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META-CHLOROPERBENZOIC ACID AS A SELECTIVE REAGENT FOR THE REMOVAL OF O-PROPENYL GROUPS. ITS USE IN THE SYNTHESIS OF SOME D-GALACTOPYRANOSIDE AND 4-DEOXY-L-*THREO*-4-HEXENOPYRANOSIDE DERIVATIVES

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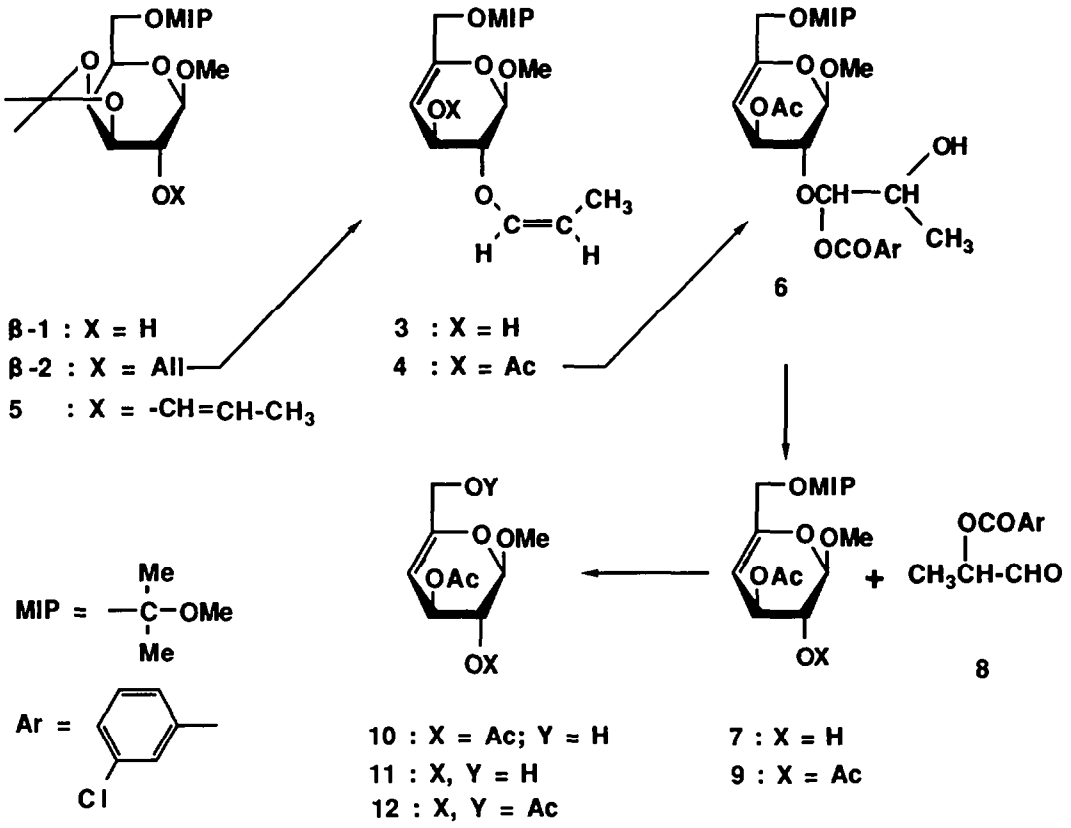
Abstract.- *Meta*-chloroperbenzoic acid can be used as a mild and selective reagent for the removal of the O-propenyl group in the deprotection sequence of allyl protected hydroxyl functions. Its use is illustrated in four synthetic pathways, leading, respectively, to methyl 3-O-acetyl-4-deoxy-6-O-(1-methoxy-1-methylethyl)-α-L-*threo*-4-hexenopyranoside, to methyl 2-O-acetyl-3,4,6-tri-O-methyl-α- and β-D-galactopyranoside and to benzyl 6-O-allyl-3,4-O-isopropylidene-β-D-galactopyranoside.

The allyl group is a frequently used protection for hydroxyl in carbohydrate synthesis, which is easily introduced, but sometimes poses some problem in its selective removal. Although a few methods are available for its direct cleavage,[1] their limited selectivity usually imposes an isomerization to the O-propenyl group that can be removed under much milder and selective conditions, because of the high reactivity of vinyl ethers with electrophiles. Many different reagents have been proposed for the latter step, ranging from dilute aqueous acids to miscellaneous oxidizing reagents. The mercury chloride-mercury oxide mixture is one of the most frequently employed reagents.[1] To the best of our knowledge, peroxyacids, that are highly reactive towards double bonds of vinyl ethers, have never been employed for this purpose.

In relation with our work on 4-deoxy-4-hexenopyranosides we needed to remove selectively the *cis*-propenyl group from compound **3**, without affecting the second, endocyclic, enol ether functionality. This was achieved as shown in Scheme I. Compound **3** was easily prepared from methyl β-D-galactopyranoside through our transacetalation method,[2] involving the use of a diluted solution of the glycoside in 2,2-dimethoxypropane for long reaction times in the presence of an acidic catalyst and giving the diacetals of type **1** as largely predominating products in the β-series. Allylation of β-**1** gave β-**2** that was reacted with *t*-BuOK in DMF to give **3**. Under these conditions the allyl group is isomerized to *cis*-propenyl and the 3,4-O-isopropylidene group is eliminated with formation of the 4,5-unsaturation.[3] As previously found for the analogous benzyl β-D-galactoside

SCHEME I

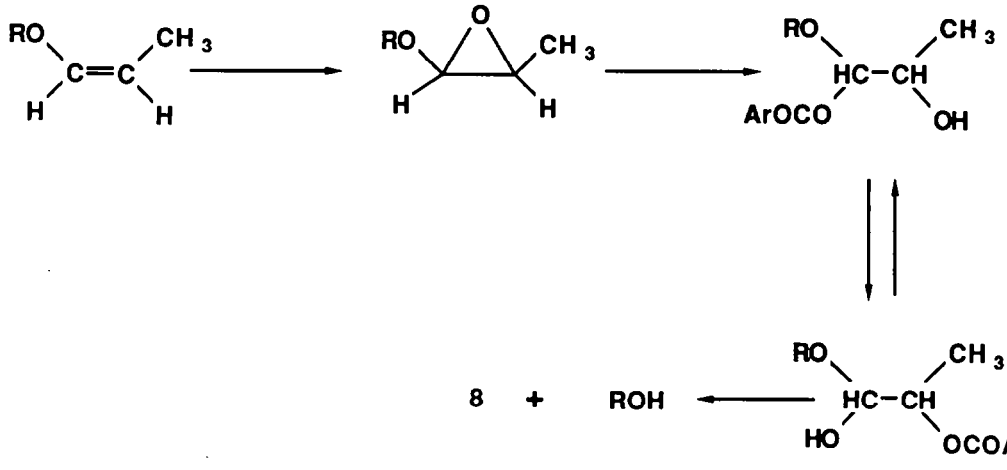


derivative,[3] a small amount of compound **5** was also formed.

