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Synthesis of α-D-(1→3) and α-D-(1→4)-C-linked Galactosides of D-Mannose Derivatives. Conformation of α-C-Galactosides.‡

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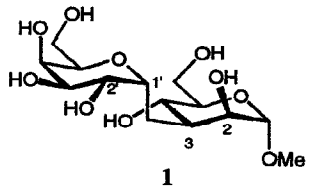
Summary: *Reductive radical α-D-galactosidation of 5-exo-(benzeneselenyl)-6-endo-chloro-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one with acetobromo-D-galactose, followed by ketone reduction led to (+)-(1R,2S,3R,4S,5S,6S)-5-exo-(benzeneselenyl)-6-endo-chloro-3-endo-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-endo-ol which was converted into (+)-methyl 3-deoxy-3-[(α-D-galactopyranosyl)methyl]-α-D-mannopyranoside* (**1**)*, (+)-3-deoxy-3-[(α-D-galactopyranosyl)methyl]-D-mannitol* (**2**) *and 4-deoxy-4-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-2,3,6-tri-O-acetyl-D-mannono-1,5-lactone* (**3**)*. ^{1}H-MNR data of the α-C-galactosides confirmed that their preferred conformations involve antiperiplanar arrangements for the C-linked substrates and bond σC(1'),C(2') of the α-(1→3)-C-galactoside unit. The α-(1→3)-C-galactoside of methyl mannopyranoside* **1** *adopts a conformation similar to that proposed for methyl 3-O-(α-D-galactopyranosyl)-α-D-mannopyranoside.*

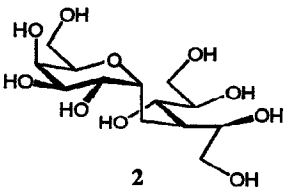
Introduction. - The replacement of the interglycosidic oxygen atom in disaccharides by a methylene group generates a class of interesting analogues of disaccharides, namely the C-disaccharides, which constitute potential inhibitors of glycosidases[2a] and disaccharidases.[2b] Inhibitors of α-amylases and other mammalian intestinal carbohydrate-splitting enzymes have aroused medical interest in the treatment of metabolic diseases such as diabetes.[2b,3] Inhibitors of sucrose as well as maltase may bring about a reduction in food consumption and weight gain.[4] A large number of cellular recognition events are thought to involve the specific binding of particular classes of oligosaccharides on one cell surface to "receptor" glycoproteins on the surface of another cell.[5,6] The immense number of structures that can be made from a relatively small number of saccharide units and the multiplicity and specificity of the enzymes which assemble them suggest that intercellular communication is encoded in oligosaccharides.[5,7] Thus, specific glycosidase inhibitors may find applications as antiviral,[8] antitumor[9] or fertility control agents.[10] Since the first synthesis of a β-(1→6)-C-disaccharide (β-D-Glc*p*-CH_2(1→6)-α-D-Glc*p*-OMe) by Rouzaud and Sinaÿ[11] several approaches to C-disaccharides and analogues have been proposed.[12-28] The synthesis of C,C-trisaccharides has also been reported by Kishi and co-workers.[29] Only two examples of (1→3)-C-disaccharides have been described thus far, i.e. α-D-Gal*p*-CH_2-(1→3)-D-Gal[14c] and α-D-Glc*p*-CH_2-(1→3)-L-Man.[27] We report here the first synthesis of α-D-Gal*p*-CH_2-(1→3)-α-D-Man*p*-OMe (**1**) which relies on the stereoselective addition[27] of 2,3,4,6-tetra-O-acetylgalactopyranosyl radical onto a 3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one derivative. The same method has allowed one to generate the C-disaccharides **2** and **3** linking centre C(1) of α-galactopyranose to the carbon centre C(3) of mannitol and carbon center C(4) of mannono-1,5-lactone, respectively. ^{1}H-NMR studies confirmed that the galactopyranosyl and mannopyranosyl moieties of **1** adopt $^4C_1$ conformations. It is found also that the C(3)-CH_2 bond of the mannoside unit is antiperiplanar with respect to the C(1')-C(2') bond

‡ "Naked Sugars" as Synthetic Intermediates, Part XXVI. Part XXV, see ref. 1a; Part XXIV, see ref. 1b

of the α-galactoside. Similar conclusions were reached for the conformation of other α-C-galactosides with their hydroxy groups being acetylated.



1



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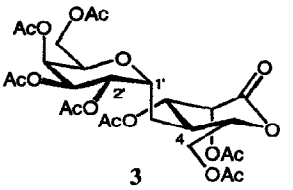
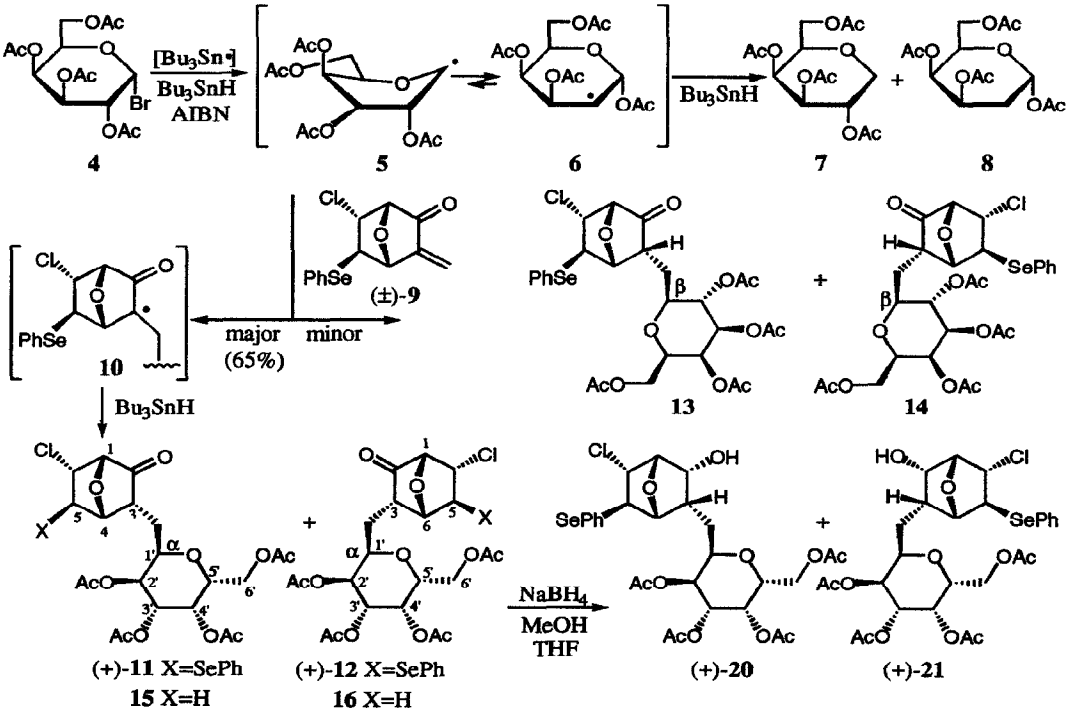


3

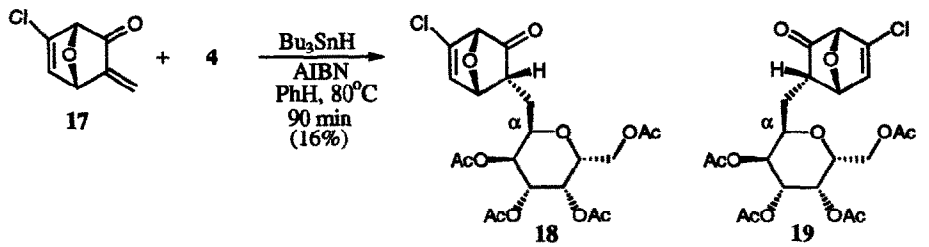
Results and discussion. - Under conditions similar to those recommended by Giese and co-workers,[13] the slow addition (2.5 h) of a molar solution of Bu_3SnH in anhydrous toluene containing 1% of AIBN (α,α'-azoisobutyronitrile) to a solution of α-acetobromogalactose (**4**, 0.2 molar, 1.3 equivalent) and enone (±)-**9**[27] (0.15 molar) in toluene maintained at 75°C afforded a mixture composed of the reduced sugars **7** and **8** (55%) resulting from the radical intermediates **5** and **6**, respectively,[30] a 1:1 mixture of the α-galactosides (+)-**11** and (+)-**12** (25%) and traces of the β-galactosides **13**, **14**, and of the product of phenylselenide reduction **15** and **16**. A significant proportion of enone (±)-**9** polymerized under the above conditions. Better yield of the desired α-galactosides (+)-**11** and (+)-**12** (42%) were obtained when the enone (±)-**9** was added to the solution of **4**



4 5 6 7 8

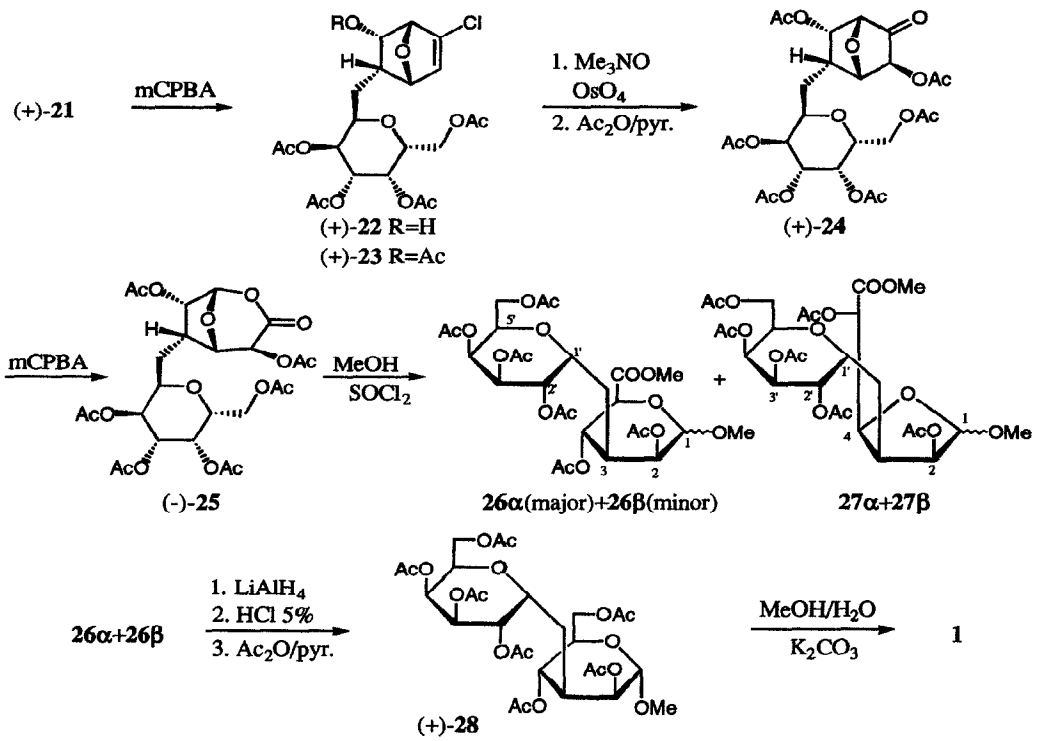
together with Bu_3SnH, AIBN in toluene. Slower addition rates and higher temperatures (>75°C) decrease the yield of (+)-**11** and (+)-**12**. The best yield was reached when a solution 0.5 molar in Bu_3SnH, 0.38 molar in

