 20 min, MeI (1.3 ml, 20.8 mmol) was injected as described for (±)-**5**. CC [eluent: $Et_2O$/*n*-pentane (1:1)] yielded 353 mg (95%) of (+)-**5** ($R_f$ = 0.54) as colourless oil. − $[\alpha]_D^{24}$ = + 68.4 (*c* = 0.59, $CHCl_3$). − The spectral data are identical to those of *rac*-**5**.

5. *(2R,3S,4R,5R,6R)-(−)-2,3,4,5-Tetrahydro-5,6-dimethoxy-3-methoxymethyl-2,4-heptanofuran* [(−)-**5**]: Compound (−)-**5** was obtained from (−)-**3** by the same procedure as described for (+)-**5**; $[\alpha]_D^{26}$ = −67.3 (*c* = 0.67, $CHCl_3$). − The spectral data are identical to those of *rac*-**5**.

6. *(2S,3R,4S,5S,6S)-(+)-2,3,4,5-Tetrahydro-5-hydroxy-6-methoxy-3-methoxymethyl-2,4-heptanofuran* [(+)-**6**]: A solution of (+)-**5** (350 mg, 1.28 mmol) in THF (10 ml) and 1 N HCl (150 ml) was treated analogously to the procedure described for *rac*-**6** to provide 280 mg (85%) of (+)-**6** ($R_f$ = 0.25) after CC [eluent: $Et_2O$/*n*-pentane (1:1)] as colourless oil. − $[\alpha]_D^{22}$ = + 36.3 (*c* = 0.50, $CHCl_3$). − The spectral data are identical to those of *rac*-**6**.

7. *(2R,3S,4R,5R,6R)-(−)-2,3,4,5-Tetrahydro-5-hydroxy-6-methoxy-3-methoxymethyl-2,4-heptanofuran* [(−)-**6**]: Compound (−)-**6** was obtained from (−)-**5** by the same procedure as described for (+)-**6**. − $[\alpha]_D^{22}$ = −36.8 (*c* = 0.48, $CHCl_3$). − The spectral data are identical to those of *rac*-**6**.

8. *(2R,3S,4R,5R,6R,2′R,3′S,4′R,5′R,6′R)-(−)-2,3,4,5-Tetrahydro-6-methoxy-3-methoxymethyl-2,4-heptanofuranosyl(5→5)-tetrahydro-6-methoxy-3-methoxymethyl-2,4-heptanofuran* [(−)-**8**]: Compound (−)-**6** (715 mg, 2.77 mmol) was treated with commercial, not purified $CHCl_3$. Removal of the solvent in vacuo (< 1 Torr) afforded (−)-**8** as the only product as colourless crystals; m.p. 116.5−117°C ($Et_2O$/*n*-pentane). − $[\alpha]_D^{23}$ = −134.5 (*c* = 0.50, $CH_2Cl_2$). − IR (KBr): $\tilde{\nu}$ = 1107 $cm^{-1}$ (ether C−O). − $^1H$ NMR (200 MHz, $CDCl_3$): δ = 1.20−1.98 (m, 24 H, $CH_2$), 2.33 (ddd, $^3J_{4,12}$ = 5.3 Hz, $^3J_{4,12}$ = 3.2 Hz, $^3J_{4,3}$ = 3.1 Hz, 2 H, 4-*H*, 4′-*H*), 2.68 (dddd, $^3J_{3,13}$ = 10.1 Hz, $^3J_{3,2}$ = 7.7 Hz, $^3J_{3,13}$ = 4.8 Hz, $^3J_{3,4}$ = 3.1 Hz, 2 H, 3-*H*, 3′-*H*), 3.26 (dd, $^3J_{13,3}$ = 10.1 Hz, $^2J_{13,13}$ = 8.7 Hz, 2 H, 13-*H*, 13′-*H*), 3.34 (s, 6 H, $OCH_3$), 3.36 (s, 6 H, $OCH_3$), 3.45 (dd, $^2J_{13,13}$ = 8.7 Hz, $^3J_{13,3}$ = 4.8 Hz, 2 H, 13-*H*, 13′-*H*), 3.55 (ddd, $^3J_{6,7}$ = 10.9 Hz, $^3J_{6,2}$ = 3.0 Hz, $^3J_{6,7}$ = 3.0 Hz, 2 H, 6-*H*, 6′*H*), 3.91 (dd, $^3J_{2,3}$ = 7.4 Hz, $^3J_{2,6}$ = 3.0 Hz, 2 H, 2-*H*, 2′-*H*), 5.09 (s, 2 H, 5-*H*, 5′ *H*). − $^{13}C$ NMR (50 MHz, $CDCl_3$): δ = 17.08/19.58/25.36/25.58/27.26 (t, *C*-8, -8′, -9, -9′, -10, -10′, -11, -11′, -12, -12′), 30.62 (t, *C*-7, -7′), 40.84 (d, *C*-3, -3′), 50.02 (d, *C*-4, -4′), 57.28/58.75 (q, 6-, 6′-, 13-, 13′-$OCH_3$), 77.46 (t, *C*-13, -13′), 79.77 (d, *C*-6, -6′), 82.24 (d, *C*-2, -2′), 103.67 (d, *C*-5, -5′). − MS (EI); *m/z* (%): 498 ($M^+$, 0.6) 240 (1/2 [$M^+$ − $H_2O$], 39). − MS (CI); *m/z* (%): 498 ($M^+$, 0.5), 241 (1/2 [$M^+$ − $H_2O$] + H, 100). − Vapour-pressure osmometry: calcd. 498 g/mol; found 480 g/mol. − $C_{28}H_{50}O_7$ (498.71): calcd. C 67.43, H 10.11; found C 66.94 H 10.10.

