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Formation of stable organometallic products during deprotection of monoallyloxyalcohols

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Abstract—Removal of the allyl group from the monoprotected vicinal diols with the Wilkinson's catalyst followed by treatment with HgO/$HgCl_2$, gave significant amounts of cyclic compounds containing the mercury species as well as the expected diols. Reduction of these organomercurials with sodium borohydride led to replacement of mercury by hydride but, provided unsaturated compounds arising from the cleavage of the C–O bond (α to the mercuric moiety) also.

1. Introduction

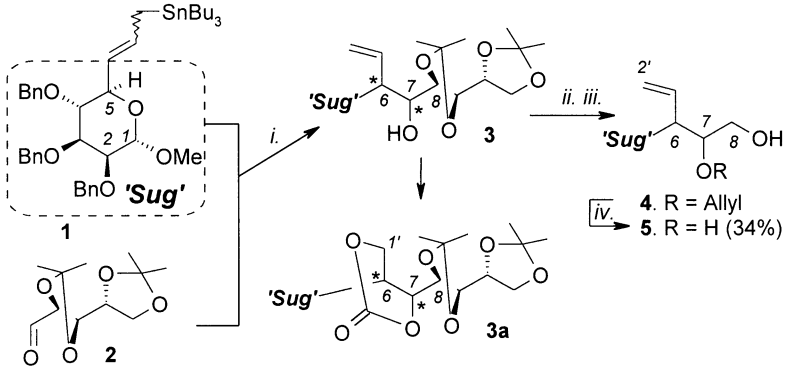
In a study on the synthesis of higher carbon sugars[1] by reaction of allyltin derivatives (e.g. **1**) with aldehydes (e.g. **2**) catalyzed by a Lewis acid we faced the problem of determination of the configuration at the newly created chiral centers in derivatives such as compound **3** (Scheme 1). Since no models are available, we decided to determine the relative configuration at the C-6–C-7 centers by NMR spectroscopy (after conversion into a cyclic derivative, e.g. **3a**), while the absolute configuration at C-7 using CD spectra[2] of the diol **5**.

Diol **5** could be prepared from precursor **3** in a few simple steps involving a temporary protection of a free hydroxyl group, transformation of the 'right' part of the molecule into a CH_2OH group and final deprotection. We decided to use the allyl group as it is stable under a wide variety of different reaction conditions and can be selectively removed by isomerization of the double bond followed by hydrolysis of the vinyl ether.[3]

However, removal of the allyl group from the monoprotected compound **4** turned out to be a rather serious problem. In this paper a study on removal of the allyl protection from vicinal monoallyloxy alcohols is described.

2. Results and discussion

The first step of removal of the allyl group in compound **4**, its isomerization into a vinyl group using Wilkinson's catalyst, proceeded as expected. However, the next stage, reaction with HgO/$HgCl_2$ in the presence of water,[3] gave significant amounts of a compound containing the mercury species as well as expected diol. The ^{13}C NMR spectrum of this derivative revealed two sets of signals (in the ratio ca



Scheme 1. (i) $BF_3{\cdot}OEt_2$; (ii) AllylBr, NaH, DMF; (iii) $H^{(+)}$ than $NaIO_4$ then $NaBH_4$; (iv) Wilkinson's catalyst, then HgO/$HgCl_2$, acetone/water (15:1).

Keywords: monosaccharides; protecting groups; organomercurial derivatives.
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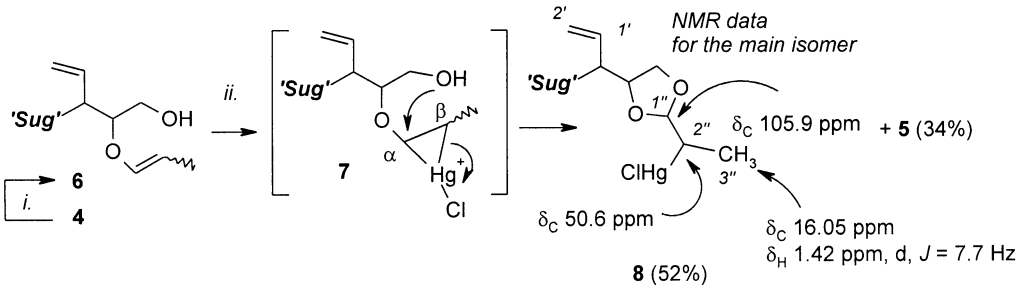
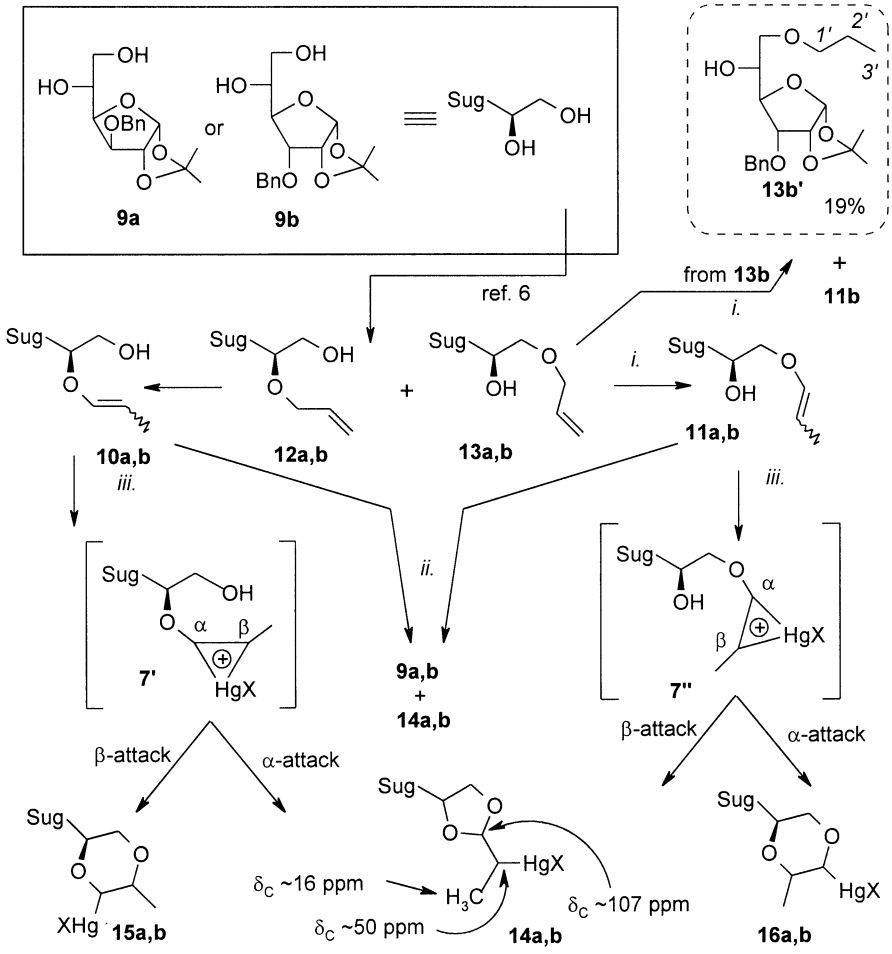