enone (±)-**9** and 0.006 molar in AIBN in benzene was added in 90 min to a boiling 0.5 molar solution of aceto-bromogalactose in benzene. Under these conditions a 1:1 mixture of (+)-**11** and (+)-**12** was isolated with a yield better than 65% after flash chromatography on silica gel. The two α-galactosides could be separated by low pressure analytical column chromatography (see Exper. Part) and fully characterized by their spectral data. The *endo* configuration of the (2',3',4',6'-tetra-O-acetyl-D-galactopyranosyl)methyl substituent at position C(3) of the 7-oxabicyclo[2.2.1]heptan-2-ones (+)-**11** and (+)-**12** was given by the vicinal coupling constants ^3J(H-C(3),H-C(4)) = 6.0 Hz in (+)-**11** and 5.0 Hz in (+)-**12**.[31] No trace of the 3-*exo*-isomer of (+)-**11** and (+)-**12** could be detected in the 400 MHz ^{1}H-NMR spectrum of the crude reaction mixture, thus demonstrating the high stereoselectivity of the reductive D-galactopyranosyl radical addition to the bicyclic enone (±)-**9**. These results can be interpreted in terms of the formation of the 7-oxabicyclo[2.2.1]heptyl radical intermediates of type **10**, the reaction of which with Bu_3SnH is expected to be highly *exo* face selective.[27] The absolute configuration of the 7-oxabicyclo[2.2.1]heptyl moieties in (+)-**11** and (+)-**12** was given by the radical galactosidation of optically pure (-)-**9**[27] which gave (+)-**11**. The above flash chromatography afforded also the 1-deoxygalactose derivative **7** (17%) and a 1:1 mixture of the deselenated derivatives **15** and **16** (10%). When $(Me_2Si)_3SiH$[32] was used instead of Bu_3SnH as hydrogen atom donor,[18] the yield in (+)-**11** and (+)-**12** never surpassed 33% (75% conversion of enone (±)-**9**). On lowering the concentration of the Bu_3SnH solution, the yield of C-galactosidation decreased (58%, 0.2 molar in benzene) and the β-C-galactosides **13** and **14** (2-4%) were formed concurrently with the α-C-galactosides.

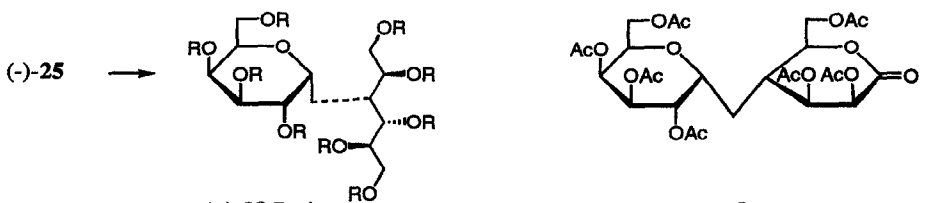


When dienone (±)-**17**[27] was used instead of enone (±)-**9** for the reductive galactosidation, a 1:1 mixture of the α-galactosides **18** and **19** was obtained in mediocre yield (16%).

Reduction of the mixture of (+)-**11** and (+)-**12** obtained above with $NaBH_4$ (THF/MeOH, 0°C, 10 min) gave a 1:1 mixture of the corresponding *endo* alcohols (+)-**20** and (+)-**21** which were separated by flash column chromatography and obtained in 32.2% and 32.3% yield, respectively. Oxidative elimination of the phenylseleno substituent of (+)-**21** with metachloroperbenzoic acid (mCPBA, CH_2Cl_2) afforded (+)-**22** (98%) the acetylation of which (Ac_2O/pyridine/DMPA) led to (+)-**23** (95%). Double hydroxylation of the chloroalkene (+)-**23** with trimethylamine oxide and a catalytic amount (1%) of OsO_4 followed by acetylation (Ac_2O/pyridine/DMPA) furnished ketone (+)-**24** (86%). Baeyer-Villiger oxidation with mCPBA/$NaHCO_3$/CH_2Cl_2 provided the uronolactone (-)-**25** (93%), the reaction of which with MeOH and $SOCl_2$ afforded a 8:1 mixture of the mannonohexopyranoside **26** and mannonohexofuranoside **27**. Reduction of **26** with an excess of $LiAlH_4$ in THF followed by acetylation gave (+)-**28** (71%). Saponification with K_2CO_3/MeOH/H_2O followed by purification of Dowex 500W 4X 200-400 mesh loaded with $CaCl_2$ provided pure methyl 3-deoxy-3-[(α-D--galactopyranosyl)methyl]-α-D-mannohexopyranoside (**1**) in 77% yield.

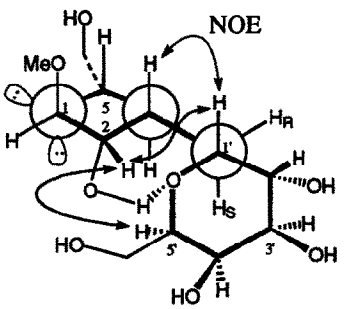


Reduction of uronolactone (-)-**25** with $NaBH_4/K_2CO_3$ in MeOH, followed by acetylation afforded the C-galactoside (+)-**29** which was deprotected (K_2CO_3/MeOH/H_2O) to give 3-deoxy-3-[(α-D-galactopyranosyl)methyl]-D-mannitol (**2**) in 78% yield. When (-)-**25** was treated first with 0.02 N HCl in dioxane/H_2O (50°C, 14 h), followed by reaction with $Na(CN)BH_3$ (20°C, 3 h), acidic treatment (pH = 1, (HCl), 60°C, 24 h) and acetylation (Ac_2O/pyridine/DMPA, 20°C, 14 h), 4-deoxy-4-[2',3',3',6'-tetra-O-acetyl-α-D-galactopyranosyl)-methyl]-2,3,6-tri-O-acetyl-D-mannono-1,5-lactone (**3**) was isolated in 30% yield.



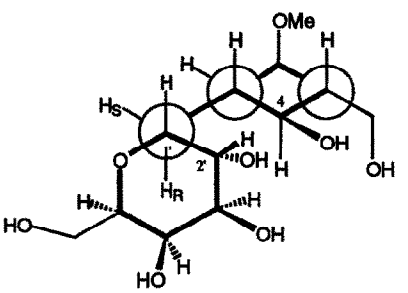
The structure of all the new compounds described above were confirmed by their elemental analyses, their spectral data and mode of formation. The vicinal proton-proton coupling constants obtained by double irradiation experiments (400 MHz ^{1}H-NMR, CD_3OD) of **1** were consistent, as expected, with $^4C_1$-chair conformations for both the α-D-galactopyranoside and α-D-mannopyranoside units. One of the two methylene protons of the CH_2-link showed relatively large vicinal coupling constants (10.2 hertz) with H-C(1') of the

galactoside moiety and with H-C(3) (9.2 hertz) of the mannoside moiety. These data are consistent with conformer **A** in which the pro-S proton (H_S) of the CH_2-link is antiperiplanar with respect to both H-C(1') and H-C(3) or with conformer **B** in which the pro-R proton (H_R) of the CH_2-link is antiperiplanar with respect to both H-C(1') and H-C(3). By analogy with the extensive work carried out by Kishi and co-workers[14] on the conformational analysis of all kinds of C-disaccharides, conformer **A** which implies a zig-zag arrangement for the σC(1')-C(2) and σC(3)-CH_2 bonds, should be preferred. This conformation corresponds also to that proposed recently by Lipkind and Kolchetkov[33] for methyl 3-O-(α-D-galactopyranosyl)-α-D-mannopyranoside and which allows for hydrogen bridging (7-membered ring) between the hydroxy group at C(2) and the oxygen atom of the ring of the galactopyranoside unit. In conformer **B** which implies a gauche arrangement for bonds σ(C(1'),C(2') and C(3)-CH_2, this stabilizing interaction is not possible. The NOESY spectrum of **1** was also consistent with conformer **A**. Most significant was the observation of a NOE between protons H-C(2) and H-C(5') indicating a relative short distance between these protons which cannot be realized with conformer **B**. This effect is also visible in the ^{1}H-NMR spectrum of the polyacetylated derivative (+)-**28**. Applying the modified Karplus equation for the calculation of vicinal proton/proton couling constants[34] we estimate the following dihedral angles in **1**: H-C(1')/H_S: 175°, H-C(1')/H_R: 64°, H-C(3)/H_S: 159° and H-C(3)/H_R: 47°. Lipkind and Kotchetkov[33] obtained a ratio of 4.33 for the intensity of the NOE's between proton pairs H-C(1')/H-C(3) and H-C(1')/H-C(2) in the case of methyl 3-0-(α-galactopyranosyl)-α-D-manno-pyranoside. We measure a ratio of 2.26 for the same proton pairs in **1**, consistent with the fact that both the O and corresponding C-linked disaccharides adopt very similar conformations.[14]



A

^3J(H-C(1'),H_S) = 10.2 hertz
^3J(H-C(1'),H_R) = 2.4
^3J(H-C(1'),H-C(2')) = 5.3
^3J(H-C(3),H_S) = 9.2
^3J(H-C(3),H_R) = 4.2
^3J(H-C(3),H-C(2)) ≤ 2.3
^3J(H-C(3),H-C(4)) = 10.0
^3J(H-C(4),H-C(5)) = 10.0

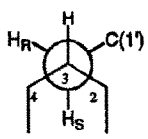


B

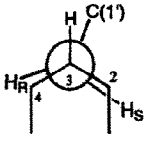
Strong NOE between:
H-C(1') (δ_H = 4.16 ppm) and
H-C(2') (3.89), H_R(1.38),
H-C(2) (4.00), H-C(3) (1.93)
H-C(5') ($\delta_H \cong$ 3.90 ppm) and H_S (1.82)
H-C(1) (δ_H = 4.57 ppm) and H-C(2)
H-C(3) and H_R, H-C(2)
H-C(3') ($\delta_H \cong$ 3.71 ppm) and H_S

The ^{1}H-NMR spectrum (see Exp. Part) of the polyacetate (+)-**28** showed that this disaccharide adopts an average conformation that is somewhat different from that of **1**. Vicinal coupling constants suggest that both the galactoside and mannoside units adopt $^4C_1$ conformations. Proton H-C(1') of the galactoside couples with the protons of the methylene link with ^3J(H-C(1'),H_S) = 11.6 hertz and ^3J(H-C(1'),H_R) = 3.0 hertz. A strong

NOE between protons H-C(2) of the mannoside and H-C(5') of the galactoside moieties confirms that bonds CH_2-C(3) and C(1')-C(2') are antiperiplanar as shown with C. The coupling constants ^3J(H-C(3),H_S) = 3.9 hertz and ^3J(H-C(3),H_R) = 4.4 hertz are consistent with a nearly eclipsed conformation about bond C(3)-CH_2. Compared with 1 (conformation A), (+)-**28** has undergone a rotation of 40-50° about the C(3)-CH_2 bond. The ratio of the NOE's measured for the proton pairs H-C(1')/H-C(3) and H-C(1')/H-C(2) amounts to 5.0; it confirms the average conformation C which is consistent also with the observation of NOE's between protons H-C(2)/H-C(5') which is significantly stronger in (+)-**28** than in **1**.