For the selective removal of the propenyl group from **3** we tried, among other reagents, the use of an equimolar amount of *meta*-chloroperbenzoic acid (MCPBA), in the expectation that the more easily accessible side-chain double bond would be more reactive than the endocyclic one, but the difference in reactivity turned out to be unsufficient: some oxidation at the 4,5-unsaturation accompanied the removal of the propenyl group. However, when the acetyl derivative **4** was subjected to the same treatment, the higher electron-withdrawing inductive effect of the allylic acetoxy substituent sufficiently reduced the nucleophilic reactivity of the endocyclic double bond to allow clean oxidation of the propenyl group without affecting the other double bond. Proton NMR analysis of the crude reaction mixture provided evidence in favour of the formation of compound **6**, even if the presence of up to four possible diastereomers, originating from the

introduction of two new chiral centres in the 2-side chain, precluded a complete analysis of the spectrum. When triethylamine was added to the solution after completion of the oxidation, a complete conversion to the deprotected compound **7** and to the 2-acyloxypropanal **8** was observed. Acetylation of **7** gave the diacetate **9**, which was deprotected in position 6 by leaving its solution in aqueous methanol for 24 h, or more rapidly in the presence of a trace of *p*-toluenesulfonic acid, to yield the 2,3-diacetate **10**. Furthermore, a similar deprotection of **7**, gave the 3-acetate **11**, the acetylation of which led to the 2,3,6-triacetate **12**. These examples illustrate the versatility of the present approach to selectively functionalized hexenopyranoside derivatives.

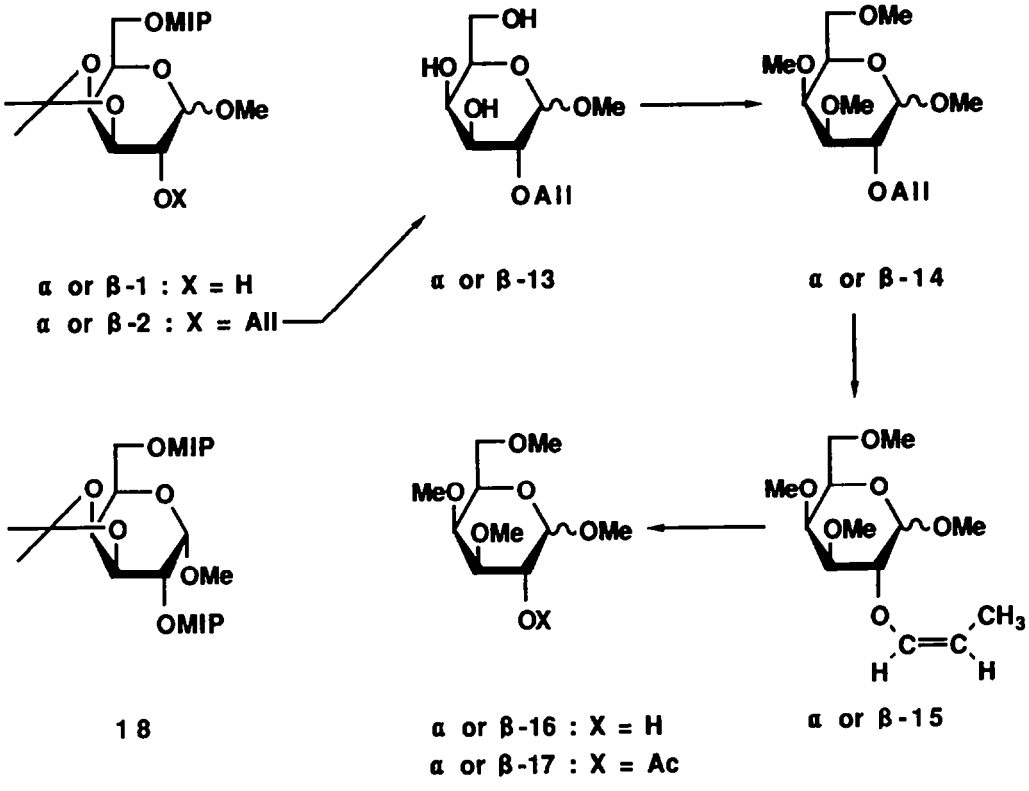
SCHEME II



The fact that the O-propenyl group is removed under these oxidative conditions, not involving a hydrolytic step, can be explained by the sequence shown in Scheme II. The primarily formed labile alkoxy epoxide is opened by the *m*-chlorobenzoic acid, deriving from the reduction of the peroxyacid, in a nucleophilic attack at the more reactive oxirane carbon to give a relatively stable ester adduct, which undergoes an 1,2 acyl shift, catalyzed by triethylamine, to produce a hemiacetal, spontaneously cleaving into free alcohol and the aldehyde **8**. Such a behaviour is in good agreement with older work by Stevens,[4] who extensively investigated the behaviour of vinyl ethers with perbenzoic acid. Only in particular cases can epoxy ethers be isolated, and often the reaction directly leads to an alcohol and a carbonyl compound. In the one particular case,[4b] involving the reaction

of 3-methoxy-2,2-dimethyloxirane with benzoic acid, the intermediate adduct was isolated and found to be converted into 2-benzoyloxy-2-methylpropanal and methanol by triethylamine. A similar case has been most recently reported for the reaction of a trialkylsilyl enol ether with MCPBA.[5]

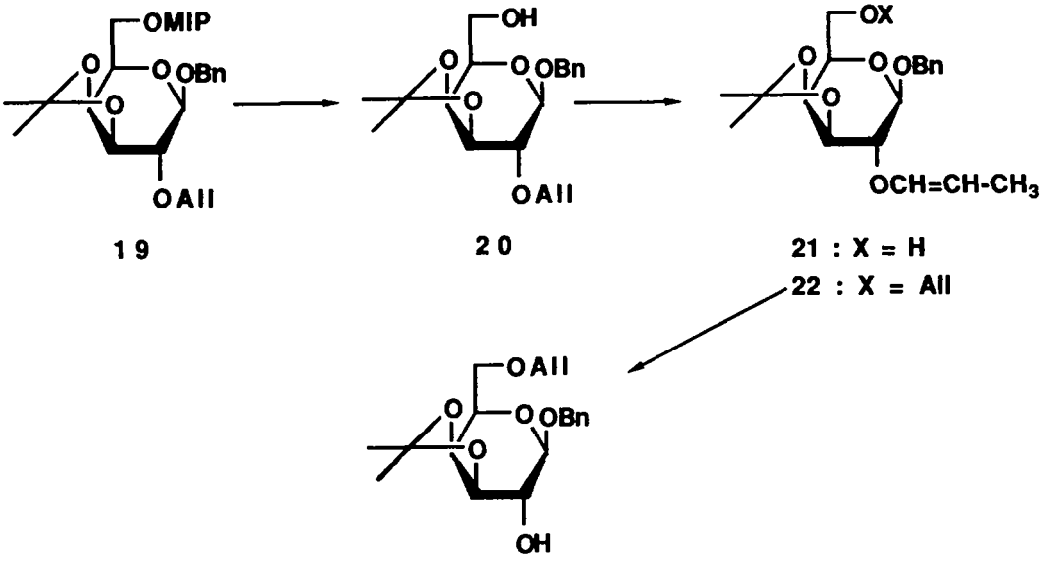
SCHEME III



A second case in which we used MCPBA for O-propenyl removal was in the synthesis, shown in Scheme III, of methyl 2-O-acetyl-3,4,6-tri-O-methyl-α and β-D-galactopyranosides (α- and β-17), which we needed for an NMR study. The preparation of the diacetal α-1, as previously mentioned in a preliminary comunication,[2] gave a lower yield than in the case of β-1, owing to a not easily explainable higher nucleophilic reactivity of the 2-OH group in the α- with respect to the β-series, that caused the formation of substantial amounts of the tris-acetal derivative **18**. Some methyl 3,4-O-isopropylidene-α-D-galactopyranoside was also isolated from the reaction mixture. Allylation to α- and β-2, followed by hydrolytic removal of both acetal

groups by heating with aqueous acetic acid gave α- and β-13. Methylation to 14 and isomerization with *t*-butoxide produced the *cis*-O-propenyl derivatives α- and β-15. Reaction with MCPBA and triethylamine gave α- and β-16 in about 95% yields, which were converted into the corresponding diacetates 17 by acetylation.