Scheme 2. (i) Wilkinson's catalyst; (ii) HgO/$HgCl_2$, acetone/water (15:1).

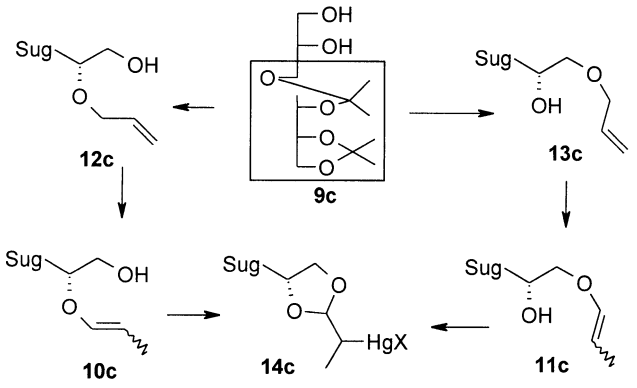
3:1) suggesting the presence of two stereoisomers (Scheme 2).

The signal at δ_C=16.05 ppm (minor isomer δ_C=16.0 ppm) could be assigned to the methyl group and the signal at δ_C=50.6 ppm (minor δ_C=50.7 ppm) to the R_2CH–HgCl grouping.[4] The ^1H NMR spectroscopic data further supported this assignment: the CH_3 group at the tertiary carbon atom showed δ_H=1.42 ppm; doublet J=7.7 Hz (minor isomer δ_H=1.22 ppm; doublet J=7.1 Hz). Evidence for the presence of the mercury species in the molecule came from the mass spectral data showing the molecular ion at m/z: 833 ($M+Na^+$) with the very characteristic isotopic pattern. On the basis of these spectral data we were able to propose the structure **8** for this unexpected organometallic derivative. Presence of a dioxolane ring rather than a six-membered one could be suggested on the basis of the ^{13}C NMR spectroscopic data (δ_C=105.9 ppm, C-1″; Scheme 2).[5]

Thus, attack of the mercury species on the double bond of **6** afforded intermediate **7** which could undergo either reaction with water (leading to the desired diol **5**) or an intramolecular process involving attack of the primary hydroxyl group of **7** either at the α (leading to **8**) or β positions.



Scheme 3. (i) Wilkinson's catalyst, EtOH/water 9:1; (ii) HgO/$HgCl_2$, acetone/water (15:1); (iii) HgO/$HgCl_2$, 100% acetone; **14a**: 54% from **12a** or 47% from **13a**; **14b**: 64% from **12b** or 39% from **13b**.



Scheme 4. Conditions as in Scheme 3. **14c**: 53% from **12c** or 70% from **13c**.

To determine whether the formation of organomercurial species during the deprotection of monoallyloxyalcohols was general, several model mono-protected derivatives of diols were prepared: (a) with the allyl protection at the secondary position (with primary hydroxy group free: **12a–c**) and (b) with the primary hydroxy group blocked as an allyl ether (**13a–c**).[6]

These two 'families' of monoallyloxy alcohols were subjected to the deprotection sequence commonly applied for removal of the allyl group. Treatment of either **12** or **13** with Wilkinson's catalyst[7] afforded the corresponding vinyl ethers **10** and **11**, respectively. Interestingly, in one case (reaction of **13b**) the reduction product **13b′** was formed besides the expected compound **11b**.

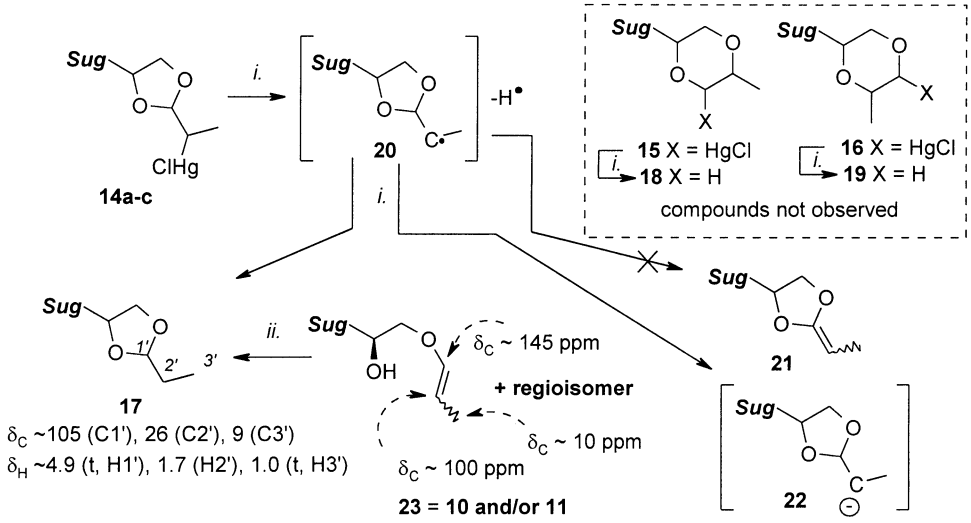
Reaction of these vinyl intermediates with $HgO/HgCl_2$ in acetone/water (15:1) provided, besides the diols, significant amounts of organometallic species. If water was excluded from this process, only derivatives containing the mercury atom in the molecule were obtained in good yields (Schemes 3 and 4).