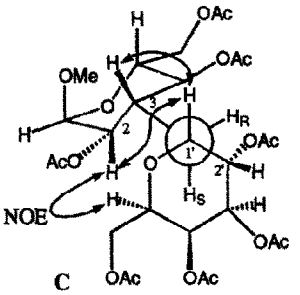


A



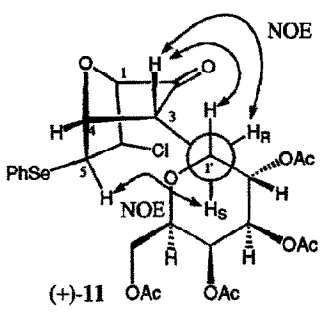
C

^3J(H-C(1'),H_S) = 11.6 hertz
^3J(H-C(1'),H_R) = 3.0 hertz
^3J(H-C(3),H_S) = 3.9 hertz
^3J(H-C(3),H_R) = 4.4 hertz



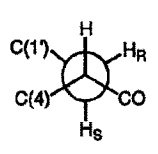
C

The NOESY ^{1}H-NMR (CD_2Cl_2) spectra of the C-galactosides (+)-**11** and (+)-**12** were consistent with the conformations **D** and **E**, respectively. The vicinal coupling constants confirmed $^4C_1$-chair conformations for the 2,3,4,6-tetra-O-acetyl galactopyranosyl moieties and antiperiplanar arrangements for the bonds σC(1'),C(2') of the galactoside and C(3)-CH_2 of the 7-oxabicyclo[2.2.1]heptanone units. The absolute configuration of the latter group does not affect, apparently, these arrangements; it affects the orientation of the bicyclic system with respect to the C(3)-CH_2 bond, as shown by the coupling constants between H-C(3) and the two methylene protons of the CH_2 link and by the NOE measurements. Most significant NOE's were those involving protons H-C(3) and H-C(5) of the 7-oxabicyclo[2.2.1]heptyl system with those of the CH_2 link and H-C(1') of the galactoside unit, as indicated with representations **D** and **E**.

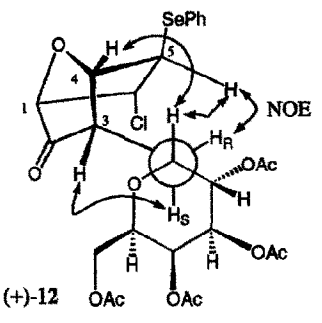


(+)-**11**

D

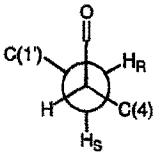


^3J(H-C(1'),H_S) = 10.8 hertz
^3J(H-C(1'),H_R) = 2.2 hertz
^3J(H-C(3),H_S) = 9.6 hertz
^3J(H-C(3),H_R) = 4.5 hertz



(+)-**12**

E



^3J(H-C(1'),H_S) = 11.8 hertz
^3J(H-C(1'),H_R) = 3.1 hertz
^3J(H-C(3),H_S) = 4.1 hertz
^3J(H-C(3),H_R) = 10.7 hertz

Conclusion. - The reductive radical galactosidation of racemic 5-*exo*-(benzeneselenyl)-6-*endo*-chloro-3--methylidene-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**9**) gives a mixture of the diastereomeric 3-*endo*-C-α--galactosides (+)-**11** and (+)-**12** which were reduced into the corresponding 2-*endo*-alcohols (+)-**20** and (+)-**21** that were readily separated and purified by flash column chromatography. Isomer (+)-**21** was converted with high stereoselectivity into α-D-(1→3) and α-D-(1→4)-C-linked galactosides of D-mannose derivatives. The ^{1}H-NMR data of the α-C-galactosides confirmed that their preferred conformations involve antiperiplanar arrangements for the C-linked substrates and bond σC(1'),C(2') of the α-galactoside unit. The conformation of methyl 3-deoxy-3-[(α-D-galactopyranosyl)methyl]-α-D-mannopyranoside (**1**) adopts a conformation similar to that proposed for methyl 3-O-(α-D-galactopyranosyl)-α-D-mannopyranoside. [33]

Experimental Part

General remarks, see ref. 35. The 400 MHz ^{1}H-NMR and 100.61 MHz ^{13}C-NMR spectra were recorded on a Bruker ARX 400 spectrometer (Aspect X32/3 computer, 1.5 MBYTE max. acquisition memory). Double irradiation experiments for the selective proton-proton decouplings used a power of 40-50 dB. NOESY spectra were recorded with various "mixing time" (0.2, 0.4, 0.8, 1.0, 1.5 s). Usually the best spectra were obtained with a mixing time of 0.6 s. The NMR signal attributions were all confirmed by the double irradiation experiments, including the NOESY spectra. The 600 MHz ^{1}H-NMR spectra were recorded on a Bruker-AMX-600 spectrometer, RISC-CPU-R-3000 computer, 3 MBYTE max. aquisition memory.

*(+)-(1S,3S,4R,5R,6R)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galacto-pyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**11**) and *(+)-(1R,3R,4S,5S,6S)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-3-*endo*-[2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one* ((+)-**12**). A solution of acetobromo-D-galactose (**4**, 5.1 g, 12.27 mmol) in anh. benzene (24 ml) was heated under reflux. Enone (±)-**9**[27] (3 g, 9.44 mmol), Bu_3SnH (3.3 ml, 12.27 mmol) and AIBN (150 mg) in solution in anh. benzene (12 ml) was added through an automatic syringe in 90 min. The mixture was then heated under reflux for 30 min and allowed to cool to 20°C. KF (4 g) was added and the mixture was stirred at 20°C for 14 h. After solvent evaporation in vacuo, the residue was purified by flash chromatography on a column of silica gel (300 g, EtOAc/light petroleum 1:2) yielding first 0.51 g of **4**, 5 g of a mixture of C-galacto-sides (+)-**11**, (+)-**12**, **7**, **8** and 0.51 g (10%) of **15** + **16**. Analytical samples of (+)-**11** and (+)-**12** could be obtained by column chromatography (Lobar®, column type A Si60, 40-63 μm, EtOAc/light petroleum 1:2.5).

Characteristics of (+)-**11**: Colourless oil $[\alpha]_D^{26}$ = +24; $[\alpha]_{677}^{26}$ = +31.5; $[\alpha]_{546}^{26}$ = +41; $[\alpha]_{435}^{26}$ = +79; $[\alpha]_{405}^{26}$ = +93 (c = 1.0 $CHCl_3$). UV (CH_3CN): $\varepsilon_{(273)}$ = 1300, $\varepsilon_{(219)}$ = 5900. IR (KBr) ν: 1740, 1370, 1220, 1110, 1040 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 7.6-7.7 (m, 2 Harom.); 7.3-7.4 (m, 3 Harom.); 5.20 (dd, ^3J = 5.1, 3.3, H-C(4')); 5.13 (dd, ^3J = 5.8, 3.3, H-C(3')); 5.00 (dd, ^3J = 5.8, 3.0, H-C(2')); 4.92 (d, $^3J(H_{exo}$-C(3),H-C(4)) = 6.0, H-C(4)); 4.54 (dd, ^2J = 12.3, ^3J = 9.3, H-C(6')); 4.45 (d, ^3J(H-C(1),H-C(6)) = 4.7, H-C(1)); 4.30 (dd, ^3J = 4.7, 3.4, H-C(6)); 4.21 (m, H-C(1')); 4.05 (dd, ^2J = 12.3, ^3J = 3.5, H'-C(6')); 3.73 (m, H-C(5')); 3.69 (d, ^3J = 3.4, H-C(5)); 2.72 (m, H-C(3)); 2.05, 2.07, 2.08, 2.09 (4s, 4 Ac); 1.84 & 1.54 (2m, CH_2-C(3)). ^{13}C-NMR (100.61 MHz, CD_2Cl_2) δ_C: 206.9 (s), 170.78, 169.85, 169.82, 169.58 (4s), 134.7, 129.7, 128.8 (3d, ^1J(C,H) ≅ 161, H-Carom.); 87.3 (d, ^1J(C,H) = 168, C(4)); 83.3 (d, ^1J(C,H) = 170, C(1)); 71.1 (d, ^1J(C,H) =

148, C(5')); 69.4 (d, ^1J(C,H) = 152, C(2')); 68.8 (d, ^1J(C,H) = 145, C(1')); 67.5 (d, ^1J(C,H) = 155, C(3')); 66.3 (d, ^1J(C,H) = 150, C(4')); 60.1 (t, ^1J(C,H) = 148, C(6')); 58.8 (d, ^1J(C,H) = 167, C(6)); 51.7 (d, ^1J(C,H) = 132, C(3)); 47.3 (d, ^1J(C,H) = 152, C(5)); 25.8 (t, ^1J(C,H) = 129, CH_2-C(3)); 20.94, 20.88, 20.83, 20.77 (4q, ^1J(C,H) = 129, 4 Me); signal attributions confirmed by 2D(^{1}H-^{13}C)-COSY-spectrum. CI-MS (NH_3) m/z: 646 ($M^{+\bullet}$, 4), 453 (14), 344 (5), 310 (12), 245 (8), 158 (16), 78 (100). Anal. calcd. for $C_{27}H_{31}ClO_{11}Se$ (645.95): C 50.20, H 4.84; found: C 50.12, H 4.72.

Characteristics of (+)-**12**: colourless oil. $[\alpha]_D^{26}$ = +41; $[\alpha]_{577}^{26}$ = +44.5; $[\alpha]_{546}^{26}$ = +55; $[\alpha]_{435}^{26}$ = +99; $[\alpha]_{405}^{26}$ = +115 (c = 1.0 $CHCl_3$). UV (CH_3CN): $\varepsilon_{(273)}$ = 2800, $\varepsilon_{(216)}$ = 10600. IR (KBr) ν: 3440, 2980, 1740, 1370, 1220, 1110, 1050, 740 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 7.6-7.7 (m, 2 H); 7.3-7.4 (m, 3 H); 5.37 (dd, ^3J = 2.8, 2.7, H-C(4')); 5.18 (dd, ^3J = 9.1, 2.7, H-C(3')); 5.14 (dd, ^3J = 9.1, 4.6, H-C(2')); 4.89 (d, ^3J(H_{exo}-C(3),H-C(4)) = 5.0, H-C(4)); 4.51 (d, ^3J = 5.8, H-C(1)); 4.32 (dd, ^3J = 5.8, 3.2, H-C(6)); 4.22 (dd, ^2J = 10.8, ^3J = 7.1, H-C(6')); 4.0-4.12 (m, H-C(5'), H'-C(6')); 3.93 (m, H-C(1')); 3.47 (d, ^3J = 3.2, H-C(5)); 2.80 (m, H-C(3)); 2.22 & 1.38 (2m, ^2J = 15.4, H_2C-C(3)); 1.9-2.1 (4s, 4 Ac). ^{13}C-NMR (100.61 MHz, CD_2Cl_2) δ_C: 207.3, 170.2, 170.03 (3s); 135.2, 130.0, 129.1 (3d, ^1J(C,H) ≈ 162; CHarom.); 85.4 (d, ^1J(C,H) = 163, H-C(4)); 83.8 (d, ^1J(C,H) = 172, C(1)); 69.7 (d, ^1J(C,H) = 151, C(1')); 69.2 (d, ^1J(C,H) = 158, C(5')); 68.4 (d, ^1J(C,H) = 154, C(2')); 67.9 (d, ^1J(C,H) = 149, C(4')); 67.6 (d, ^1J(C,H) = 153, C(3')); 61.5 (t, ^1J(C,H) = 150, C(6')); 58.9 (d, ^1J(C,H) = 167, C(6)); 49.8 (d, ^1J(C,H) = 133, C(3)); 46.9 (d, ^1J(C,H) = 155, C(5)); 23.4 (t, ^1J(C,H) = 131, CH_2-C(3)); 20.9 (q, ^1J(C,H) = 130, Ac); signal attributions confirmed by 2D(^{1}H-^{13}C)-COSY-spectrum. CI-MS (NH_3) m/z: 646 ($M^{+\bullet}$, 8), 453 (5), 386 (18), 316 (16), 231 (17), 158 (51), 103 (18), 78 (100). Anal. calcd. for $C_{27}H_{31}ClO_{11}Se$ (645.95): C 50.20, H 4.84; found: C 50.06, H 4.81.