SCHEME IV



A further illustration of the usefulness of the peracid method is shown in Scheme IV. Benzyl 6-O-allyl-3,4-O-isopropylidene-β-D-galactopyranoside **23** was needed as an acceptor for a disaccharide synthesis. The previously described compound **19**[3] was selectively hydrolyzed to **20**. In this case *t*-butoxide was avoided in the allyl-propenyl isomerization since it could have caused some elimination of the 3,4-isopropylidene group and the anomeric O-benzyl group is less resistant than O-alkyl groups to the strongly basic reaction conditions. Wilkinson's catalyst[6] was therefore employed for this purpose to yield **21** as a mixture of *cis*- and *trans*-O-propenyl derivatives, that was directly allylated to **22**. Treatment of **22** with an equimolar amount of MCPBA, followed by triethylamine, produced **23** in 70% overall yield from **19**. The same reaction, carried out with the usual $HgCl_2/HgO$[7] reagent had produced **23** in 60% overall yield. This example further illustrates the selectivity of peroxyacid reagent, exhibiting a pronounced

preference for attack at the enol ether rather than at the allyl ether double bond.

In conclusion, we believe that the use of peroxyacid can provide a valid alternative to other methods available for the removal of propenyl, or other vinyl ether groups, in allyl deprotection sequences, since it avoids the use of toxic mercury reagents, or of, often incompatible, strong acids, and exhibits satisfactory selectivities and yields.

EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. Optical rotations were measured on (1.0±0.1)% solutions in $CHCl_3$ at 20±2°C on a Perkin-Elmer 241 polarimeter. ^1H NMR spectra (internal Me_4Si) were recorded with a Bruker AC 200 instrument at 200 MHz. First order spectral analysis was performed whenever possible, otherwise spectra were simulated with PANIC (Bruker) computer program. Chemical shift values were confirmed, when necessary, with COSY or J-RES experiments. In some cases signal overlapping prevented a complete analysis. ^{13}C NMR spectra were recorded with the same spectrometer at 50 MHz. Assignments were made with the aid of DEPT and HETCOR experiments. All reactions were followed by TLC on Kieselgel 60 F_{254} with detection by UV light or with ethanolic 10% phosphomolybdic or sulphuric acid and heating. Kieselgel 60 (Merck, 70-230 or 230-400 mesh) was used for column and flash chromatography. Solvents were distilled and stored over 4 Å molecular sieves activated by heating for at last 24 h at 400°C. All reactions were conducted under argon.

Methyl 3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-β-D-galactopyranoside (β-1). A suspension of methyl β-D-galactopyranoside (220 mg, 1.13 mmol) and camphosulfonic acid (10 mg) in 2,2-dimethoxypropane (20 mL) was shaken at room temp for 48 h. The product slowly dissolved, and TLC (1:1 hexane/AcOEt) showed that the starting material had completely disappeared and one major product had formed, accompanied by only trace amounts of side-products. Triethylamine (0.1 mL) was added, the solution was evaporated under reduced pressure (bath temp 30°C), three portions of toluene (10 mL) being added during the last stages of evaporation. The residue was subjected to flash chromatography (1:4 hexane/AcOEt containing 0.1% Et_3N) to yield 291 mg (84% yield) of pure **β-1**. R_f 0.36 (3:7 hexane/AcOEt), $[\alpha]_D$ +1.6°, ^1H NMR (C_6D_6): δ 1.23 and 1.44 (2 s, 6H, 2 dioxolanic Me), 1.30 (s, 6H, 2 MIP Me[a]), 3.18 and 3.33 (2 s, 6H, 2 OMe), from 3.64 to 4.06 (m, 7H, H-1 to H-6'). Anal. Calcd. for $C_{14}H_{26}O_7$: C, 54.9; H, 8.5. Found: C, 55.0; H, 8.8.

Methyl 3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-α-D-galactopyranoside (α-1). Methyl α-D-galactopyranoside (1.48 g, 7.63 mmol) was treated as described above for the preparation of **β-1**. After 48 h TLC (1:4 hexane/AcOEt) revealed the presence of one major and two minor products with R_f, respectively, of 0.55, 0.79, and 0.19 and of trace impurities. After work-up, chromatography (1:4 hexane/AcOEt) yielded methyl 3,4-O-isopropylidene-2,6-di-O-(1-methoxy-1-methylethyl)-α-D-galactopyranoside **18**, 385 mg (13.5% yield), compound **α-1** (1.30 g, 56% yield), and methyl 3,4-O-isopropylidene-α-D-galactopyranoside (235 mg, 13% yield), m.p. 103-104°C $[\alpha]_D$ +161°; lit.[9], m.p. 103-104°C $[\alpha]_D$ +161°.
α-1: $[\alpha]_D$ +101°; ^1H NMR (C_6D_6): δ 1.20 and 1.46 (2 s, 6H, 2 dioxolanic Me),

1.31 (s, 6H, 2 MIP Me), 2.50 (bs, 1H, OH), 3.15 and 3.18 (2 s, 6H, 2 OMe), 3.84 (dd, 1H, $J_{5,6'}$ 5.89 Hz, H-6'), 3.92 (dd, 1H, $J_{6,6'}$ 9.74 Hz, H-6), 3.98 (dd, $J_{2,3}$ 5.85 Hz, H-2), 4.10 (dd, 1H, $J_{4,5}$ 2.17 Hz, H-4), 4.23 (ddd, 1H, $J_{5,6}$ 6.64 Hz, H-5), 4.31 (dd, 1H, $J_{3,4}$ 6.63 Hz, H-3), 4.69 (d, 1H, $J_{1,2}$ 3.88 Hz, H-1). Anal. Calcd. for $C_{14}H_{26}O_7$: C, 54.9; H, 8.5. Found: C, 54.6; H, 8.3.