Again, two reaction pathways should be considered in the former process (with H_2O), involving (a) an attack of a molecule of water (leading to diol **9**) or (b) intramolecular process leading to an organometallic intermediate. Attack of the free hydroxy group at the α-carbon atom would lead to organomercurial **14** in both cases, while attack at the β-atom would afford six-membered ring products: **15** (from **7′**) or **16** (from **7″**). On the basis of the ^{13}C NMR spectroscopic data (δ_C ~107 ppm) we were able to suggest structure **14** containing a five membered ring rather than structure with the six membered one (**15** or **16**) to the newly formed organometalic derivatives. This assumption was verified by the ^1H NMR spectroscopic data of the borohydride reduction products **17**, derived from the corresponding organomercurials (Scheme 5) which pointed unambiguously at the presence of the $CH_3CH_2CH(OR)_2$ grouping [signals at δ_H ~1.0 (t, 3H), 1.7 (2H) and 4.9 (d, 1H)]. No signals for the six-membered derivatives **18** or **19** were seen in the ^1H NMR spectrum.

However, compounds **17** were not the major products of the reduction of organomercurials. From the post-reaction mixture we isolated derivatives with the same molecular formula as **17**, but undergoing acetylation with Ac_2O. Their ^{13}C NMR spectrum revealed signals at δ_C ca 145 and 100 ppm, strongly suggesting the presence of the O–CH=CH– group (see e.g. Ref. 8) and were identical with compounds prepared by isomerization of either **12**(**a–c**) or **13**(**a–c**) with Wilkinson's catalyst.

In order to explain this we suggest the following. The first step, reaction with sodium borohydride, provides radical[9] **20** which is further converted into the desired product **17**. Another possibility is the rearrangement of such a radical, the most evident route being abstraction of a hydrogen atom from the α-position with formation of unsaturated derivative **21**. This process was, however, not observed. Since cleavage of the C–O bond under these conditions is not very likely,[10] further reduction of the radical **20** to anion **22** should be rather postulated, with the latter undergoing the β-elimination process (with a cleavage of either C–O bond) leading to mixture of vinyl ethers **23** (=**10** and/or **11**).

One of these vinyl ethers, compound **23a** underwent cyclization to **17a** (mixture of two stereoisomers) after storage for two months at room temperature (Scheme 5).



Scheme 5. (i) $NaBH_4$, MeOH, rt. (**a** 24% of **17** and 47% of **23**; **b** 16% of **17** and 52% of **23**; **c** 48% of **17** and 19% of **23**); (ii) Storage for two months.

3. Conclusion

Removal of the allyl group from monoprotected 1,2-diols by isomerization of a double bond with Wilkinson's catalyst followed by treatment of the resulting vinyl ether with HgO/$HgCl_2$ can be problematic. The organomercurial complex formed in the latter stage is attacked rather by a free hydroxy group of the monoprotected diol (to give the 5-membered cyclic derivatives containing the mercury species) than water (which should remove the protecting group and afford the free diol) leading to a complicated mixture of products.

4. Experimental

4.1. General

^1H- and ^{13}C NMR spectra were recorded with Bruker AM 500 MHz or Varian Gemini 200 MHz spectrometers for solutions in $CDCl_3$ (internal Me_4Si). Mass spectra (LSIMS; *m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added or ESI) were recorded with an AMD-604 or PE SCIEX API 365. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 for solutions in $CHCl_3$ at room temperature. Column chromatography was performed on silica gel (Merck, 70–230 or 230–400 mesh). For chromatography purposes a fraction of mineral oil with boiling point in range of 70–90°C was used as a mixture of hexanes. Organic solutions were dried over anhydrous sodium sulfate.

4.1.1. Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-C-(vinyl)-7-*O*-allyl-α-D-*manno*-octose[†] (4). The titled compound was prepared according to Ref. 1 as colorless oil; R_f (25% AcOEt/hexanes) 0.3; δ_H (200 MHz) 7.40–7.20 (15H, m, Ph), 6.01–5.78 [2H, m, C(6)C*H*=CH_2 and OCH_2CH=CH_2], 5.25–5.02 [4H, m, C(6)CH=CH_2 and OCH_2CH=CH_2], 5.91 (1H, d, *J*=11 Hz, CH_aH_bPh), 4.79–4.53 (6H, m, H-1, CH_aH_bPh and 2×CH_2Ph), 4.22–3.48 (9H, m, H-2, H-3, H-4, H-5, H-7, both H-8 and OCH_2CH=CH_2), 3.27 (3H, s, O*Me*), 2.98 (1H, m, H-6), 2.75 (O*H*); δ_C (50 MHz) 138.7, 138.4, 138.2 (3×quat. Bn), 136.3 and 135.0 [C(6)*C*H=CH_2 and OCH_2CH=CH_2], 117.5 and 116.6 [C(6)CH=CH_2 and OCH_2CH=CH_2], 99.1 (C-1), 80.8, 78.5, 76.4, 75.0, 73.7, 74.5 (OCH_2CH=CH_2), 72.9, 72.0, 70.7 (3×CH_2Ph), 62.3 (C-8), 54.8 (O*Me*), 45.4 (C-6); *m*/*z* 597.2832; calcd for $C_{35}H_{42}O_7Na$ ($M+Na^+$): 597.2828].