*Characteristics of the 1:1 mixture of (1S,3S,4S,6S)-6-*endo*-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one* (**15**) and *(1R,3R,4R,6R)-6-*endo*-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-one* (**16**). IR (KBr) ν: 1740, 1360, 1220, 1110, 1040 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6) of **15**, δ_H: 5.55 (t, ^3J = 3.0, H-C(4')); 5.40-5.52 (m, H-C(2'),H-C(3')); 4.75 (t, ^3J = 5.6, H-C(4)); 4.44 (dd, ^2J = 11.8, ^3J = 8.4, H-C(6')); 4.39 (m, H-C(1')); 4.17 (m, H-C(1)); 4.13 (dd, ^2J = 11.8, ^3J = 4.3, H'-C(6')); 3.94 (m, H-C(5')); 3.84 (m, H-C(6)); 2.58 (m, H-C(3)); 2.43 (m, H_{exo}-C(5)); 2.02 & 1.65 (2m, CH_2-C(3)); 1.84 (m, H_{endo}-C(5)); 1.6-1.7 (4s, 4 Ac). ^{1}H-NMR (400 MHz, C_6D_6) of **16**, δ_H: 5.40-5.52 (m, H-C(2'), H-C(3'), H-C(4')); 4.59 (t, ^3J = 5.4, H-C(4)); 4.32 (dd, ^2J = 11.2, ^3J = 8.0, H-C(6')); 4.16-4.25 (m, H-C(1), H-C(1')); 4.01 (dd, ^2J = 11.2, ^3J = 4.7, H'-C(6')); 3.75 (m, H-C(6)); 3.68 (m, H-C(5')); 2.82 (m, H-C(3)); 2.48 & 1.54 (2m, CH_2-C(3)); 1.93 (m, H_{exo}-C(5)); 1.6-1.8 (4s, 4 Ac); 1.54 (m, H_{endo}-C(5)). ^{13}C-NMR (100.61 MHz, $CDCl_3$) of **15**, δ_C: 207.4, 170.5, 169.8, 169.6, 169.5 (5s), 82.0 (d, ^1J(C,H) = 171), 80.1 (d, ^1J(C,H) = 163), 70.4 (d ^1J(C,H) = 147), 69.5 (d, ^1J(C,H) = 149), 68.3 (d, ^1J(C,H) = 147), 67.3 (d, ^1J(C,H) = 149), 66.6 (d, ^1J(C,H) = 149), 60.6 (t, ^1J(C,H) = 149), 50.9 & 50.8 (2d, ^1J(C,H) = 135), 34.6 (t, ^1J(C,H) = 135), 24.1 (t, ^1J(C,H) = 137), 20.6 (4q, ^1J(C,H) = 130). ^{13}C-NMR (100.61 MHz, $CDCl_3$) of **16**, δ_C: 207.9, 170.3, 169.8, 169.7, 169.4 (5s), 82.3 (d, ^1J(C,H) = 171); 78.8 (d, ^1J(C,H) = 163); 69.4 (d, ^1J(C,H) = 148); 68.4 (2d, ^1J(C,H) = 147), 67.4 (2d, ^1J(C,H) = 148); 61.2 (t, ^1J(C,H) = 150); 50.9 (d, ^1J(C,H) = 135); 48.5 (d, ^1J(C,H) = 133); 34.4 & 22.8 (2t, ^1J(C,H) = 132), 20.6 (4q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 508 (M+17, 4), 491 ($M^{+\bullet}$, 2), 431 (2), 386 (8), 269 (1), 205 (3), 169 (10), 84 (100). Anal. calc. for $C_{21}H_{27}O_{11}Cl$ (490.9): C 51.38, H 5.54; found: C 51.35, H 5.52.

*Mixture of (1S,3S,4R)-6-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**18**) and *(1R,3R,4S)-6-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]hept-5-en-2-one* (**19**). This mixture was prepared according to the procedure described for the preparation of (+)-**11** and (+)-**12**, starting with **4** (0.68 g, 1.65 mmol) in PhH (8 ml), Bu_3SnH (0.44 ml, 1.65 mmol), AIBN (20 mg) and **17**[27] (0.2 g, 1.27 mmol) in anh. PhH (4 ml). Column chromatography on silica gel (EtOAc/CH_2Cl_2 1:10) gave 101 mg (16%) of a 1:1 mixture of **18** and **19** that could not be separated.

Characteristics of **18**: IR (KBr) ν: 1745, 1360, 1220, 1050 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 6.63 (d, ^3J = 1.9, H-C(5)); 5.33-5.45 (m, H-C(4), H-C(4')); 5.13 (m, 2 H, H-C(3'), H-C(2')); 4.54 (m, H-C(6')); 4.50 (d, ^4J (H-C(1),H-C(4)) = 1.0, H-C(1)); 4.38 (dd, ^2J = 11.6, ^3J = 7.8, H-C(6')); 4.31 (m, H-C(1')); 4.22-4.00 (m, H-C(5')); 2.41 (m, H-C(3)); 2.2-2.0 (4s, 4 Ac); 1.9 & 1.28 (2m, CH_2-C(3)); ^{13}C-NMR (100.61 MHz, CD_2Cl_2) δ_C: 206.8, 170.7, 170.2, 169.9, 169.8 (5s), 136.1 (s), 134.5 (d, ^1J(C,H) = 182), 85.4 (d, ^1J(C,H) = 176); 83.7 (d, ^1J(C,H) = 173); 71.3 (d, ^1J(C,H) = 146); 70.3 (d, ^1J(C,H) = 147); 68.9, 67.8, 67.0 (3d, ^1J(C,H) = 146); 61.1 (t, ^1J(C,H) = 149); 40.4 (d, ^1J(C,H) = 135); 29.2 (t, ^1J(C,H) = 128); 20.8 (q, ^1J(C,H) = 130).

Characteristics of **19**: ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 6.54 (d, ^3J = 1.9, H-C(5)); 5.36 (m, H-C(4)); 5.33-5.45 (m, H-C(4')); 5.20 (m, H-C(2'), H-C(3')); 4.54 (d, ^4J = 1.0, H-C(1)); 4.22-4.00 (m, H-C(1'), H-C(5'),H_2-C(6')); 2.53 (m, H-C(3)); 2.24 & 1.02 (2m, CH_2-C(3)); 2.2-2.0 (4s, 4 Ac). ^{13}C-NMR (100.61 MHz, CD_2Cl_2) δ_C: 207.5, 170.8, 170.1, 170.0, 169.9 (5s); 136.8 (s); 133.3 (d, ^1J(C,H) = 182); 85.9 (d, ^1J(C,H) = 176); 82.5 (d, ^1J(C,H) = 170); 69.3 (d, ^1J(C,H) = 147); 68.9 (d, ^1J(C,H) = 146); 68.7 (d, ^1J(C,H) = 150); 67.9, 67.6 (2d, ^1J(C,H) = 146); 61.4 (t, ^1J(C,H) = 150); 40.8 (d, ^1J(C,H) = 135); 28.2 (t, ^1J(C,H) = 129); 20.8 (q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 489 ($M^{+\bullet}$, 11), 427 (7), 386 (100), 266 (8), 210 (19), 169 (24), 98 (51), 73 (57). Anal. calc. for $C_{21}H_{25}ClO_{11}$ (488.90): C 51.59, H 5.15; found: C 51.48, H 5.15.

*(+)-(1S,2R,3S,4R,5R,6R)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo[2.2.1]heptan-2-*endo*-ol* ((+)-**20**) and *(+)-(1R,2S,3R,4S,5S,6S)-5-*exo*-(Benzeneselenyl)-6-*endo*-chloro-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo-[2.2.1]heptan-2-*endo*-ol* ((+)-**21**). $NaBH_4$ (90 mg, 2.35 mmol) was added to a solution of the 1:1 mixture of (+)-**11** and (+)-**12** obtained above (0.5 g, 0.77 mmol) in THF/MeOH 1:1 (20 ml) cooled to 0°C. After stirring at 0°C for 10 min, the mixture was neutralized with 10% aq. HCl and extracted with CH_2Cl_2 (25 ml). The organic extract was washed with H_2O (25 ml) and then with brine (25 ml, twice). The combined aqueous phases were extracted with CH_2Cl_2 (25 ml, 3 times). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated in vacuo. The residue was purified and separated by flash column chromatography on silica gel (60 mg, CH_2Cl_2/EtOAc 5:1) giving 0.22 g (44%) of (+)-**21** and 0.25 g (50%) of (+)-**20**.