18: m.p. 66-67°C (from hexane), $[\alpha]_D$ +94.5°; ^{1}H NMR (C_6D_6): δ 1.20 and 1.46 (2 s, 6H, 2 dioxolanic Me), 1.31 and 1.49 (2 s, 6H, 2 MIP Me), 1.33 (s, 6H, 2 MIP Me), 3.21, 3.22, and 3.25 (3 s, 9H, 3 OMe), 3.91 (dd, 1H, $J_{5,6'}$ 5.73 Hz, H-6'), 3.99 (dd, 1H, $J_{6,6'}$ 9.63 Hz, H-6), 4.08 (dd, $J_{2,3}$ 8.00 Hz, H-2), 4.09 (dd, 1H, $J_{4,5}$ 2.59 Hz, H-4), 4.18 (ddd, 1H, $J_{5,6}$ 6.34 Hz, H-5), 4.43 (dd, 1H, $J_{3,4}$ 5.44 Hz, H-3), 4.90 (d, 1H, $J_{1,2}$ 3.45 Hz, H-1). Anal. Calcd. for $C_{18}H_{34}O_8$: C, 57.1; H, 9.0. Found: C, 57.4; H, 9.3.

Methyl 2-O-allyl-3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-β-D-galactopyranoside (β-2). To a suspension of NaH (60 mmol, obtained by washing with hexane 1.6 g of 80% NaH in mineral oil) in DMF (30 mL), cooled at 0°C was added through a double-tipped needle a solution of β-1 (3.8 g, 12.4 mmol) in DMF (50 mL). After stirring for 15 min at 0°C and 30 min at room temp, the suspension was cooled again at 0°C, then treated with allyl bromide (3.5 mL, 40 mmol), left at 0°C 15 min and 2 h at room temp. Addition of methanol to decompose excess NaH, evaporation *in vacuo*, addition of iced water (30 mL), extraction with CH_2Cl_2, evaporation of the dried extract and chromatography of the residue on silica (3:1 hexane/AcOEt containing 0.1% Et_3N) led to pure β-2 (3.9 g, 91% yield). R_f 0.55 (2:3 hexane/AcOEt), $[\alpha]_D$ +4.2°, ^{1}H NMR (C_6D_6): δ 1.23 and 1.42 (2 s, 6H, 2 dioxolanic Me), 1.30 (s, 6H, 2 MIP Me), 3.18 and 3.36 (2 s, 6H, 2 OMe), 3.60 (dd, 1H, $J_{2,3}$ 6.8 Hz, H-2), 3.64 (ddd, 1H, $J_{5,6}$ 6.8 Hz, H-5), 3.82 (dd, 1H, $J_{5,6'}$ 5.2 Hz, H-6'), 3.84 (dd, 1H, $J_{4,5}$ 2.3 Hz, H-4), 3.97 (dd, 1H, $J_{6,6'}$ 11.0 Hz, H-6), 4.04 (dd, 1H, $J_{3,4}$ 5.8 Hz, H-3), 4.10 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.39 (m, 2H, OCH_2), 5.07 (2 m, 2H, $=CH_2$), 6.00 (m, 1H, =CH-). Anal. Calcd. for $C_{17}H_{30}O_7$: C, 59.0; H, 8.7. Found: C, 59.2; H, 9.0.

Methyl 2-O-allyl-3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-α-D-galactopyranoside (α-2). Compound α-1 was allylated as described above for the preparation of β-2 to produce a 90% yield of α-2, R_f 0.41 (7:3 hexane/AcOEt), $[\alpha]_D$ +96.6°, ^{1}H NMR (C_6D_6): δ 1.21 and 1.46 (2 s, 6H, 2 dioxolanic Me), 1.31 (s, 6H, 2 MIP Me), 3.19 and 3.22 (2 s, 6H, 2 OMe), 3.66 (dd, 1H, $J_{2,3}$ 7.67 Hz, H-2), 3.90 (dd, 1H, $J_{5,6'}$ 5.66 Hz, H-6'), 3.98 (dd, $J_{6,6'}$ 9.62 Hz, H-6), 4.02 (dd, 1H, $J_{4,5}$ 2.82 Hz, H-4), 4.10 (m, 1H, J_{gem} 13.13 Hz, J_{vic} 5.55 Hz, 1/2 OCH_2), 4.19 (ddd, 1H, $J_{5,6}$ 6.61 Hz, H-5), 4.25 (m, 1H, J_{vic} 5.24 Hz, J_{all} 1.66 Hz, 1/2 OCH_2), 4.47 (dd, 1H, $J_{3,4}$ 5.60 Hz, H-3), 4.81 (d, 1H, $J_{1,2}$ 3.50 Hz, H-1), 5.01 (m, 1H, J_{cis} 10.46 Hz, J_{gem} 1.81 Hz, 1/2 $=CH_2$), 5.26 (m, 1H, J_{trans} 17.26 Hz, 1/2 $=CH_2$), 5.89 (m, 1H, =CH-). Anal. Calcd. for $C_{17}H_{30}O_7$: C, 59.0; H, 8.7. Found: C, 59.5; H, 8.7.

Methyl 4-deoxy-6-O-(1-methoxy-1-methylethyl)-2-O-(*cis*-1-propenyl)-α-L-*threo*-4-hexenopyranoside (3). A solution of β-2 (530 mg, 1.53 mmol) and *t*-BuOK (675 mg, 6.0 mmol) in DMF (20 mL) was heated at 80°C under stirring for 4 h. TLC (3:2 hexane/AcOEt) showed that the starting material had completely been transformed into two products, a major one with R_f 0.46 and a minor with R_f 0.68. The solvent was removed under reduced pressure, the residue token up in iced water and extracted with CH_2Cl_2. Evaporation of the dried extract and chromatography over silica (4:1 hexane/AcOEt containing 0.1% of Et_3N) gave in the first fractions methyl 3,4-O-isopropylidene-6-O-(1-methoxy-1-methylethyl)-2-O-(*cis*-1-propenyl)-β-D-galactopyranoside (5, 12 mg, 5% yield) $[\alpha]_D$ +16.3°, ^{1}H NMR (C_6D_6): δ 1.18 and 1.36 (2 s, 6H, 2 dioxolanic Me), 1.29 (s, 6H, 2 MIP Me), 1.78 (dd, 3H, J_{vic} 6.8

Hz, J_{all} 1.7 Hz, C-Me), 3.17 and 3.33 (2 s, 6H, 2 OMe), 3.63 (m, 1H, H-5), from 3.78 to 4.06 (m, 5H, H-2, H-3, H-4, H-6, and H-6'), 4.10 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4.43 (dq, 1H, =CH-C), 6.42 (dq, 1H, J_{cis} 6.2 Hz, =CH-O). The later fractions of the chromatography gave product **3** (310 mg, 70% yield), $[\alpha]_D$ -62.4°, ^{1}H NMR (C_6D_6): δ 1.23 and 1.25 (2 s, 6H, 2 MIP Me), 1.62 (dd, 3H, J_{vic} 6.8 Hz, J_{all} 1.7 Hz, C-Me), 2.54 (d, 1H, $J_{3,OH}$ 11.2 Hz, OH), 3.08 and 3.11 (2 s, 6H, 2 OMe), 3.83 (m, 1H, H-6'), 3.87 (m, 1H, H-2), 3.95 (m, 1H, $J_{4,6}$ 0.9 Hz, H-6), 4.09 (m, 1H, H-3), 4.40 (dq, 1H, J_{cis} 6.2 Hz, =CH-C), 4.82 (dd, 1H, $J_{1,2}$ 2.8 Hz, $J_{1,3}$ 1.3 Hz, H-1), 5.31 (dd, 1H, $J_{3,4}$ 4.7 Hz, H-4), 5.81 (dq, 1H, =CH-O). Anal. Calcd. for $C_{14}H_{24}O_6$: C, 58.3; H, 8.4. Found: C, 58.6; H, 8.6.