4.1.2. Deprotection of methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-C-(vinyl)-7-*O*-allyl-α-D-*manno*-octose (4). To a solution of the monoprotected diol derivative **4**; (1.48 g, 2.6 mmol) in ethanol–water (9:1 v/v, 5 mL), diazabicyclo[2.2.2]octane (DABCO, 90 mg, 0.79 mmol) was added and the mixture was warmed to ca 70°C. Wilkinson's catalyst (0.244 g, 0.26 mmol) was added and the mixture was boiled under reflux for 2 h (TLC monitoring in 20% EtOAc/hexanes two developments; the product was slightly less polar than the starting allyl ether). The mixture was cooled to room temperature, diluted with acetone (10 mL), filtered through Celite, concentrated, and the crude material was used directly in the next step without any further purification.

The crude vinyl ether was dissolved in acetone (10 mL) and water (0.75 mL) to which yellow HgO (0.63 g, 2.9 mmol) and $HgCl_2$ (0.79 g, 2.9 mmol) were added, the mixture was stirred at room temperature for 2 h (TLC monitoring in 25% EtOAc/hexanes, two developments), diluted with acetone (10 mL), filtered through Celite, concentrated and the products were separated by column chromatography (15–25% EtOAc/hexanes). Isolated first was compound **8** (colorless oil, 1.37 g, 2.54 mmol, 52%) containing the mercury species. Isolated second was diol **5** (0.436 g, 1.66 mmol, 34%) which was characterized as diacetate **5–Ac**.

Compound **8**; A 2:1 mixture of isomers as colorless oil; R_f (25% AcOEt/hexanes) 0.35; ν_{max} (liquid film) 3087–2919, 1639, 1603, 1497, 1454, 1363, 1324, 1196–927 (br), 843, 807, 738, 698, 605, 462 cm^{-1}; δ_H (200 MHz) 7.40–7.20 (15H, m, Ph), 5.80–6.00 [1H, m, C(6)C*H*=CH_2], 5.37–3.60 [18H, m, H-1, H-2, H-3, H-4, H-5, H-6, H-7, both H-8, C(6)CH=CH_2, H-1″, 3×CH_2Ph], 3.26 (3H, s, O*Me*), 2.75–3.05 (2H, m, H-6, H-2″), 1.42 (3H, d, *J*=7.7 Hz, CH_3″); δ_C (50 MHz) *main isomer* 138.4, 138.35, 138.3 (3×quat. Bn), 134.5 [C(6)*C*H=CH_2], 120.2 [C(6)CH=*C*H_2], 105.9 (C-1″),[‡] 98.6 (C-1), 80.5, 75.5, 75.4, 75.1, and 73.0, 74.8, 72.6, and 72.4 (3×O*C*H_2Ph), 67.1 (C-8), 54.9 (O*Me*), 50.6 (C-2″), 46.1 (C-6), 16.05 (CH_3″); *minor isomer* 138.4, 138.3, 138.2 (3×quat. Bn), 134.6 [C(6)*C*H=CH_2], 119.8 [C(6)CH=*C*H_2], 105.6 (C-1″), 98.5 (C1), 80.5, 75.6, 75.1, 74.7, and 73.0, 74.8, 72.5, and 72.4 (3×O*C*H_2Ph), 67.1 (C-8), 54.9 (O*Me*), 50.7 (C-2″), 45.6 (C-6), 16.0 (CH_3″); (several signals of both isomers overlapped); *m*/*z* 833 [$M(C_{35}H_{41}O_7{}^{202}Hg^{35}Cl)+Na^+$], 775 [$(C_{35}H_{41}O_7{}^{202}Hg)^-$=M−Cl, main signal]. The isotopic patterns of both ions (resulting from the presence of seven stable isotopes of Hg and two of Cl) matched perfectly well with the calculated ones.

Methyl 6,7-di-O-acetyl-2,3,4-tri-O-benzyl-6-deoxy-6-C-(vinyl)-α-D-manno-octose (**5–Ac**); colorless oil; (98%); R_f (25% AcOEt/hexanes) 0.45; $[\alpha]_D{}^{20}$=5.50 (*c* 1.2, $CHCl_3$); δ_H (200 MHz) 7.42–7.25 (15H, m, Ph), 5.87 [1H, dt, *J*=9.9, 17.1 Hz, C(6)C*H*=CH_2], 5.45 (1H, ddd, *J*=8.5, 2.3 and 6.5 Hz, H-7), 5.14 [2H, m, C(6)CH=CH_2], 4.96 and 4.76 (1H, d, *J*=11.0 Hz, CH_2Ph), 4.62 (4H, m, 2×CH_2Ph), 4.69 (1H, d, *J*=1.5 Hz, H-1), 4.44 (1H, dd, *J*=12.2 Hz, H-8_a), 4.09 (1H, t, *J*=9.5 Hz, H-4), 4.02 (1H, dd, H-8_b), 3.79 (1H, dd, *J*=3.0 Hz, H-3), 3.73 (1H, dd, H-2), 3.61 (1H, dd, *J*=1.6 Hz, H-5), 3.26 (3H, s, O*Me*), 3.02 (1H, m, H-6), 1.97 and 1.90 (6H, 2×s, 2×CH_3CO_2); δ_C (50 MHz) 170.7 and 170.0 (2×C=O), 138.6, 138.4, 138.1 (3×quat. Bn), 135.9 [C(6)*C*H=CH_2], 118.2 [C(6)CH=*C*H_2], 98.6 (C-1), 80.4, 76.5, 75.1, 73.5 and 70.4, 74.7, 72.7 and 71.9 (3×*C*H_2Ph), 64.6 (C-8), 54.8 (O*Me*), 43.8 (C-6), 21.1 and 20.7 (2×*C*H_3CO_2). *m*/*z* 641.2727; calcd for $C_{36}H_{42}O_9Na$ ($M+Na^+$): 641.2727.

[†] The configuration at the C-6 and C-7 centers is not known.

[‡] Additional signals observed at δ_C 105.6, 45.6, and 16.0 ppm pointed at the presence of a second stereoisomer.