Characteristics of (+)-**20**: yellow crystals, m.p. 61-67°C (dec.). $[\alpha]_D^{27}$ = +33.7; $[\alpha]_{577}^{27}$ = +35.6; $[\alpha]_{546}^{27}$ = +43.3; $[\alpha]_{436}^{27}$ = +76.3; $[\alpha]_{405}^{27}$ = +86.5 (c = 1.2, $CHCl_3$). IR (KBr) ν: 3500, 1740, 1370, 1220, 1040 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 7.75-7.85 (m, 2 H); 7.30-7.40 (m, 3 H); 5.26 (m, H-C(4')); 5.16 (dd, ^3J = 6.8, 3.1, H-C(3')); 5.07 (dd, ^3J = 6.8, 4.1, H-C(2')); 4.62 (d, ^3J = 5.6, H-C(4)); 4.48 (m, H-C(1), H-C(2), H-C(6')); 4.31 (m, H-C(6)), 4.22 (m, H-C(1')); 4.05 (dd, ^2J = 12.4, ^3J = 4.1, H'-C(6')); 3.85 (m, H-C(5')); 3.71 (d, ^3J = 4.9, H-C(5)); 2.70 (d, $^3J \equiv 8$, OH), 2.48 (m, H-C(3)), 2.0-2.2 (4s, 4 Ac); 1.76 & 1.50 (2m, CH_2-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.5, 169.6, 169.5, 169.4 (4s), 134.6 (d, ^1J(C,H) = 170); 129.2 (d, ^1J(C,H) = 167);

128.3 (s); 128.1, 89.1 (2d, ^1J(C,H) = 167); 78.3 (d, ^1J(C,H) = 159); 72.9 (d, ^1J(C,H) = 156); 69.5 (d, ^1J(C,H) = 155); 69.2 (d, ^1J(C,H) = 150); 68.9 (d, ^1J(C,H) = 166); 67.2 (d, ^1J(C,H) = 162); 66.4 (d, ^1J(C,H) = 165); 62.7 (d, ^1J(C,H) = 162); 60.2 (t, ^1J(C,H) = 149); 46.8 (d, ^1J(C,H) = 150); 40.7 (d, ^1J(C,H) = 135); 22.5 (t, ^1J(C,H) = 124); 20.50-20.75 (4q, ^1J(C,H) = 129). CI-MS (NH_3) m/z: 648 ($M^{+\bullet}$, 17), 595 (2), 455 (19), 395 (8), 312 (68), 234 (10), 157 (14), 78 (100). Anal. calc. for $C_{27}H_{33}ClO_{11}Se$ (647.97): C 50.05, H 5.13; found: C 50.01, H 5.17.

Characteristics of (+)-**21**: yellow crystals, m.p. 79-85°C (dec.). $[\alpha]_D^{27}$ = +41.2; $[\alpha]_{577}^{27}$ = +43; $[\alpha]_{546}^{27}$ = +53; $[\alpha]_{435}^{27}$ = +100; $[\alpha]_{405}^{27}$ = +119 (c = 0.92, $CHCl_3$). IR (KBr) ν: 3490, 1740, 1370, 1220 cm-1. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ_H: 7.65 (m, 2 H); 7.35 (m, 3 H); 5.39 (dd, ^3J = 3.6, 3.5, H-C(4')); 5.20 (dd, ^3J = 7.5, 3.5, H-C(3')); 5.11 (dd, ^3J = 7.5, 4.0, H-C(2')); 4.52 (d, ^3J = 5.5, H-C(4)); 4.47 (m, H-C(6'), H-C(2), H-C(1)); 4.25 (m, H-C(5')); 4.20 (m, H-C(6)); 4.05 (m, H-C(1'), H-C(6')); 3.49 (d, ^3J = 5.4, H-C(5)); 2.94 (d, ^3J = 5, OH); 2.37 (m, H-C(3)); 2.02-2.20 (4s, 4 Ac), 2.00 & 1.78 (2m, CH_2-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.7, 169.8, 169.6, 169.3, 138.8 (5s); 127.7 (d, ^1J(C,H) = 178); 83.6 (d, ^1J(C,H) = 174); 83.2 (d, ^1J(C,H) = 173); 70.7 (d, ^1J(C,H) = 172); 70.3 (d, ^1J(C,H) = 169); 70.0 (d, ^1J(C,H) = 167); 69.2 (d, ^1J(C,H) = 172); 67.5 (d, ^1J(C,H) = 165); 66.3 (d, ^1J(C,H) = 167); 60.1 (t, ^1J(C,H) = 148); 41.7 (d, ^1J(C,H) = 135); 24.0 (t, ^1J(C,H) = 127); 20.7-20.5 (4q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 648 ($M^{+\bullet}$, 7), 455 (3.8), 395 (7), 314 (39), 236 (43), 188 (11), 157 (53), 117 (17), 78 (100). Anal. calc. for $C_{27}H_{33}ClO_{11}Se$ (647.97): C 50.05, H 5.13; found: C 50.04, H 5.16.

*(+)-(1*R*,2*S*,3*R*,4*S*)-6-Chloro-3*-endo-*[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo-[2.2.1]hept-5-en-2*-endo-*ol* ((+)-**22**). A solution of mCPBA (75% 3-$ClC_6H_4CO_3H$ in 3-$ClC_6H_4CO_2H$, 371 mg) in anh. CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of (+)-**21** (1.17 g, 1.8 mmol) in anh. CH_2Cl_2 (30 ml) cooled to -78°C in 30 min. After stirring at -75°C for 3 h, the mixture was allowed to warm up to 20°C in 10 h. CH_2Cl_2 (50 ml) was added and the solution was washed with sat. aq. soln. of $NaHCO_3$ (50 ml). The aqueous phase was extracted with CH_2Cl_2 (50 ml, 3 times). The combined org. phases were washed with brine (50 ml) and dried ($MgSO_4$). After solvent evaporation in vacuo the residue was purified by flash column chromatography on silica gel (120 g, CH_2Cl_2/EtOAc 1:5), yielding 0.87 g (98%), colourless crystals, m.p. 61-67°C (dec.). $[\alpha]_D^{27}$ = +61; $[\alpha]_{577}^{27}$ = +64; $[\alpha]_{546}^{27}$ = +75; $[\alpha]_{435}^{27}$ = +133; $[\alpha]_{405}^{27}$ =+157 (c = 1.3, $CHCl_3$). IR (KBr) ν: 1740, 1370, 1220, 1050 cm-1. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 6.21 (d, ^3J = 2.0, H-C(5)); 5.37 (dd, ^3J = 3.3, 3.2, H-C(4')); 5.18 (dd, ^3J = 6.8, 3.2, H-C(3')); 5.08 (dd, ^3J = 6.8, 3.5, H-C(2')); 4.81 (m, H-C(4)); 4.74 (d, ^3J = 4.4, H-C(1)); 4.63 (dd, ^2J = 12.1, ^3J = 9.0, H-C(6')); 4.53 (m, H-C(2)); 4.20-4.30 (m, H-C(1'), H-C(5')); 4.03 (dd, ^2J = 12.1, ^3J = 3.9, H'-C(6')); 3.0 (d, ^3J = 3, OH); 2.28 (m, H-C(3)); 2.12, 2.11, 2.10, 2.09 (4s, 4 Ac); 1.58 & 1.25 (2m, CH_2-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.8, 169.8, 169.6, 169.3, 138.9 (5s); 127.8 (d, ^1J(C,H) = 179); 83.6, 83.3 (2d, ^1J(C,H) = 173); 70.7, 70.5 (2d, ^1J(C,H) = 168); 70.1 (d, ^1J(C,H) = 170), 69.3 (d, ^1J(C,H) = 167); 67.5 (d, ^1J(C,H) = 170); 66.3 (d, ^1J(C,H) = 165); 60.0 (t, ^1J(C,H) = 144); 42.0 (d, ^1J(C,H) = 136); 24.2 (t, ^1J(C,H) = 127); 20.7, 20.6 (2q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 491 ($M^{+\bullet}$, 8), 473 (5), 431 (3), 389 (6), 328 (25), 297 (8), 251 (15), 226 (6), 148 (14), 102 (100), 75 (30). Anal. calc. for $C_{21}H_{27}ClO_{11}$ (490.90): C 51.38, H 5.54; found: C 51.24, H 5.55.

*(+)-(1*R*,2*S*,3*R*,4*S*)-6-Chloro-3*-endo-*[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo-[2.2.1]hept-5-en-2*-endo-*yl Acetate* ((+)-**23**). A mixture of (+)-**22** (0.87 g, 1.77 mmol), anh. pyridine (10 ml),

Ac_2O (0.85 ml, 8.8 mmol) and 4-(dimethylamino)pyridine (10 mg) was stirred at 20°C for 15 h. The solvent was evaporated in vacuo and the residue washed with toluene several times. Purification by flash column chromatography on silica gel (120 g, CH_2Cl_2/EtOAc 1:1) gave 905 mg (95%), colourless crystals, m.p. 62-63°C (dec.). $[\alpha]_D^{24}$ = +47; $[\alpha]_{577}^{24}$ = +49; $[\alpha]_{546}^{24}$ = +59; $[\alpha]_{435}^{24}$ = +105; $[\alpha]_{405}^{24}$ = +123 (c = 1.07, $CHCl_3$). UV (CH_3CN): $\varepsilon_{(218)}$ = 1400. IR (KBr) ν: 1750, 1370, 1230, 1100 cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$) δ_H: 6.21 (d, ^3J = 2.0, H-C(5)); 5.38 (t, ^3J = 2.4, H-C(4')); 5.10-5.30 (m, H-C(2'), H-C(3'), H-C(2)); 4.95 (m, H-C(4)); 4.25 (m, H-C(6')); 4.17 (m, H-C(1')); 4.05 (m, H-C(5'), H-C(6')); 2.54 (m, H-C(3)); 2.11, 2.07, 2.04, 2.03, 2.01 (5s, 5 Ac); 1.73 & 1.00 (2m, CH_2-C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ_C: 170.6, 170.5, 169.9, 169.9, 169.8, 169.8 (5s); 137.9 (s), 128.3 (d, ^1J(C,H) = 178); 82.1 (d, ^1J(C,H) = 166); 81.8 (d, ^1J(C,H) = 171); 71.0 (d, ^1J(C,H) = 161); 70.0 (d, ^1J(C,H) = 151); 68.5, 68.4 (2d, ^1J(C,H) = 155); 67.6 (d, ^1J(C,H) = 150); 67.3 (d, ^1J(C,H) = 152); 61.2 (t, ^1J(C,H) = 149); 38.1 (d, ^1J(C,H) = 137); 23.3 (t, ^1J(C,H) = 127); 20.7, 20.6, 20.5 (3q, ^1J(C,H) = 123). CI-MS (NH_3) m/z: 550 (21), 533 ($M^{+\cdot}$, 9), 473 (31), 413 (14), 370 (22), 331 (99), 268 (62), 251 (19), 225 (12), 169 (20), 109 (100), 81 (84). Anal. calc. for $C_{23}H_{29}ClO_{12}$ (532.93): C 51.84, H 5.48; found: C 51.73, H 5.44.