Methyl 3-O-acetyl-4-deoxy-6-O-(1-methoxy-1-methylethyl)-2-O-(*cis*-1-propenyl)-α-L-*threo*-4-hexenopyranoside (4). Compound **3** was converted into the corresponding 3-O-acetate **4** in 95% yield by 7 h treatment with Ac_2O in pyridine at room temp followed by coevaporation of the solvent with toluene under reduced pressure. R_f 0.33 (4:1 hexane/AcOEt), $[\alpha]_D$ +30.4°, ^{1}H NMR (C_6D_6): δ 1.21 (s, 6H, 2 MIP Me), 1.65 (s, 3H, OAc), 1.66 (dd, 3H, J_{vic} 6.82 Hz, J_{all} 1.71 Hz, C-Me), 3.06 and 3.19 (2 s, 6H, 2 OMe), 3.89 (m, 2H, H-6 and H-6'), 3.98 (m, 1H, $J_{2,3}$ 4.02 Hz, $J_{2,4}$ 0.81 Hz, H-2), 4.44 (dq, 1H, J_{cis} 6.23 Hz, =CH-C), 4.76 (dd, 1H, $J_{1,2}$ 4.55 Hz, $J_{1,3}$ 0.75 Hz, H-1), 5.25 (m, 1H, $J_{4,6}$ 1.2 Hz, H-4), 5.28 (m, 1H, $J_{3,4}$ 3.92 Hz, $J_{3,6}$ 1.4 Hz, H-3), 6.20 (m, 1H, =CH-O). Anal. Calcd. for $C_{16}H_{26}O_7$: C, 58.2; H, 7.9. Found: C, 58.1; H, 8.1.

Reaction of compound 4 with MCPBA. Methyl 3-O-acetyl-4-deoxy-6-O-(1-methoxy-1-methylethyl)-α-L-*threo*-4-hexanopyranoside (7). A solution of compound **4** (111 mg, 0.33 mmol) in CH_2Cl_2 (1 mL) was treated at 0°C with 83% MCPBA (71 mg, 0.34 mmol) in CH_2Cl_2 (2 mL). After 15 min the starting compound had completely disappeared (TLC, 3:7 hexane/AcOEt). The solution was immediately filtered through a silica column (3:7 hexane/AcOEt) to give a product (116 mg, 69% yield). The following ^{1}H NMR (C_6D_6) signals in the spectrum of the crude product provided evidence for the structure of the 2-O-substituent: δ 1.21 (d, 3H, Me), 4.41 (m, 1H, Me-C*H*), 6.42 and 6.62 (2 d, 1H, O-CH-OCO), 6.70, 7.07, 7.87, and 8.23 (4 m, 4H, aromatic H). The doubling of most signals in the ^{13}C NMR spectrum confirmed the presence of at least two diastereomeric forms of **6**. The product **6** was dissolved in CH_2Cl_2 and Et_3N (0.5 mL) was added. After 12 h at room temp the solution was evaporated *in vacuo* and the residue chromatographed over silica (1:4 hexane/AcOEt) to give the aldehyde **8** and compound **7** as the only products. The reaction was repeated with 0.72 mmol of **4** and 0.72 mmol of MCPBA, without isolation of the intermediate **6**, but adding Et_3N (0.1 mL) to the reaction solution after 15 min at 0°C. Work up as above yielded **8** (90%) and **7** (85% yield). 2-(*m*-Chlorobenzoyloxy)propanal (**8**): R_f 0.23 (4:1 hexane/AcOEt), ^{1}H NMR (C_6D_6): δ 0.91 (d, 3H, J 7.12 Hz, Me), 4.80 (dq, 1H, CH), 6.68, 7.06, 7.77, and 8.09 (4 m, 4H, aromatic H), 9.01 (d, 1H, J 0.5 Hz, O=CH). Compound **7**: R_f 0.41 (1:1 hexane/AcOEt), $[\alpha]_D$ +16.7°, ^{1}H NMR (C_6D_6): δ 1.22 (s, 6H, 2 MIP Me), 1.65 (s, 3H, OAc), 2.35 (bs, 1H, OH), 3.07 and 3.18 (2 s, 6H, 2 OMe), 3.87 (m, 2H, $J_{4,6}$ 1.0 Hz, $J_{5,6}$ 1.5 Hz, H-6 and H-6'), 3.98 (m, 1H, $J_{2,3}$ 5.4 Hz, H-2), 4.53 (dd, 1H, $J_{1,2}$ 6.4 Hz, $J_{1,3}$ 0.4 Hz, H-1), 5.22 (m, 1H, H-4), 5.54 (m, 1H, $J_{3,4}$ 3.2 Hz, H-3). Anal. Calcd. for $C_{13}H_{22}O_7$: C, 53.8; H, 7.6. Found: C, 53.5; H, 7.5.

Methyl 2,3-di-O-acetyl-4-deoxy-6-O-(1-methoxy-1-methylethyl)-α-L-*threo*-4-hexenopyranoside (9). Acetylation of **7** with Ac_2O/pyridine gave **9**: R_f 0.67 (1:1 hexane/AcOEt), $[\alpha]_D$ +30.8°, ^{1}H NMR (C_6D_6): δ 1.21 (s, 6H, 2 MIP Me), 1.57 and 1.65 (2 s, 6H, 2 OAc), 3.05 and 3.19 (2 s, 6H, 2 OMe), 3.90

(m, 2H, H-6 and H-6'), 4.92 (dd, 1H, $J_{1,2}$ 3.5 Hz, $J_{1,3}$ 0.8 Hz, H-1), from 5.38 to 5.51 (m, 3H, H-2 to H-4). Anal. Calcd. for $C_{18}H_{24}O_6$: C, 54.2; H, 7.3. Found: C, 53.9; H, 7.2.

Methyl 2,3-di-O-acetyl-4-deoxy-α-L-*threo*-4-hexenopyranoside (10). Compound **9** (129 mg, 0.38 mmol) in 10:1 MeOH/H_2O mixture was left at room temp until the starting material had disappeared (TLC, 24-36 h). In the presence of a trace of *p*-toluenesulfonic acid the reaction was complete after 30 min and the yield only slightly lower. Evaporation *in vacuo* followed by chromatography on silica (1:1 hexane/AcOEt) gave **10** (79 mg, 80% yield), R_f 0.33 (1:1 hexane/AcOEt), $[\alpha]_D$ +39.6°, ^1H NMR (C_6D_6): δ 1.61 and 1.67 (2 s, 6H, 2 OAc), 3.12 (s, 3H, OMe), 3.78 (m, 2H, H-6 and H-6'), 4.85 (dd, 1H, $J_{1,2}$ 3.3 Hz, $J_{1,3}$ 1.2 Hz, H-1), 5.19 (m, 1H, H-4), 5.43 (m, 2H, H-2 and H-3). Anal. Calcd. for $C_{11}H_{16}O_7$: C, 50.8; H, 6.2. Found: C, 50.6; H, 6.9.