4.1.3. Conversion of monoallyloxy-alcohols 12a–c and 13a–c into organomercurials 14a–c. To a solution of **12a–c** or **13a–c** (2.6 mmol each) in ethanol–water (9:1 v/v, 5 mL), DABCO (90 mg, 0.79 mmol) was added, and the mixture was warmed to ca 70°C.

Wilkinson's catalyst (0.244 g, 0.26 mmol) was added and the mixture was boiled under reflux for 2–5 h (TLC monitoring in 20% AcOEt/hexanes, two developments), cooled to room temperature, diluted with acetone (10 mL), filtered through Celite, concentrated, and the crude material (vinyl ethers **10a–c** and **11a–c**) was dried by co-evaporation with toluene (3×) and finally under high vacuum (0.1 torr) for 3 h.

When these vinyl ethers were treated under standard conditions (as for **4**, i.e. in the presence of water) besides the diols **9** also significant amounts of compounds containing mercury atom in the molecule were formed. To better characterize these organometallic derivatives this reaction was repeated without water.

The crude vinyl ether was dissolved in acetone (10 mL) to which yellow HgO (0.63 g, 2.9 mmol) and $HgCl_2$ (0.79 g, 2.9 mmol) were added, the mixture was stirred at room temperature for 2–5 h (TLC monitoring in 25% EtOAc/hexanes, two developments), then was diluted with acetone (10 mL), filtered through Celite, concentrated and the products were purified by column chromatography (15–25% EtOAc/hexanes). Only traces of the diols were detected; the main products being organomercurials **14a–c**.

*From **12a**, single isomer*[§] *of* **14a**; colorless oil (54%); R_f (25% AcOEt/hexanes), 0.4; δ_H (200 MHz) 7.45–7.16 (5H, m, Ph), 5.95 (1H, d, J=3.7 Hz, H-1), 5.06 (1H, d, J=2.3 Hz, H-1′), 4.75–3.90 (8H, m, H-2, H-3, H-4, H-5, both H-6 and CH_2Ph), 2.85 (1H, m, H-2′), 1.51, 1.31 (6H, 2×s, CMe_2), 1.44 (3H, d, J=7.7 Hz, CH_3′); δ_C (50 MHz) 137.3 (quat. Bn), 111.9 (*C*Me$_2$), 106.9 and 105.0 (C-1 and C-1′), 82.4, 81.6, 80.0, and 75.6, 73.6 and 67.2 (*C*H$_2$Ph and C-6), 50.6 (C-2′), 26.8 and 26.7 (CMe_2) 15.4 (*C*H$_3$′); *m/z* 609=M($C_{19}H_{25}O_6{}^{202}Hg^{35}Cl$)+$Na^+$.

*From **13a**, two isomers of* **14a**; colorless oil (47%) in the ratio ca 2:1 (from NMR); R_f (25% AcOEt/hexanes) 0.4; δ_H (200 MHz) 7.45–7.16 (5H, m, Ph), 5.96 (d, J=3.8 Hz, H-1 of main isomer), 5.92 (d, J=3.7 Hz, H-1 of minor isomer), 5.10 (d, J=2.5 Hz, H-1′ of minor isomer), 5.05 (d, 1H, J=2.5 Hz, H-1′ of main isomer), 4.75–3.90 (m, H-2, H-3, H-4, H-5, both H-6 and CH_2Ph of both isomers), 2.85 (m, H-2′ of both isomers), 1.55–1.30 (m, CMe_2, CH_3′ of both isomers); δ_C (50 MHz) 107.1 and 107.0 (C-1′ of both isomers), 105.2 and 105.1 (C-1 of both isomers), 83.0, 82.4, 81.0, 74.3 (main isomer), 82.9, 82.6, 81.0, 74.7 (minor isomer), 72.9 (*C*H$_2$Ph of both isomers), 68.1 (C-6 of minor isomer), 68.0 (C-6 of main isomer), 51.0 and 50.9 (C-2′), 16.0 and 15.9 (*C*H$_3$′), 27.0, 26.3 (CMe_2 of both isomers); *m/z* 609=M($C_{19}H_{25}O_6{}^{202}Hg^{35}Cl$)+$Na^+$.

*From **12b**, single isomer of* **14b** (contaminated with small amounts of other stereoisomer); colorless oil (64%); R_f (25% AcOEt/hexanes) 0.5; δ_H (200 MHz) 7.43–7.28 (5H, m, Ph), 5.84 (1H, d, J=3.9 Hz, H-1), 5.06 (1H, d, J=2.3 Hz, H-1′), 4.85–4.52 (3H, m, J=4.0 Hz, H-2, CH_2Ph), 4.33 (1H, m, H-5), 4.07–3.67 (5H, m, H-1′, H-3, H-4 and both H-6), 2.80 (1H, m, H-2′), 1.60, 1.37 (6H, 2×s, CMe_2), 1.39 (3H, d, J=7.7 Hz, CH_3′); δ_C (50 MHz): 137.3 (quat. Bn), 113.0 (*C*Me$_2$), 107.4 (C-1′) 104.0 (C-1), 78.2, 77.6, 76.3, and 75.4, 72.0 (*C*H$_2$Ph), 65.0 (C-6), 49.8 (C-2′), 26.8 and 26.7 (CMe_2) 16.0 (*C*H$_3$′); *m/z* 609=M($C_{19}H_{25}O_6{}^{202}Hg^{35}Cl$)+$Na^+$.