*(+)-(1R,2S,3S,4S,5S)-6-Oxo-3-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-7-oxabicyclo-[2.2.1]hept-2-*endo*,5-*exo*-diyl Diacetate* ((+)-**24**). Me_3NO (67 mg, 0.6 mmol) in THF/H_2O 5:1 (2 ml) was added dropwise to a stirred solution of (+)-**23** (160 mg, 0.3 mmol), $NaHCO_3$ (90 mg, 1.2 mmol), and 0.156 molar soln. of OsO_4 in CCl_4 (0.02 ml), THF/H_2O 5:1 (2 ml). After stirring at 20°C for 2 h, EtOAc (20 ml) was added and the solution was washed with a sat. aq. soln. of $NaHSO_3$ (20 ml, 3 times), than with brine (20 ml, twice). The combined aq. phases were extracted with EtOAc (25 ml, twice). The combined org. phases were dried ($MgSO_4$). After solvent evaporation in vacuo, the residue was dissolved in anh. pyridine (5 ml) and Ac_2O (0.2 ml) and 4-(Me_2N)C_5H_4N (5 mg) were added. After stirring at 20°C for 14 h, the solvent was evaporated in vacuo and the residue washed with toluene. Purification by flash column chromatography on silica gel (50 g, CH_2Cl_2/EtOAc 5:1) yielded 148 mg (86%), colourless crystals, m.p. 66-75°C (dec.). $[\alpha]_D^{24}$ = +28.3; $[\alpha]_{577}^{24}$ = +29; $[\alpha]_{546}^{24}$ = +35; $[\alpha]_{435}^{24}$ = +43 (c = 1.1, $CHCl_3$). UV (CH_3CN): $\varepsilon_{(279)}$ = 2000. IR (KBr) ν: 1780, 1740, 1370, 1220 cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$) δ_H: 5.40 (t, ^3J = 3.4, H-C(4')); 5.24 (m, H-C(1), H-C(2')); 5.18 (dd, ^3J = 7.5, 3.4, H-C(3')); 4.75 (s, H-C(5)); 4.65 (d, ^3J = 5.5, H-C(4), H-C(2)); 4.36-4.46 (m, H-C(1'), H-C(6')); 4.08-4.17 (m, H-C(5'), H'-C(6')); 2.73 (m, H-C(3)); 2.15, 2.11, 2.10, 2.08, 2.05, 2.03 (6s, 6 Ac); 1.87 & 1.50 (2m, CH_2-C(3)). ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ_C: 201.3, 170.6, 170.5, 169.8, 169.7, 169.6, 169.5 (7s); 82.6 (d, ^1J(C,H) = 165); 80.7 (d, ^1J(C,H) = 171); 70.4 (d, ^1J(C,H) = 168); 69.9 (d, ^1J(C,H) = 164), 68.6, 68.1 (2d, ^1J(C,H) = 165); 67.6 (d, ^1J(C,H) = 167); 66.6 (d, ^1J(C,H) = 164); 60.7 (t, ^1J(C,H) = 150); 38.7 (d, ^1J(C,H) = 137); 22.3 (t, ^1J(C,H) = 103); 20.6-20.5 (6q, ^1J(C,H) = 126). CI-MS (NH_3) m/z: 573 ($M^{+\cdot}$, 7), 530 (5), 425 (9), 366 (7), 212 (14), 170 (21), 97 (32), 71 (100). Anal. calc. for $C_{25}H_{32}O_{15}$ (572.52): C 52.45, H 5.63; found: C 52.50, H 5.70.

*(-)-(1S,4S,5S,6S,7S)-3-Oxo-6-*endo*-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-2,8-dioxabi-cyclo[3.2.1]octa-4-*exo*,7-endo-diyl Diacetate* ((-)-**25**). A mixture of (+)-**24** (110 mg, 0.19 mmol), $NaHCO_3$ (20 mg), mCPBA (80%, 48 mg, 0.19 mmol) and anh. CH_2Cl_2 (5 ml) was stirred at 20°C for 14 h. CH_2Cl_2 (20 ml) was added and the mixture washed with sat. aq. soln. of $NaHCO_3$ (25 ml, twice), than with brine (25 ml, twice). The combined aq. phases were extracted with CH_2Cl_2 (25 ml, 3 times). The combined org. phases were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was purified by flash column chromato-

graphy on silica gel (50 g, CH_2Cl_2/EtOAc 5:1) yielding 105 mg (93%), colourless crystals, m.p. 85-90°C (dec.). $[\alpha]_D^{24}$ = -20.3; $[\alpha]_{577}^{24}$ = -21; $[\alpha]_{546}^{24}$ = -22.4; $[\alpha]_{435}^{24}$ = -35.3; $[\alpha]_{405}^{24}$ = -46 (c = 1.4, $CHCl_3$). IR (KBr) ν: 1750, 1370, 1230, 1100 cm-1. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 6.10 (d, ^3J = 4.2, H-C(1)); 5.40 (t, ^3J = 3.6, H-C(4')); 5.18-5.30 (m, H-C(2'), H-C(3')); 5.15 (dd, ^3J = 9.3, 4.2, H-C(7)); 4.52 (d, ^3J = 6.6, H-C(5)); 4.46 (dd, ^2J = 11.8, ^3J = 8.4, H-C(6)); 4.33 (m, H-C(1')); 4.14 (m, H-C(5')); 4.07 (dd, ^2J = 11.8, ^3J = 4.1, H-C(6')); 2.73 (m, H-C(6)); 2.17, 2.14, 2.12, 2.10, 2.09, 2.08, 2.04 (6s, 6 Ac); 1.94 & 1.67 (2m, CH_2-C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.5, 169.77, 169.7, 169.6 (4s); 163.0 (s), 100.4 (d, ^1J(C,H) = 185); 80.7, 72.8, 69.9, 68.3 (4d, ^1J(C,H) ≡ 168); 68.0 (d, ^1J(C,H) = 166), 67.4 (d, ^1J(C,H) = 168); 67.0 (d, ^1J(C,H) = 170); 66.5 (d, ^1J(C,H) = 171); 60.6 (t, ^1J(C,H) = 147); 37.7 (d, ^1J(C,H) = 134); 21.8 (t, ^1J(C,H) = 132); 20.7-20.3 (6q, ^1J(C,H) = 127). CI-MS (NH_3) m/z: 606 (100), 589 ($M^{+\cdot}$, 23), 548 (7), 456 (15), 350 (23), 273 (10), 169 (8), 97 (23). Anal. calc. for $C_{25}H_{32}O_{16}$ (588.52): C 51.02, H 5.48; found: C 51.10, H 5.52.

Methyl {Methyl 2,4-di-O-Acetyl-3-deoxy-3-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-α- and -β-D-mannopyranosid}uronate (**26α** + **26β**) and *Methyl {Methyl 2,4-di-O-acetyl-3-deoxy-3-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-α- and -β-D-mannofuranosid}uronate* (**27α** + **27β**). Freshly distilled $SOCl_2$ (0.11 ml, 1.53 mmol) was added dropwise to a stirred solution of (-)-**25** (150 mg, 0.25 mmol) in anh. MeOH (3 ml) cooled to 0°C. After stirring at 20°C for 18 h, the solvent was evaporated in vacuo. The residue was dissolved in pyridine (3 ml), then Ac_2O (0.7 ml) and DMAP (10 mg) were added. After stirring at 20°C for 14 h, the solvent was evaporated in vacuo and the residue taken with toluene. The solvent was evaporated in vacuo (3 times). The residue was purified by filtration through a pad of silica gel (10 g, EtOAc) and then by column chromatography on silica gel (Lobar®, column type A, EtOAc/light petroleum 1:2) yielding 99 mg (62%) of **26α** + **26β** and 12 mg (7%) of **27α** +**27β**.

Characteristics of **26α** + **26β** (9:1): colourless oil. IR (KBr) ν: 1730, 1440, 1370, 1220, 1020 cm-1. ^{1}H-NMR (400 MHz, C_6D_6) of **26α**, δ_H: 5.80 (t, ^3J = 10.0, H-C(4)); 5.58 (dd, ^3J = 9.1, ^3J = 5.3, H-C(2')); 5.50 (t, ^3J = 3.3, H-C(4')); 5.47 (dd, ^3J = 9.1, 3.3, H-C(3')); 5.22 (m, H-C(2)); 4.83 (d, ^3J = 1.3, H-C(1)); 4.61 (m, H-C(1')); 3.72 (dd, ^2J = 11.2, ^3J = 8.2, H-C(6')); 4.41 (d, ^3J = 10.0, H-C(5)); 4.06 (dd, ^2J = 11.5, ^3J = 4.3, H'-C(6')); 3.91 (m, H-C(5')); 3.39 (s, MeOOC); 2.98 (s, MeO); 2.74 (m, H-C(3)); 1.99 (m, CH_2-C(3)); 1.88, 1.86, 1.75, 1.70, 1.56, 1.55 (6s, 6 Ac). ^{13}C-NMR (100.61 MHz, C_6D_6) of **26α**, δ_C: 171, 170.7, 170.5, 170.4, 170.2, 169.9, 169.3 (7s); 98.2 (d, ^1J(C,H) = 170); 73.1, 72.7, 71.1, 70.4, 69.7, 69.5, 68.5 (7d, ^1J(C,H) = 152-154); 62.3 (t, ^1J(C,H) = 148); 55.3 (q, ^1J(C,H) = 143); 52.4 (q, ^1J(C,H) = 147); 36.3 (d, ^1J(C,H) = 169); 25.5 (t, ^1J(C,H) = 126); 20.7 (6q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 652 (M+18, 73), 603 (84), 543 (9), 515 (46), 455 (100), 412 (25), 350 (9), 251 (7), 145 (5), 105 (15). Anal. calc. for $C_{27}H_{38}O_{17}$ (643.59): C 51.10, H 6.04; found: C 51.14, H 6.12.

Characteristics of **27α** + **27β** (α:β 10:1). Colourless oil. IR (KBr) ν: 1740, 1440, 1370, 1220, 1040 cm-1. ^{1}H-NMR (400 MHz, C_6D_6) of **27α**, δ_H: 5.65 (t, ^3J = 9.5, H-C(4)); 5.5-5.6 (m, H-C(2'), H-C(2), H-C(3'), H-C(4')); 4.70 (m, H-C(1')); 4.56 (dd, ^2J = 10.7, ^3J = 6.7, H-C(6')); 4.25 (m, H-C(5'), H'-C(6')); 4.14 (s, H-C(1)); 3.95 (d, ^3J = 9.5, H-C(5)); 3.40 (s, MeOOC); 3.21 (s, MeO); 2.29 (m, H-C(3)); 2.08 & 1.98 (2m, H_2C-C(3)); 1.89, 1.80, 1.74, 1.73, 1.69, 1.65 (6s, 6 Ac). ^{13}C-NMR (100.61 MHz, C_6D_6) of **27α**, δ_C: 170.4, 170.0, 169.9, 169.4, 169.1, 168.1 (6s), 101.4 (d, ^1J(C,H) = 158, C(1)); 76.0 (d, ^1J(C,H) = 146, C(5)); 71.7 (d, ^1J(C,H) = 164, C(1')); 69.3, 69.2, 69.1, 68.5, 68.2 (5d, ^1J(C,H) = 140, C(2), C(2'), C(3'), C(4), C(4')); 61.2 (t, ^1J(C,H) =

150, C(6')); 56.6 (q, ^1J(C,H) = 139), 51.9 (q, ^1J(C,H) = 148); 39.8 (d, ^1J(C,H) = 127, C(3)); 25.0 (t, ^1J(C,H) = 128); 20.2 (6q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 652 (M+18, 50), 603 (67), 543 (11), 515 (52), 455 (100), 412 (35), 339 (15), 279 (8), 225 (8), 97 (23). Anal. calc. for $C_{27}H_{38}O_{17}$ (643.59): C 51.10, H 6.04; found: C 51.21, H 6.21.