Methyl 3-O-acetyl-4-deoxy-α-L-*threo*-4-hexenopyranoside (11). Deprotection of **7**, as described for **9**, gave **11** in 92% yield, R_f 0.32 (1:4 hexane/AcOEt), $[\alpha]_D$ +9.3°, ^1H NMR (C_6D_6): δ 1.67 (s, 3H, OAc), 2.71 (bs, 2H, 2 OH), 3.15 (s, 3H, OMe), 3.77 (m, 2H, $J_{4,6}$ 0.9 Hz, $J_{3,6}$ 1.7 Hz, H-6 and H-6'), 3.97 (m, 1H, $J_{2,3}$ 5.1 Hz, H-2), 4.54 (dd, 1H, $J_{1,2}$ 5.8 Hz, $J_{1,3}$ 0.6 Hz, H-1), 5.03 (m, 1H, H-4), 5.44 (m, 1H, $J_{3,4}$ 3.4 Hz, H-3). Anal. Calcd. for $C_8H_{14}O_6$: C, 49.5; H, 6.5. Found: C, 49.4; H, 6.5.

Methyl 2,3,6-tri-O-acetyl-4-deoxy-α-L-*threo*-4-hexenopyranoside (12). It was prepared in 90% yield from **11** with Ac_2O/pyridine. R_f 0.65 (1:1 hexane/AcOEt), $[\alpha]_D$ +35.7°, ^1H NMR (C_6D_6): δ 1.58, 1.59, and 1.64 (3 s, 9H, 3 OAc), 3.12 (s, 3H, OMe), 4.42 (m, 2H, H-6 and H-6'), 4.86 (m, 1H, H-1), 5.28 (m, 1H, H-4), 5.37 (m, 2H, H-2 and H-3). Anal. Calcd. for $C_{13}H_{18}O_8$: C, 51.7; H, 6.0. Found: C, 52.0; H, 6.1.

Methyl 2-O-allyl-β-D-galactopyranoside (β-13). A solution of **β-2** (1.63 g, 4.71 mmol) in 100 mL of acetic acid and 25 mL of water was heated at 90°C. After 10 min the reaction was complete (TLC, 3:2 hexane/AcOEt). Toluene (10 mL) was added and the solution was evaporated in vacuo, the residue being evaporated again twice after two further additions of toluene. The residue (1.08 g, 96% yield) crystallized, m.p. 75-77°C (from AcOEt/hexane). R_f 0.45 (4:1 hexane/AcOEt), $[\alpha]_D$ -2.1°; lit[10] m.p. 85°C, $[\alpha]_D$ -9° (CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 2.73 (bs, 3H, 3 OH), from 3.36 to 4.07 (m, 6H, H-2 to H-6'), 3.55 (s, 3H, OMe), 4.16 (m, 1H, 1/2 OCH_2), 4.24 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 4.39 (m, 1H, 1/2 OCH_2), 5.19 (m, 1H, J_{cis} 10.3 Hz, 1/2 $=CH_2$), 5.29 (m, 1H, J_{trans} 17.2 Hz, 1/2 $=CH_2$), 5.95 (m, 1H, =CH-). Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.2; H, 7.7. Found: C, 51.0; H, 8.0.

Methyl 2-O-allyl-3,4,6-tri-O-methyl-β-D-galactopyranoside (β-14). A solution of compound **β-13** (1.00 g, 4.3 mmol) in DMF (30 mL) was added at 0°C through a double-tipped needle to NaH (43 mmol obtained by washing with hexane 1.3 g of 80% NaH in mineral oil) in DMF (30 mL). The suspension was stirred 15 min at 0°C and 30 min at room temp, then cooled again at 0°C. An 1:4 (vol/vol) MeI/DMF mixture (9 mL) was added and stirring was continued 15 min at 0°C and 2 h at room temp. Methanol was added to dextroy excess NaH, volatiles were removed under reduced pressure and iced water (30 mL) was added. The product was extracted with CH_2Cl_2 (4 x 30 mL), dried and evaporated. Chromatography (1:1 hexane/AcOEt) yielded **β-14** (1.07 g, 90% yield), m.p. 45-46°C (from hexane). R_f 0.38 (1:1 hexane/AcOEt), $[\alpha]_D$ -22.2°, ^1H NMR (C_6D_6): δ 3.01 (dd, 1H, $J_{3,4}$ 3.06 Hz, H-3), 3.12, 3.30, 3.37, and 3.48 (4 s, 12H, 4 OMe), 3.36 (m, 1H, $J_{5,6'}$ 5.43 Hz, H-5), 3.46 (m, 1H, $J_{4,5}$ 1.20 Hz, H-4), 3.50 (dd, 1H, $J_{6,6'}$ 9.0 Hz, H-6'), 3.65 (dd, 1H, $J_{5,6}$

7.42 Hz, H-6), 3.85 (dd, 1H, $J_{2,3}$ 9.68 Hz, H-2), 4.17 (d, 1H, $J_{1,2}$ 7.61 Hz, H-1), 4.26 (m, 1H, J_{gem} 13.04 Hz, J_{vic} 5.45 Hz, J_{all} 1.57 Hz, 1/2 OCH_2), 4.46 (m, 1H, J_{vic} 5.14 Hz, J_{all} 1.62 Hz, 1/2 OCH_2), 5.03 (m, 1H, J_{cis} 10.48 Hz, J_{gem} 1.89 Hz, 1/2 $=CH_2$), 5.28 (m, 1H, J_{trans} 17.26 Hz, 1/2 $=CH_2$), 5.98 (m, 1H, =CH-). Anal. Calcd. for $C_{13}H_{24}O_6$: C, 56.5; H, 8.8. Found: C, 56.9; H, 8.9.

Methyl 3,4,6-tri-O-methyl-2-O-(*cis*-1-propenyl)-β-D-galactopyranoside (β-**15**). A solution of β-**14** (307 mg, 1.12 mmol) and *t*-BuOK (565 mg, 5.0 mmol) in DMF (10 mL) was heated at 80°C under stirring for 3 h, water was added and the product extracted into CH_2Cl_2. The residue obtained from the dried extract was chromatographed on silica (7:3 hexane/AcOEt) to yield β-**15** (236 mg, 77% yield) m.p. 76-78°C (from hexane), R_f 0.33 (7:3 hexane/AcOEt). $[\alpha]_D$ -6.3°, ^1H NMR (C_6D_6): δ 1.74 (dd, 3H, J_{vic} 6.8 Hz, J_{all} 1.7 Hz, C-Me), 3.03 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{2,3}$ 9.1 Hz, H-3), 3.10, 3.26, 3.33, and 3.46 (4 s, 12H, 4 OMe), 3.34 (m, 1H, H-5), 3.44 (m, 1H, H-4), 3.48 (dd, 1H, $J_{6,6'}$ 5.4 Hz, H-6'), 3.63 (dd, 1H, $J_{5,6}$ 7.4 Hz, $J_{6,6'}$ 9.0 Hz, H-6), from 4.09 to 4.19 (m, 2H, H-1 and H-2), 4.32 (dq, 1H, =CH-C), 6.29 (dq, J_{cis} 6.2 Hz, =CH-O). Anal. Calcd. for $C_{13}H_{24}O_6$: C, 56.5; H, 8.8. Found: C, 57.0; H, 9.0.