*From **13b**, two isomers of* **14b;** colorless oil (39%) in the ratio ca 1:1 (from NMR); R_f (25% AcOEt/hexanes) 0.5; δ_H (200 MHz) 7.43–7.28 (5H, m, Ph), 5.82 (d, J=3.8 Hz, H-1 of one isomer), 5.75 (d, J=3.7 Hz, H-1 of second isomer), 5.07 (d, J=3.1 Hz, H-1′ of one isomer), 4.85–3.62 (m, H-2, H-3, H-4, H-5, both H-6, CH_2Ph of both isomers and H-1′of second isomer), 2.82 (m, H-2′ for both isomers), 1.59–1.37 (m, CMe_2, CH_3′ of both isomers); δ_C (50 MHz) 137.7, 136.9 (quat. Bn of both isomers), 113.0, 112.9 (*C*Me$_2$ of both isomers), 107.3 and 107.0 (C-1′ of both isomers), 104.0, 103.8 (C-1 of both isomers), 78.2, 78.1, 77.9, 77.8, 77.2, 77.0, 75.5, 75.2 (4 C of both isomers), 71.9 (*C*H$_2$Ph of both isomers), 66.1, 65.3 (C-6 of both isomers), 50.5 and 49.6 (C-2′), 26.7 (double), 26.6, 26.5 (CMe_2 of both isomers), 15.9 and 15.6 (*C*H$_3$′ of both isomers); *m/z* 609=M($C_{19}H_{25}O_6{}^{202}Hg^{35}Cl$)+$Na^+$.

From the post reaction mixture, 3-O-benzyl-1,2-O-isopropylidene-6-O-n-propyl-α-D-ribofuranose (**13b′**); resulting from reduction of **13b** in the very first step of this sequence was obtained as colorless oil (40 mg, 0.113 mmol, 19%); R_f (25% AcOEt/hexanes) 0.5; δ_H (200 MHz) 7.44–7.28 (5H, m, Ph), 5.75 (1H, d, J=3.7 Hz, H-1), 4.80–4.50 (2H, m, J=11.5 Hz, CH_2Ph), 4.55 (1H, dd, J=3.1 Hz, H-2), 4.10–3.93 (3H, m, H-3, H-4, H-5), 3.45–3.55 (2H, m, both H-6), 3.40 (2H, t, J=6.6 Hz, both H-1′), 2.57 (O*H*), 1.59 (2H, m, both H-2′), 1.59 and 1.32 (6H, 2×s, CMe_2), 0.90 (3H, t, J=7.0 Hz, CH_3′); δ_C (50 MHz) 137.3 (quat. Bn), 113.0 (*C*Me$_2$), 104.1 (C-1), 78.3, 77.7, 77.3 and 70.1, 73.0, 72.1, and 70.9 (*C*H$_2$Ph, C-6 and C-1′), 26.8 and 26.6 (CMe_2), 22.8 (C-2′), 10.5 (*C*H$_3$′).

Acetate **13b′–Ac**; colorless oil; R_f (25% AcOEt/hexanes) 0.55; $[\alpha]_D{}^{20}$=101.3 (*c* 1.0, $CHCl_3$); δ_H (200 MHz) 7.42–7.28 (5H, m, Ph), 5.71 (1H, d, J=3.7 Hz, H-1), 5.25 (1H, m, H-5), 4.75–4.45 (2H, m, J=11.5 Hz, CH_2Ph), 4.55 (1H, dd, J=3.1 Hz, H-2), 4.15 (1H, dd, J=8.8, 4.8 Hz, H-6), 3.90 (1H, dd, J=4.3 Hz, second H-6), 3.70–3.30 (4H, m, H-3, H-4, both H-1′), 1.97 (3H, s, CH_3CO_2), 1.59 (2H, m, both H-2′), 1.58 and 1.35 (6H, 2×s, CMe_2), 0.87 (3H, t, J=7.4 Hz, CH_3′); δ_C (50 MHz) 170.3 (C=O), 137.3 (quat. Bn), 113.1 (*C*Me$_2$), 104.1 (C-1), 79.2, 77.2, 76.7 and 71.3, 73.4, 72.1, and 68.9 (*C*H$_2$Ph, C-6 and C-1′), 26.8 and 26.6 (CMe_2), 22.7 (C-2′), 21.0 (*C*H$_3$CO$_2$), 10.4 (*C*H$_3$′); *m/z* 417.18764; calcd for $C_{21}H_{30}O_7Na$ (M+Na^+): 417.18892.

*From **12c**, two isomers of* **14c**; colorless oil (53%; 3:1); R_f (25% AcOEt/hexanes) 0.5; δ_H (200 MHz) 5.14 (d, J=2.6 Hz, H-1′ of minor isomer), 5.12 (d, J=2.6 Hz, H-1′ of main isomer), 4.30–3.74 (m, H-2, H3, H-4, H-5, both H-1 and both H-6 of both isomers), 2.93 (m, H-2′ of both

[§] Small amounts of other isomer was seen in the ^{13}C NMR spectrum.

isomers), 1.50–1.30 (2×C*Me*$_2$ and C*H*$_3$′ of both isomers); δ_C (50 MHz) *main isomer* 110.6 (2×*C*Me$_2$), 108.0 (C-1′), 80.8, 78.7, 78.3, and 77.6, 68.5, 66.9 (C-1 and C-6), 51.1 (C-2′), 27.9, 27.7, 27.2, 25.8 (2×C*Me*$_2$), 16.6 (*C*H$_3$′); *minor isomer* 110.4 (2×*C*Me$_2$), 107.7 (C-1′), 80.2, 77.8, 77.6, and 76.7, 68.4, 67.2 (C-1 and C-6), 51.0 (C-2′), 27.9, 27.7, 27.2, 25.8 (2×C*Me*$_2$), 16.3 (*C*H$_3$′); *m/z* (of a mixture) 561=M($C_{15}H_{25}O_6{}^{202}Hg^{35}Cl$)+Na$^+$.