(+)-Methyl 3-Deoxy-3-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-2,4,6-tri-O-acetyl-α-D-mannopyranoside ((+)-**28**). $LiAlH_4$ (140 mg, 3.7 mmol) was added portionswise to a stirred solution of **26α** + **26β** (168 mg, 0.26 mmol) in anh. THF cooled to 0°C. After stirring at 20°C for 3 h 3% aq. soln. of HCl was added until pH=3 at 0°C. The solvent was evaporated in vacuo at 60°C until dryness. Pyridine (5 ml), Ac_2O (1 ml) and DMAP (10 mg) were added and the mixture stirred at 20°C for 14 h. The solvent was evaporated in vacuo and the residue taken with toluene which was evaporated to dryness (3 times). The residue was purified by filtration through a pad of silica gel (EtOAc) and then by column chromatography (Lobar®, column type B, EtOAc/light petroleum 2:1) yielding 122 mg (71%), colourless crystals; m.p. 69-71°C (dec.). $[\alpha]_D^{25}$ = +62; $[\alpha]_{577}^{25}$ = +64; $[\alpha]_{546}^{25}$ = +76; $[\alpha]_{435}^{25}$ = +132; $[\alpha]_{405}^{25}$ = +154 (c = 1.35, $CHCl_3$). IR (KBr) ν: 1740, 1370, 1220 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6) δ_H: 5.58 (dd, ^3J = 9.0, 5.3, H-C(2')); 5.54-5.40 (m, H-C(3'), H-C(4), H-C(4')); 5.23 (s, H-C(2)); 4.77 (s, H-C(1)); 4.55 (m, H-C(1')); 4.47 (dd, ^2J = 11.4, ^3J = 8.2, H-C(6')); 4.42 (dd, ^2J = 12.1, ^3J = 4.9, H-C(6)); 4.11 (m, H-C(6), H-C(6')); 3.99 (m, H-C(5')); 3.85 (m, H-C(5)); 3.03 (s, MeO); 2.68 (m, H-C(3)); 2.02 & 1.89 (2m, CH_2-C(3)); 1.89, 1.87, 1.79, 1.78, 1.75, 1.65, 1.61 (7s, 7 Ac). ^{13}C-NMR (100.61 MHz, C_6D_6) δ_C: 171.1, 170.9, 170.5, 170.4, 170.2, 169.9 (6s); 98.1 (d, ^1J(C,H) = 173, C(1)); 73.7 (d, ^1J(C,H) = 153); 72.8 (d, ^1J(C,H) = 149); 69.9, 69.7, 69.5, 68.58, 68.52 (5d, ^1J(C,H) = 152-153); 63.2 (t, ^1J(C,H) = 148); 62.4 (t, ^1J(C,H) = 150); 54.9 (q, ^1J(C,H) = 140); 36.5 (d, ^1J(C,H) = 130, C(3)); 25.4 (t, ^1J(C,H) = 127); 21.0, 20.8, 20.7, 20.4 (4s, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 666 (M+18, 100); 617 (95), 557 (10), 529 (55), 496 (23), 468 (69), 443 (59), 369 (7), 331 (23), 196 (7), 81 (24). Anal. calc. for $C_{28}H_{40}O_{17}$ (648.62): 51.85, H 6.22; found: C 51.86, H 6.09.

(+)-Methyl 3-Deoxy-3-[(α-D-galactopyranosyl)methyl]-α-D-mannopyranoside (**1**). A mixture of (+)-**28** (90 mg, 0.138 mmol), anh. K_2CO_3 (268 mg, 1.9 mmol) and 1:1 MeOH/H_2O (4 ml) was stirred at 20°C for 3 h. After solvent evaporation the residue was purified by column chromatography on DOWEX 500 W 4X 200-400 mesh/Ca++ (H_2O) yielding 38 mg (77%), colourless oil. $[\alpha]_D^{23}$ = +49.6; $[\alpha]_{577}^{23}$ = +58.4; $[\alpha]_{546}^{23}$ = +72; $[\alpha]_{435}^{23}$ = +127; $[\alpha]_{405}^{23}$ = +147 (c = 0.75, MeOH). IR (film) ν: 3400, 1660, 1630 cm^{-1}. ^{1}H-NMR (600 MHz, CD_3OD) δ_H: 4.57 (d, ^3J = 1.5, H-C(1)); 4.16 (m, H-C(1')); 4.0 (t, ^3J = 2.3, H-C(2)); 3.95-3.83 (m, H-C(2'), H-C(6'), H-C(6), H-C(4'), H-C(5')); 3.73 (dd, ^3J = 11.7, 5.9, H-C(6)); 3.70-3.66 (m, H-C(3'), H-C(6')); 3.55 (m, H-C(5)); 3.47 (t, ^3J = 10, H-C(4)); 3.43 (s, OMe); 2.15 (m, HproR-CH_2-C(3)); 1.93 (m, H-C(3)); 1.82 (m, HproS-CH_2-C(3)). ^{13}C-NMR (100.61 MHz, CD_3OD) δ_C: 102.2 (d, ^1J(C,H) = 169); 76.7 (d, ^1J(C,H) = 148); 75.2 (d, ^1J(C,H) = 145); 74.2 (d, ^1J(C,H) = 140); 72.0 (d, ^1J(C,H) = 142), 70.4, 70.3, 70.2 (3d, ^1J(C,H) = 159); 67.6 (d, ^1J(C,H) = 144); 63.2, 62.5 (2t, ^1J(C,H) = 142); 55.0 (q, ^1J(C,H) = 142); 42.6 (d, ^1J(C,H) = 127); 22.5 (t, ^1J(C,H) = 126). CI-MS (NH_3) m/z: 372 (M+17, 61), 355 ($M^{+\bullet}$, 78), 337 (13), 323 (51), 287 (23), 236 (100), 134 (47), 97 (63), 74 (80). MS [electrospray, LiCl]: 361 (M+ +Li, 100), 329 (32). Anal. calc. for $C_{14}H_{26}O_{10}$ (354.36): C 47.45, H 7.40; found: C 47.30, H 7.38.

(+)-3-Deoxy-3-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-1,2,4,5,6-penta-O-acetyl-D-mannitol ((+)-**29**). A mixture of (-)-**25** (100 mg, 0.165 mmol), anh. K_2CO_3 (10 mg) and anh. MeOH (4 ml) was

stirred at 20°C for 30 min. The soln. was cooled to 0°C and $NaBH_4$ (80 mg, 2.3 mmol) was added. After stirring at 20°C for 2 h 45 min the solvent was evaporated in vacuo and the residue taken with 1 N HCl (2 ml). After stirring at 40°C for 14 h, the solvent was evaporated in vacuo to dryness and pyridine (2 ml), Ac_2O (0.2 ml) and DMAP (5 mg) were added. After stirring at 20°C for 14 h, the solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel (30 g, EtOAc/light petroleum 1:1) yielding 64 mg (53%), colourless crystals, m.p. 82-83°C. $[\alpha]_D^{24}$ = +66.5; $[\alpha]_{577}^{24}$ = +72.5; $[\alpha]_{546}^{24}$ = +87; $[\alpha]_{435}^{24}$ = +155; $[\alpha]_{405}^{24}$ = +183 (c = 1.0, $CHCl_3$). IR (KBr) ν: 1740, 1360, 1220, 1040 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6) δ_H: 5.73 (dd, ^3J = 7.1, 4.2, H-C(4)); 5.67 (t, ^3J = 3.3, H-C(4')); 5.57-5.43 (m, H-C(2), H-C(2'), H-C(3'), H-C(5)); 4.76 (dd, ^2J = 12.1, ^3J = 3.4, H-C(6)); 4.65 (dd, ^2J = 11.1, ^3J = 7.3, H-C(6')); 4.55 (m, H-C(1')); 4.45 (dd, ^2J = 12.4, ^3J = 2.9, H-C(1)); 4.30-4.21 (m, H-C(1), H-C(5'), H-C(6')); 4.18 (dd, ^2J = 12.1, ^3J = 7.5, H-C(6)); 2.50 (m, H-C(3)); 2.05 & 1.95 (2m, CH_2-C(3)); 1.88, 1.87, 1.86, 1.79, 1.78, 1.65, 1.64, 1.60 (8s, 9 Ac). ^{13}C-NMR (100.61 MHz, C_6D_6) δ_C: 170.6, 170.5, 170.4, 170.2, 170.1, 169.9 (6s); 72.3, 71.5, 71.0, 70.3, 69.7, 68.7, 67.7 (7d, ^1J(C,H) = 152-154); 64.4, 62.4, 61.2 (3t, ^1J(C,H) = 148); 37.7 (d, ^1J(C,H) = 129); 24.9 (t, ^1J(C,H) = 127); 21.1, 21.0, 20.8, 20.6, 20.5 (5q, ^1J(C,H) = 130). CI-MS (NH_3) m/z: 739 ($M^{+\cdot}$, 99), 737 (100), 661 (85), 540 (23), 498 (45), 485 (18), 425 (7), 299 (3), 169 (9), 81 (8). Anal. calc. for $C_{31}H_{62}O_{19}$ (738.83): C 50.40, H 8.46; found: C 50.54, H 8.23.

(+)-3-Deoxy-3-[(α-D-galactopyranosyl)methyl]-D-mannitol (**2**). A mixture of (+)-**29** (100 mg, 0.135 mmol), K_2CO_3 (20 mg) and MeOH/H_2O 1:1 (2 ml) was stirred at 20°C for 24 h. The solvent was evaporated and the residue purified by flash chromatography on silica gel (15 g, EtOAc/MeOH/AcOH 100:100:1) giving 36.3 mg (78%), colourless oil. $[\alpha]_D^{25}$ = +33; $[\alpha]_{577}^{25}$ = +37; $[\alpha]_{546}^{25}$ = +47; $[\alpha]_{435}^{25}$ = +88; $[\alpha]_{405}^{25}$ = +102 (c = 0.9, MeOH). IR (film) ν: 3350, 1570, 1440 cm^{-1}. ^{1}H-NMR (400 MHz, CD_3OD) δ_H: 4.20 (m, H-C(1')); 3.96-3.80 (m, H-C(1), H-C(2), H-C(2'), H-C(4'), H-C(4), H-C(6), H-C(6')); 3.57-3.77 (m, H-C(1), H-C(3'), H-C(5), H-C(5'), H-C(6), H-C(6')); 2.18 (m, H-C(3)); 1.99 & 1.83 (2m, CH_2-C(3)). ^{13}C-NMR (100.61 MHz, CD_3OD) δ_C: 75.4, 74.9, 74.2, 73.2, 72.0, 71.3, 70.2 (7d, ^1J(C,H) = 141); 69.9 (d, ^1J(C,H) = 145); 64.9 (2t, ^1J(C,H) = 142); 62.0 (t, ^1J(C,H) = 142); 39.0 (d, ^1J(C,H) = 126); 21.3 (t, ^1J(C,H) = 124). CI-MS (NH_3) m/z: 343 (M+1, 7), 325 (8), 307 (2), 223 (8), 189 (13), 125 (31), 111 (78), 81 (100). MS [electrospray, LiCl]: 349 (M^+ +Li, 82), 348 (100).

4-Deoxy-4-[(2',3',4',6'-tetra-O-acetyl-α-D-galactopyranosyl)methyl]-2,3,6-tri-O-acetyl-D-mannono-1,5-lactone (**3**). A mixture of (-)-**25** (50 mg, 0.082 mmol), 50% aq. dioxane (10 ml) and 1 N HCl (0.2 ml) was heated to 50°C for 14 h. Aq. NH_3 was added until pH=3 and $Na(CN)BH_3$ (7 mg) was added at 20°C. After stirring at 20°C for 3 h, 1 N HCl was added until pH=1 and the mixture heated to 60°C for 24 h. The solvent was evaporated in vacuo (10^{-3} Torr) to dryness. Pyridine (5 ml), Ac_2O (0.5 ml) and DMAP (5 mg) were added and the mixture was stirred at 20°C for 14 h. The solvent was evaporated in vacuo and the residue purified by flash column chromatography on silica gel (10 g, EtOAc/light petroleum 2:1) giving 16 mg (30%), colourless oil. IR (CH_2Cl_2) ν: 1740, 1360, 1200, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H: 6.14 (d, ^3J = 1.5, H-C(2)); 5.41 (m, H-C(4')); 5.30-5.10 (m, H-C(5), H-C(2'), H-C(3')); 4.95 (dd, ^3J(H-C(2),H-C(3)) = 1.5, ^3J(H-C(3),H-C(4)) < 3, H-C(3)); 4.40-4.21 (m, H-C(6), H-C(6'), H-C(1')); 4.14-3.99 (m, H-C(5'), H-C(6), H-C(6')); 2.43 (m, H-C(4)); 2.18, 2.15, 2.14, 2.11, 2.09, 2.08, 2.07 (7s, 7 Ac); 1.70 & 1.53 (2m, CH_2-C(4)). ^{13}C-NMR (100.61 MHz, $CDCl_3$) δ_C: 170.1, 169.7, 167.9 (3s), 88.7 (d, ^1J(C,H) = 177); 71.5, 70.9, 69.9, 69.3, 68.7, 68.4, 66.7 (7d, ^1J(C,H) = 150-156); 67.5 (t, ^1J(C,H) = 154); 60.3 (t, ^1J(C,H) = 153); 36.2 (d, ^1J(C,H) = 128); 24.2 (t,

^1J(C,H) = 130); 20.8 (q, ^1J(C,H) = 129). CI-MS (NH_3) m/z: 683 (M+3 NH_3, 100), 655 (M-CO+3 NH_3, 30), 634 (M+1, 1), 606 (M+1-CO, 39), 485 (7), 443 (13) 399 (13), 331 (7). MS [electrospray, LiCl, injection MeOH/H_2O]: 673 (M+ +Li+MeOH, 92), 647 (M+ +2Li, 26); 640 (M+ +Li, 14.6), 612 (M+ +Li+MeOH-AcOH, 100). Anal. calc. for $C_{27}H_{36}O_{17}$ (633.58): C 51.27, H 5.74; found: C 51.06, H 5.91.

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1. a) Allemann, S.; Vogel, P. *Helv. Chim. Acta* **1994**, *77*, 1, 2487; b) Chen, Y; Vogel, P. *J. Org. Chem.* **1994**, *59*, 2487.
2. a) Lagerie, P.; Legler, G.; Yon, D. M. *Biochemie* **1982**, *64*, 977; b) Truscheit, E.; Frommer, W.; Junge, B.; Müller, L.; Schmid, D. D.; Wingender, W. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 744; Sinnott, M. L. In *Enzyme Mechanisms*; Page, M. I., Williams, A., Eds.; The Royal Society of Chemistry; London, 1987; p 259.
3. Bennet, P. H.; Rushforth, N. B.; Miller, M.; Le-Compte, P. M. *Rec. Prog. Horm. Res.* **1976**, *32*, 333.
4. See, e.g.: Puls, W.; Krause, H. P.; Müller, L.; Schutt, H.; Sitt, R.; Thomas, G. *Int. J. Obesity* **1984**, *8*, 181. Layer, P.; Carlson, G. L.; Di-Magno, E. P. *Gastroenterology* **1985**, *88*, 1895.
5. See, e.g.: Rademacher, T. W.; Parekh, R. B.; Dwek, R. A. *Annu. Rev. Biochem.* **1988**, *57*, 785. Hindsgaul, O.; Khare, D. P.; Bach, M.; Lemieux, R. U. *Can. J. Chem.* **1985**, *63*, 2653.
6. Feizi, T. In *Carbohydrate Recognition in Cellular Function*; Ciba Geigy Symposium 145; Wiley: Chichester, 1989; p 62.
7. Kornfeld, R.; Kornfeld, S. *Ann. Rev. Biochem.* **1985**, *54*, 651 and references cited therein; Morenem, K. W.; Trimble, R. B.; Herscovics, A. *Glycobiology*, **1994**, *4*, 113.
8. Datema, R.; Olofsson, S.; Romero, P. A. *Pharmacol. Ther.* **1987**, *33*, 221; Klenk, H.-D.; Schwarz, R. T. *Antiviral Res.* **1982**, *2*, 177; Walker, B. D.; Kowalski, M; Goh, W. C.; Kozarsky, K.; Krieger, M.; Rosen, G.; Rohrschneider, L.; Haseltine, W. A.; Sodroski, *J. Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 8120; Gruters, R. A.; Neefjes, J. J.; Tersmete, M.; de Goede, R. E. Y.; Tulp, A.; Huisman, H. G.; Miedema, F.; Ploegh, H. L. *Nature* **1987**, *330*, 74.
9. See, e.g.: Hadwiger-Fangmeier, A.; Niemann, H.; Tamura, T. *Arch. Virol.* **1989**, *104*, 339; Nichols, E.V.; Manger, R.; Hakomori, S.; Rohrschneider, L. R. *Exp. Cell. Res.* **1987**, *173*, 486; Humphries, M. J.; Matsumoto, K.; White, S.L.; Olden, K. *Proc Natl. Acad. Sci. U.S.A.* **1986**, *83*, 1752; Humphries, M. J.; Matsumoto, K.; White, S.L.; Olden, K. *Cancer Res.* **1986**, *46*, 5215.
10. See, e.g.: Wassarman, P. M. *Science* **1987**, *235*, 553. *Annu. Rev. Cell. Biol.* **1987**, *3*, 109. *Sci. Ann.* **1988**, *255*, 78; Yanagimachi, R. In *The Physiology of Reproduction*; Kobil, E.; Neill, J. D.; Eds.; Raven Press: New York, 1988; Vol. 1, p 35.
11. Rouzaud, D.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1353.
12. a) Babirad, S. A.; Wang, Y.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 1370; b) Babirad, S. A.; Wang, Y.; Kishi, Y.; Goekjian, P.G. *Ibid.* **1987**, *52*, 4825.
13. Giese, B.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 450.

14. a) Wu, T. C.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 4823; b) Goekjian, P. G.; Wu, T. C.; Kang, H. Y.; Kishi, Y. *Ibid.* **1991**, *56*, 6422; c) Wang, Y.; Goekjian, P. G.; Ryckman, D. M.; Miller, W. H.; Bacbirad, S. A.; Kishi, Y. *Ibid.* **1992**, *57*, 482; d) Oyer, U. C.; Kishi, Y. *Ibid.* **1988**, *53*, 3383; e) O'Leary, D. J.; Kishi, Y. *Ibid.* **1993**, *58*, 304; f) Wei, A.; Kishi, Y. *Ibid.* **1994**, *59*, 88.
15. a) Giese, P.; Hoch, M.; Lamberth, C.; Schmidt, R. R. *Tetrahedron Lett.* **1988**, *29*, 1375; Giese, P. *Pure Appl. Chem.* **1988**, *60*, 1655; b) Giese, B.; Dupuis, J.; Nix, M. *Org. Synth.* **1987**, *65*, 236.
16. Carcano, M.; Nicotra, F.; Panza, C.; Russo, G. *J. Chem. Soc. Chem. Commun.* **1989**, 642; Nicotra, F.; Pangrario, C.; Panza, L.; Russo, G. *J. Chem. Soc. Perkin Trans. I.* **1994**, 333; Lay, L.; Nicotra, F.; Panza, L.; Russo, G.; Caneia, E.; *J. Org. Chem.* **1992**, *57*, 1304.
17. Boschetti, A.; Nicotra, F.; Panza, L.; Russo, G.; Zuchetti, L. *J. Chem. Soc. Chem. Commun.* **1989**, 1085.
18. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.
19. a) Martin, O. R.; Lai, W. *J. Org. Chem.* **1990**, *55*, 5188; b) Martin, O. R.; Lai, W. *Ibid.* **1993**, *58*, 176; c) Martin, O. R.; Xie, F.; Kakarta, R.; Benhamza, R. *Synlett* **1993**, 165.
20. Aebischer, B.; Bieri, J. H.; Prewo, R.; Vasella, A. *Helv. Chim. Acta* **1982**, *65*, 2251.
21. Beau, J. M.; Sinaÿ P. *Tetrahedron Lett.* **1985**, *26*, 6185, 6189, 6193.
22. Danishefsky, S. J.; Pearson, W. H.; Harvey, F. D.; Maring, C. J.; Spinger, J.P. *J. Am. Chem. Soc.* **1985**, *107*, 1256.
23. Jarosz, S.; Mootoo, D.; Fraser-Reid, B. *Carbohydr. Res.* **1986**, *147*, 59.
24. Dawson, I. M.; Johnson, T.; Paton, R. M.; Rennie, R. A. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1339.
25. Schmidt, R. R.; Preuss, R. *Tetrahedron Lett.* **1989**, *30*, 3409; Preuss, R.; Schmidt, R. R.; *J. Carbohydr. Chem.* **1991**, *10*, 887; Schmidt, R. R.; Beyerbaeh, A. *Liebigs Ann. Chem.* **1992**, 983; Preuss, R.; Jung; K. H. Schmidt, R. R. *Ibid.* **1992**, 377.
26. Motherwell, W. B.; Ross, B. K.; Tozer, M. J. *Synlett* **1989**, 68.
27. Bimwala, R. M.; Vogel, P. *J. Org. Chem.* **1992**, *57*, 2076.
28. Xin, Y. C.; Mallet, J. M.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1993**, 864; Vanzeilles, B.; Cravo, D.; Mallet, J. M.; Sinaÿ, P. *Synlett* **1993**, 522.
29. Haneda, T.; Goekjian, P. F.; Kim, S. H.; Kishi, Y. *J. Org. Chem.* **1992**, *57*, 490.
30. Giese, B.; Gröninger, K. S.; Witzel, T.; Korth, H. G.; Sustmann, R. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 233; Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615.
31. Gagnaire, D.; Payo-Subiza, E. *Bull. Soc. Chim. Fr.* **1963**, 2627; Ramey, K. C.; Lini, D.C. *J. Magn. Reson.* **1970**, *3*, 94; Nelson, W. L.; Allen, D. G. *J. Heterocycl. Chem.* **1972**, *9*, 561; Kienzle *Helv. Chem. Acta.* **1975**, *58*, 1180; Mahaim, C.; Vogel, P. *Ibid.* **1982**, *65*, 866.
32. Chatgilialoglu, C.; Griller, D.; Lesage, M. *J. Org. Chem.* **1988**, *53*, 3641; Giese, B.; Kopping, B.; Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681.
33. Lipkind, G. M.; Kochetkov, N. K. *Bioorg. Khim.* **1984**, *10*, 690.
34. Haasnoot, C. A. G.; Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.
35. Gasparini, F.; Vogel, P. *J. Org. Chem.* **1990**, *55*, 2451; Wagner, J.; Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1988**, *71*, 624.

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