Methyl 3,4,6-tri-O-methyl-β-D-galactopyranoside (β-**16**). A solution of β-**15** (134 mg, 0.49 mmol) and 83% MCPBA (105 mg, 0.51 mmol) had reacted completely after 20 min at 0°C. Addition of Et_3N (0.1 mL) followed by evaporation *in vacuo* and chromatography on silica (2:3 hexane/AcOEt) gave the aldehyde **8** and product β-**16** both in 95% yield. β-**16**, a low melting solid, R_f 0.30 (2:3 hexane/AcOEt), $[\alpha]_D$ -9.8°; lit.[10], m.p. 40°C, $[\alpha]_D$ -7.5°. ^1H NMR (C_6D_6): δ 1.41 (bs, 1H, OH), 2.96 (m, 1H, H-3), 3.11, 3.28, 3.37, and 3.44 (4 s, 12H, 4 OMe), from 3.38 to 3.42 (m, 2H, H-4 and H-5), 3.50 (m, 1H, H-6'), 3.63 (m, 1H, H-6), from 4.07 to 4.10 (m, 2H, H-1 and H-2). Anal. Calcd. for $C_{10}H_{20}O_6$: C, 50.8; H, 8.5. Found: C, 50.0; H, 8.2.

Methyl 2-O-acetyl-3,4,6-tri-O-methyl-β-D-galactopyranoside (β-**17**). Acetylation of β-**16** with Ac_2O/pyridine gave β-**17** (97% yield), m.p. 95-97°C (from hexane), R_f 0.46 (3:2 hexane/AcOEt), $[\alpha]_D$ -16.3°, ^1H NMR (C_6D_6): δ 1.78 (s, 3H, OAc), 3.07, 3.11, 3.35, and 3.38 (4 s, 12H, 4 OMe), 3.00 (dd, 1H, $J_{3,4}$ 2.87 Hz, H-3), 3.35 (ddd, 1H, $J_{5,6}$ 7.45 Hz, H-5), 3.48 (dd, 1H, $J_{4,5}$ 1.08 Hz, H-4), 3.50 (dd, 1H, $J_{5,6'}$ 5.43 Hz, H-6'), 3.63 (dd, 1H, $J_{6,6'}$ 9.03 Hz, H-6), 4.27 (d, 1H, $J_{1,2}$ 7.93 Hz, H-1), 5.79 (dd, 1H, $J_{2,3}$ 10.13 Hz, H-2). ^{13}C NMR (C_6D_6): δ 20.78 (OAc), 55.25, 57.43, 58.84, and 60.76 (4 OMe), 70.89 (C-6), 71.14 (C-2), 73.71 (C-5), 74.57 (C-4), 82.93 (C-3), 102.18 (C-1), 168.91 (C=O). Anal. Calcd. for $C_{12}H_{22}O_7$: C, 51.8; H, 8.0. Found: C, 51.9; H, 8.1.

The series of reactions leading from β-**2** to β-**17** has also been applied to the α series, under the same conditions. The following compounds were thus obtained:

Methyl 2-O-allyl-α-D-galactopyranoside (α-**13**). 98% yield from α-**2**, m.p. 61-63°C (from AcOEt/hexane), R_f 0.38 (3:1 hexane/AcOEt), $[\alpha]_D$ +152.2°, ^1H NMR ($CDCl_3$): δ 3.42 (s, 3H, OMe), 3.71 (dd, 1H, $J_{2,3}$ 9.8 Hz, H-2), from 3.78 to 4.00 (m, 4H, H-3, H-5, H-6, and H-6'), 4.11 (m, 1H, H-4), 4.14 and 4.18 (2 m, 2H, OCH_2), 4.91 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 5.23 and 5.31 (2 m, 2H, $=CH_2$), 5.95 (m, 1H, =CH-). Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.2; H, 7.7. Found: C, 51.1; H, 7.5.

Methyl 2-O-allyl-3,4,6-tri-O-methyl-α-D-galactopyranoside (α-14). 72% yield, R_f 0.39 (3:2 hexane/AcOEt), $[\alpha]_D$ +114.3°, ^{1}H NMR (C_6D_6): δ 3.16, 3.23, 3.30, and 3.50 (4 s, 12H, 4 OMe), from 3.52 to 3.72 (m, 4H, H-3, H-4, H-6, and H-6'), from 3.93 to 4.08 (m, 3H, H-2, H-5, and 1/2 OCH_2), 4.13 (m, 1H, J_{gem} 13.1 Hz, J_{vic} 5.0 Hz, J_{all} 1.6 Hz, 1/2 OCH_2), 4.81 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.98 (m, 1H, J_{cis} 10.4 Hz, 1/2 $=CH_2$), 5.22 (m, 1H, J_{trans} 17.2 Hz, 1/2 $=CH_2$), 5.85 (m, 1H, =CH-). Anal. Calcd. for $C_{13}H_{24}O_6$: C, 56.5; H, 8.8. Found: C, 56.9; H, 9.0.

Methyl 3,4,6-tri-O-methyl-2-O-(*cis*-1-propenyl)-α-D-galactopyranoside (α-15). 60% yield, R_f 0.37 (7:3 hexane/AcOEt), $[\alpha]_D$ +104.2°, ^{1}H NMR (C_6D_6): δ 1.74 (dd, 3H, J_{vic} 6.80 Hz, J_{all} 1.67 Hz, C-Me), 3.14, 3.17, 3.27, and 3.48 (4 s, 12H, 4 OMe), 3.53 (dd, 1H, $J_{4,5}$ 1.30 Hz, H-4), 3.54 (dd, 1H, $J_{6,6'}$ 9.15 Hz, H-6'), 3.64 (dd, 1H, $J_{5,6}$ 6.88 Hz, H-6), 3.70 (dd, 1H, $J_{3,4}$ 3.00 Hz, H-3), 3.95 (ddd, 1H, $J_{5,6'}$ 6.10 Hz, H-5), 4.26 (dd, 1H, $J_{2,3}$ 10.11 Hz, H-2), 4.34 (dq, 1H, =CH-C), 4.73 (d, 1H, $J_{1,2}$ 3.65 Hz, H-1), 6.05 (dq, 1H, J_{cis} 6.50 Hz, =CH-O). Anal. Calcd. for $C_{13}H_{24}O_6$: C, 56.5; H, 8.8. Found: C, 56.4; H, 8.9.

Methyl 3,4,6-tri-O-methyl-α-D-galactopyranoside (α-16). 95% yield, m.p. 83-85°C (from hexane), R_f 0.32 (2:3 hexane/AcOEt), $[\alpha]_D$ +159.3°, ^{1}H NMR (C_6D_6): δ 1.79 (d, 1H, $J_{2,OH}$ 8.3 Hz, OH), 3.07, 3.12, 3.23, and 3.45 (4 s, 12H, 4 OMe), 3.29 (dd, 1H, $J_{3,4}$ 2.9 Hz, H-3), 3.53 (dd, 1H, $J_{4,5}$ 1.2 Hz, H-4), 3.52 (dd, 1H, $J_{6,6'}$ 9.1 Hz, H-6'), 3.63 (dd, 1H, $J_{5,6}$ 6.9 Hz, H-6), 3.87 (m, 1H, $J_{5,6}$ 6.1 Hz, H-5), 4.32 (ddd, 1H, $J_{2,3}$ 10.0 Hz, H-2), 4.67 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1). Anal. Calcd. for $C_{10}H_{20}O_6$: C, 50.8; H, 8.5. Found: C, 51.1; H, 8.7.