From ***13c****, two isomers of* **14c** in a 1:1 ratio; colorless oil (70%); R_f (25% AcOEt/hexanes) 0.5; δ_H (200 MHz) 5.14 and 5.12 (2×d, *J*=2.8 Hz, H-1′ of both isomers), 4.34–3.78 (m, H-2, H-3, H-4, H-5, both H-1 and both H-6 of both isomers), 2.87 (m, H-2′ of both isomers), 1.51–1.36 (2×C*Me*$_2$ and C*H*$_3$′ of both isomers); δ_C (50 MHz) 108.9 and 108.6 (C-1′ of both isomers), 107.3 and 106.9 (C-1′ of both isomers), 80.0, 79.4, 77.8, 77.4 (double), 76.9, 76.8, 75.9 (4 C of both isomers), 67.7 (double) and 66.4 (double) (C-1 and C-6 of both isomers), 50.3 and 50.2 (C-2′ of both isomers), 27.2, 27.0 (double), 26.9 (double), 26.5, 25.1 (double) (2×C*Me*$_2$ of both isomers), 15.8 and 15.5 (*C*H$_3$′ of both isomers); *m/z* (of a mixture) 561=M($C_{15}H_{25}O_6{}^{202}Hg^{35}Cl$)+Na$^+$.

4.1.4. Reduction of organometallic derivatives with sodium borohydride. To a solution of **14a** (0.380 g, 0.65 mmol) in methanol (6 mL) sodium borohydride (50 mg) was added and the mixture was stirred for 1 h at rt. Solvent was evaporated to dryness, the product was extracted with ethyl acetate (twice), dried, and purified by column chromatography (20% EtOAc/hexanes) to afford:

*Compound 3-O-benzyl-1,2-O-isopropylidene-5,6-O-n-propylidene-α-*D*-ribofuranose* (**17a**) as a mixture of two isomers in a 3:2 ratio (colorless oil, 53 mg, 0.151 mmol, 24%); R_f (25% AcOEt/hexanes) 0.3; *m/z* 373.16296; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373. 16271; the NMR spectra were recorded for the mixture from which the individual signals (at 500 MHz for ^{1}H and 125 MHz for ^{13}C) of each isomer were assigned on the basis of the ^{1}H–^{1}H and ^{1}H–^{13}C correlations; *main isomer* δ_H 7.42–7.16 (m, Ph), 5.91 (d, *J*=3.7 Hz, H-1), 4.97 (t, *J*=4.7 Hz, H-1′), 4.59 (d, C*H*$_2$Ph), 4.58 (d, H-2), 4.33 (m, H-5), 4.25 (dd, *J*=6.9 Hz, H-4), 4.18 (dd, H-6$_a$), 4.03(d, *J*=3.19 Hz, H-3), 3.91 (dd, *J*=8.6, 7.0 Hz, H-6$_b$), 1.68 (m, H-2′), 1.49 and 1.31 (2×s, C*Me*$_2$), 0.95 (t, *J*=7.5 Hz, C*H*$_3$′); δ_C 137.5 (quat. Bn), 111.9 (*C*Me$_2$), 105.4 (C-1′), 105.35 (C-1), 82.5 (C-2), 81.7 (C-3), 81.1 (C-4), 72.4 (C-5), 72.2 (*C*H$_2$Ph), 68.2 (C-6), 27.1 and 26.8 (C*Me*$_2$), 26.2 (C-2′), 7.9 (*C*H$_3$′); *minor isomer* δ_H 7.42–7.16 (m, Ph), 5.90 (d, *J*=3.7 Hz, H-1), 4.85 (t, *J*=4.7 Hz, H-1′), 4.60 (d, C*H*$_2$Ph), 4.58 (d, H-2), 4.33 (m, H-5), 4.10 (m, *J*=3.2, 7.0, 8.6, 6.4 Hz, H-4 and H-6$_a$), 4.03 (d, H-3), 3.91 (dd, *J*=6.8 Hz, H-6$_b$), 1.68 (m, H-2′), 1.49 and 1.30 (2×s, C*Me*$_2$), 0.96 (t, *J*=7.5 Hz, C*H*$_3$′); δ_C 137.7 (quat. Bn), 111.8 (*C*Me$_2$), 105.6 (C1′), 105.3 (C-1), 82.7 (C-2), 81.5 (C-3), 81.2 (C-4), 72.5 (C-5), 72.3 (O*C*H$_2$Ph), 68.0 (C-6), 27.0 (C-2′), 26.8 and 26.3 (C*Me*$_2$), 8.0 (*C*H$_3$′).

Product **23a** (=**10a**+**11a**)[¶] (106 mg, 0.302 mmol, 47%); *m/z* 373.1628; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373.1627. This product underwent cyclization to **17a** (two stereoisomers identical with those obtained directly after reduction of **14a**) after storage for two months.

Similarly, reduction of **14b** gave **17b** and **23b** (=**10b**+**11b**) and reduction of **14c** provided **17c** and **23c** (mixture of **10c**+**11c**).

Compound **17b** (single isomer); colorless oil(16%); R_f (25% AcOEt/hexanes) 0.3; $[\alpha]_D{}^{20}$=87.1 (*c* 1.2, $CHCl_3$); δ_H (200 MHz) 7.43–7.28 (5H, m, Ph), 5.74 (1H, d, *J*=3.7 Hz, H-1), 4.87 (1H, t, *J*=4.7 Hz, H-1′), 4.77, 4.61 (2×1H, 2×d, *J*=11.7 Hz, C*H*$_2$Ph), 4.44 (1H, t, *J*=4.1 Hz, H-2), 4.33 (1H, m, *J*=5.8 Hz, H-5), 4.19–3.76 (4H, m, H-3, H-4, both H-6), 1.65 (2H, m, both H-2′), 1.59 and 1.36 (6H, 2×s, C*Me*$_2$), 0.98 (3H, t, *J*=7.5 Hz, C*H*$_3$′); δ_C (50 MHz) 137.5 (quat. Bn), 112.9 (*C*Me$_2$), 106.1 and 103.8 (C-1, C-1′), 78.2, 77.9, 77.6, 75.0, 72.3 (O*C*H$_2$Ph), 65.7 (C-6), 26.9 and 26.5 (C*Me*$_2$), 26.6 (C-2′), 8.2 (CH$_3$′); *m/z* 373.16330; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373. 16271.