9. *(2S,3R,4S,5S,6S,2′S,3′R,4′S,5′S,6′S)-(+)-2,3,4,5-Tetrahydro-6-methoxy-3-methoxymethyl-2,4-heptanofuranosyl(5→5)-tetrahydro-6-methoxy-3-methoxymethyl-2,4-heptanofuran* [(+)-**8**]: (+)-**8** was obtained as the only product from (+)-**6** (280 mg, 1.08 mmol) by the same procedure as described for (−)-**8**; m.p. 117−117.5°C ($Et_2O$/*n*-pentane). − $[\alpha]_D^{23}$ = + 139.4 (*c* = 0.52, $CH_2Cl_2$). − $C_{28}H_{50}O_7$ (498.71): calcd. C 67.43, H 10.11; found C 66.94, H 10.02. − The spectral data are identical to those of (−)-**8**.

10. *(2R,3S,4R,5R,6R)-(−)-2,3,4,5-Tetrahydro-6-methoxy-3-methoxymethyl-2,4-heptanofuranosyl(5→6)1,2;3,4-di-O-isopropylidene-D-galactopyranose* [(−)-**10**]: Under cooling with an ice bath a solution of (−)-**6** (235 mg, 0.91 mmol) in anhydrous MeCN (2 ml) was injected to 60% NaH/mineral oil suspension (80 mg, 2.00 mmol) that had been washed before with 1.5 ml of *n*-pentane under nitrogen. After 15 min of stirring at room temp., a solution of crude 1,2;3,4-di-*O*-isopropylidene-D-galactopyranosyl triflate (**9**)[9] (1.0 g, ca. 2.53 mmol) in anhydrous MeCN (5 ml) was slowly (during 8 h) added. The brown mixture was stirred at room temp. for 46 h and then hydrolyzed with water (5 ml) and satd. aq. NaCl and diluted with $CH_2Cl_2$ (10 ml). The organic layer was separated and the aqueous one was extracted with $CH_2Cl_2$ (4 × 10 ml). The combined organic layers were dried ($MgSO_4$) and filtered through silica gel. Concentration in vacuo and silica-gel CC [eluent: $Et_2O$/*n*-pentane (1:3)] of the yellow residue yielded 105 mg of crude (−)-**10** [$R_f$ = 0.42, $Et_2O$/*n*-pentane (1:1)] as colourless oil, which was purified by CC [toluene/$Et_2O$(10:1)] to furnish 74 mg (16%) of (−)-**10** ($R_f$ = 0.10) as colourless oil. − $[\alpha]_D^{23}$ = − 45.1 (*c* = 0.51, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 1107, 1070 $cm^{-1}$ (ether C−O). − $^1H$ NMR (300 MHz, $C_6D_6$, ref. $C_6D_6$): δ = 1.02−2.03 [m, 12 H, $CH_2$, therein at δ = 1.06 (q, $^4J_{Me,Me}$ = 0.6 Hz, 3 H, $CH_3$), 1.18 (q, $^4J_{Me,Me}$ = 0.6 Hz, 3 H, $CH_3$), 1.46 (q, $^4J_{Me,Me}$ = 0.6 Hz, 3 H, $CH_3$) and 1.48 (q, $^4J_{Me,Me}$ = 0.6 Hz, 3 H, $CH_3$)], 2.76 (ddd, $^3J_{4,12}$ = 4.7 Hz, $^3J_{4,12}$ = 3.4 Hz, $^3J_{4,3}$ = 3.4 Hz, 1 H, 4-*H*), 2.91 (m, 1 H, 3-*H*), 3.166 (s, 3 H, $OCH_3$), 3.169 (s, 3 H, $OCH_3$), 3.49 (dd, $^3J_{13,3}$ = 10.3 Hz, $^2J_{13,13}$ = 8.4 Hz, 1 H, 13-*H*), 3.63 (ddd, $^3J_{6,7}$ = 11.2 Hz, $^3J_{6,2}$ = 3.2 Hz, $^3J_{6,7}$ = 3.2 Hz, 1 H, 6-*H*), 3.73 (dd, $^2J_{13,13}$ = 8.4 Hz, $^3J_{13,3}$ = 4.4 Hz, 1 H, 13-*H*), 3.81 (dd, $^2J_{6',6'}$ = 9.8 Hz, $^3J_{6',5'}$ = 6.4 Hz, 1 H, 6′-*H*), 4.15 (dd, $^2J_{6',6'}$ = 9.8 Hz, $^3J_{6',5'}$ = 6.4 Hz, 1 H, 6′-*H*), 4.16 (dd, $^3J_{4',3'}$ = 8.0 Hz, $^3J_{4',5'}$ = 1.8 Hz, 1 H, 4′-*H*), 4.19 (dd, $^3J_{2',1'}$ = 5.0 Hz, $^3J_{2',3'}$ = 2.3 Hz, 1 H, 2′-*H*), 4.26 (td, $^3J_{5',6'}$ = 6.4 Hz, $^3J_{5',4'}$ = 1.8 Hz, 1 H, 5′-*H*), 4.32 (dd, $^3J_{2,3}$ = 7.4 Hz, $^3J_{2,6}$ = 3.2 Hz, 1 H, 2-*H*), 4.52 (dd, $^3J_{3',4'}$ = 8.0 Hz, $^3J_{3',2'}$ = 2.3 Hz, 1 H, 3′-*H*), 4.93 (s, 1 H, 5-*H*), 5.54 (d, $^3J_{1',2'}$ = 4.9 Hz, 1 H, 1′-*H*). − $^{13}C$ NMR (75 MHz, $C_6D_6$, ref. $C_6D_6$): δ = 17.45/20.01/25.59/25.89/27.81 (t, *C*-8, -9, -10, -11, -12), 24.42/24.88/26.21/26.25 (q, $CH_3$), 30.92 (t, *C*-7), 41.47 (d, *C*-3), 50.70 (d, *C*-4), 56.88/58.39 (q, 6-, 13-$OCH_3$), 65.50 (t, *C*-6′), 67.68/71.19/71.30/71.70 (d, *C*-2′, -3′, -4′, -5′), 77.65 (t, *C*-13), 80.13 (d, *C*-6), 82.16 (d, *C*-2), 96.79 (d, *C*-1′), 108.25/108.70 (s, *C*-7′,-8′), 109.05 (d, *C*-5). − MS (CI); *m/z* (%): 241 ($M^+$ + H − diisopropylidene-D-galactose, 100).

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[11] The atomic coordinates for this work are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U. K. Any request should be accompanied by the full literature citation for this communication and the deposition number CCDC-100876.

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