Methyl 2-O-acetyl-3,4,6-tri-O-methyl-α-D-galactopyranoside (α-17). 94% yield, R_f 0.46 (2:3 hexane/AcOEt), $[\alpha]_D$ +102.2°, ^{1}H NMR (C_6D_6): δ 1.71 (s 3H, OAc), 3.38, 3.41, 3.48, and 3.56 (4 s, 12H, 4 OMe), 3.53 (dd, 1H, $J_{5,6'}$ 5.99 Hz, H-6'), 3.59 (dd, 1H, $J_{4,5}$ 1.28 Hz, H-4), 3.64 (dd, 1H, $J_{6,6'}$ 9.12 Hz, H-6), 3.70 (dd, 1H, $J_{3,4}$ 2.94 Hz, H-3), 3.92 (ddd, 1H, $J_{5,6}$ 6.95 Hz, H-5), 5.09 (d, 1H, $J_{1,2}$ 3.69 Hz, H-1), 5.68 (dd, 1H, $J_{2,3}$ 10.46 Hz, H-2). ^{13}C NMR (C_6D_6): δ 20.61 (OAc), 54.87, 57.67, 58.84, and 60.88 (4 OMe), 69.67 (C-5), 71.53 (C-2), 71.59 (C-6), 76.19 (C-4), 78.84 (C-3), 97.98 (C-1), 169.87 (C=O). Anal. Calcd. for $C_{13}H_{22}O_7$: C, 51.8; H, 8.0. Found: C, 51.5; H, 7.7.

Benzyl 2-O-allyl-3,4-O-isopropylidene-β-D-galactopyranoside (20). Compound 19[3] (780 mg, 1.77 mmol) in 5:1 (vol/vol) of MeOH/H_2O was left at room temp for 24 h, after which time the reaction was complete. Evaporation and crystallization from hexane gave **20** (520 mg, 80% yield), as needles, m.p. 62-63°C, R_f 0.58 (2:3 hexane/AcOEt), $[\alpha]_D$ +11.2°, ^{1}H NMR ($CDCl_3$): δ 1.34 and 1.52 (2 s, 6H, 2 dioxolanic Me), 2.05 (dd, 1H, J 3.5 and 9.2 Hz, OH), 3.42 (m, 1H, H-2), 3.80 (m, 1H, H-5), 3.82 (m, 1H, H-6'), 3.98 (m, 1H, H-6), 4.13 (m, 2H, H-3 and H-4), 4.27 and 4.33 (2 m, 2H, OCH_2), 4.38 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 4.70 and 4.92 (ABq, 2H, J 12.2 Hz, CH_2-ø), 5.18 (m, 1H, J_{cis} 10.3 Hz, 1/2 $=CH_2$), 5.29 (m, 1H, J_{trans} 17.2 Hz, 1/2 $=CH_2$), 5.94 (m, 1H, =CH-), 7.36 (m, 5H, aromatic H). Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.1; H, 7.4. Found: C, 64.9; H, 7.3.

Benzyl 6-O-allyl-3,4-O-isopropylidene-β-D-galactopyranoside (23). A solution of **20** (1.30 g, 3.71 mmol), tris-(triphenylphosphine)rhodium(I) chloride (170 mg, 0.184 mmol) and diazabicyclo[2,2,2]octane (180 mg, 1.60 mmol)

in 9:1 (vol/vol) EtOH/H_2O (80 mL) was heated at 85°C for 4 h. Water (6 mL) was added and the product extracted into CH_2Cl_2 (4 x 50 mL), the organic layer, dried and evaporated, gave 1.23 g of a crude mixture of the *cis* and *trans* forms of benzyl 3,4-O-isopropylidene-2-O-(1-propenyl)-β-D-galactopyranoside (**21**) that was not separated into its components, but used as such for the subsequent step. The ^1H NMR (C_6D_6) signals corresponding to the *cis* and *trans* forms of the O-propenyl group were detected in this mixture: *cis*-**21**: δ 1.78 (dd, 3H, J_{all} 1.7 Hz, Me), 4.45 (dq, 1H, J_{vic} 6.8 Hz, =CH-C), 6.40 (dq, 1H, J_{cis} 6.4 Hz, =CH-O); *trans*-**21**: δ 1.46 (dd, 3H, J_{all} 1.6 Hz, Me), 5.23 (dq, 1H, J_{vic} 6.8 Hz, =CH-C), 6.45 (dq, 1H, J_{trans} 12.0 Hz, =CH-O). The crude product **21** (1.23 g) was subjected to allylation under the conditions described for the conversion of β-**1** into β-**2**, to yield a mixture of the *cis*/*trans* forms of benzyl 6-O-allyl-3,4-O-isopropylidene-2-O-(1-propenyl)-β-D-galactopyranoside (**22**) (1.30 g). The ^1H NMR spectrum exibited the signals expected for the presence of the allyl group: δ 5.08 (m, 1H, J_{cis} 10.3 Hz, 1/2 $=CH_2$), 5.29 (m, 1H, J_{trans} 17.2 Hz, 1/2 $=CH_2$), 5.88 (m, 1H, =CH-). Crude **22** (1.30 g) was oxidized with MCPBA (3.6 mmol) in CH_2Cl_2, as reported above, for 20 min at 0°C, then treated with Et_3N (0.5 mL). Evaporation and chromatography (7:3 hexane/AcOEt) yielded pure **23** (0.91 g, 70% yield), R_f 0.27 (7:3 hexane/AcOEt), $[\alpha]_D$ +43.8°, ^1H NMR ($CDCl_3$): δ 1.34 and 1.52 (2 s, 6H, 2 dioxolanic Me), 3.60 (dd, 1H, $J_{2,3}$ 7.3 Hz, H-2), 3.78 (d, 2H, $J_{5,6'}$ 5.8 Hz, H-6 and H-6'), 3.92 (ddd, 1H, $J_{5,6}$ 6.9 Hz, H-5), 4.05 (dd, 1H, $J_{3,4}$ 5.4 Hz, H-3), 4.10 (m, 2H, OCH_2), 4.15 (dd, 1H, $J_{4,5}$ 2.2 Hz, H-4), 4.25 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.62 and 4.93 (ABq, 2H, J_{AB} 13.0 Hz, CH_2-ø), 5.21 and 5.32 (2 m, 2H, $=CH_2$), 5.95 (m, 1H, =CH-), 7.35 (m, 5H, aromatic protons). ^{13}C NMR ($CDCl_3$): δ 26.28 and 28.12 (2 Me), 69.62 (C-6), 70.86 (CH_2-ø), 72.43 (OCH_2), 72.72 (C-5), 73.70 (C-2), 73.78 (C-4), 78.67 (C-3), 100.96 (C-1), 110.17 (dioxolanic C), 117.00 ($=CH_2$), 128.03 (aromatic *para* C), 128.31 and 128.48 (aromatic *ortho* and *meta* C), 134.58 (=CH-), 136.82 (substituted aromatic C). Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.1; H, 7.4. Found: C, 64.8; H, 7.2.

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