Compound **17c** (single isomer, but contaminated with **10c** and/or **11c**); colorless oil (48%); R_f (25% AcOEt/hexanes) 0.4; δ_H (200 MHz) 4.91 (1H, t, *J*=4.8 Hz, H-1′), 4.26–3.79 (8H, m, H-2, H-3, H-4, H-5, both H-1 and both H-6), 1.70 (2H, m, both H-2′), 1.42 (double), 1.39, 1.34 (12H, m, 2×C*Me*$_2$), 0.98 (3H, t, *J*=7.5 Hz, C*H*$_3$′); δ_C (50 MHz) 109.9 and 109.8 (2×*C*Me$_2$), 106.1 (C-1′), 80.7, 78.0, 77.1, and 76.3, 67.8 and 66.5 (C-1, C-6), 27.3, 27.0, 26.5, and 25.2 (2×C*Me*$_2$), 26.8 (C-2′), 8.1 (*C*H$_3$′); *m/z* 325.16398; calcd for $C_{15}H_{26}O_6Na$ (M+Na$^+$): 325. 16271.

4.1.5. Spectral data for the vinyl ethers 10a–c and 11a–c prepared by isomerization of 12a–c, 13a–c with the Wilkinson catalyst. *Compound* **10a**; colorless oil (48%; *trans*/*cis* ~1:1.5); R_f (25% AcOEt/hexanes) 0.25; *m/z* 373.16146; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373.16271; isomer *trans* δ_H (200 MHz) 7.41–7.28 (m, Ph), 6.03 (dq, *J*=12.1, 1.6 Hz, OC*H*=CHCH$_3$), 5.90 (d, *J*=3.8 Hz, H-1), 4.95 (m, OCH=C*H*CH$_3$), 4.70–3.68 (m, H-2, H-3, H-4, H-5, both H-6 and C*H*$_2$Ph), 2.20 (O*H*), 1.49 (m, OCH=CHC*H*$_3$), 1.50, 1.35 (2×s, C*Me*$_2$); δ_C (50 MHz) 145.8 (O*C*H=CHCH$_3$), 137.2 (quat. Bn), 111.9 (*C*Me$_2$), 105.0 (C-1), 101.4 (OCH=*C*HCH$_3$), 81.8, 81.4, 79.1, and 76.7, 62.7 (C-6), 26.7, 26.2 (C*Me*$_2$), 12.2 (OCH=CH*C*H$_3$); isomer *cis* δ_H (200 MHz) 7.41–7.28 (m, Ph), 6.07 (dq, *J*=6.0, 1.6 Hz, OC*H*=CHCH$_3$), 5.90 (d, *J*=3.6 Hz, H-1), 4.70–3.68 (m, H-2, H-3, H-4, H-5, both H-6 and C*H*$_2$Ph), 2.20 (O*H*), 1.58 (m, OCH=CHC*H*$_3$), 1.50, 147 (2×s, C*Me*$_2$); δ_C (50 MHz) 145.0 (O*C*H=CHCH$_3$), 137.2 (quat. Bn), 111.9 (*C*Me$_2$), 105.1 (C-1), 101.5 (OCH=*C*HCH$_3$), 81.8, 81.4, 79.2, and 77.9, 63.3 (C-6), 26.7, 26.2 (C*Me*$_2$), 9.2 (OCH=CH*C*H$_3$); (several signals of the *trans* and *cis* isomers overlapped).

Compound **11a**; colorless oil (53%; *trans*/*cis* ~1:2); R_f (25% AcOEt/hexanes) 0.25; *m/z* 373.16194; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373.16271; isomer *trans* δ_H (200 MHz) 7.44–7.30 (m, Ph), 6.26 (dq, *J*=12.2, 1.6 Hz, OC*H*=CHCH$_3$), 5.93 (d, *J*=3.6 Hz, H-1), 4.80 (m, OCH=C*H*CH$_3$), 4.77–4.56 and 4.22–3.80 (m, H-2, H-3, H-4, H-5, both H-6 and C*H*$_2$Ph), 2.54 (O*H*), 1.52 (m, OCH=CHC*H*$_3$), 1.48, 1.31 (2×s, C*Me*$_2$); δ_C (50 MHz)

[¶] Compounds **23** were identified by comparison of their NMR spectra with the spectra of **10**/**11**.

146.3 (O*C*H=CHCH$_3$), 137.2 (quat. Bn), 111.8 (*C*Me$_2$), 105.1 (C-1), 99.2 (OCH=*C*HCH$_3$), 82.2, 81.9, 79.5, 68.1, 72.2 (C-6), 26.7, 26.6 (C*Me*$_2$), 9.2 (OCH=CHC*H*$_3$); isomer *cis* δ_H (200 MHz) 7.44–7.30 (m, Ph), 5.99 (dq, *J*=6.2, 1.6 Hz, OC*H*=CHCH$_3$), 5.93 (d, *J*=3.6 Hz, H-1), 4.77–4.56 and 4.22–3.80 (m, H-2, H-3, H-4, H-5, both H-6 and C*H*$_2$Ph), 4.42 (m, OCH=C*H*CH$_3$), 2.54 (O*H*), 1.55 (m, OCH=CHC*H*$_3$), 1.48, *J*=1.31 Hz (2×s, C*Me*$_2$); δ_C (50 MHz) 145.8 (O*C*H=CHCH$_3$), 137.2 (quat. Bn), 111.8 (*C*Me$_2$), 105.1 (C1), 101.5 (OCH=*C*HCH$_3$), 82.2, 81.9, 67.7, 70.8 (C-6), 26.7, 26.2 (C*Me*$_2$), 12.4 (OCH=CH*C*H$_3$); (several signals of the *trans* and *cis* isomers overlapped).

Compound **10b**; colorless oil (52%; *trans*/*cis* ~1:2.5); R_f (25% AcOEt/hexanes) 0.2; *m*/*z* 373.16114; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373.16271; isomer *trans* δ_H (200 MHz) 7.48–7.25 (m, Ph), 6.13 (dq, *J*=12.2, 1.7 Hz, OC*H*=CHCH$_3$), 5.72 (d, *J*=3.6 Hz, H-1), 4.92 (m, OCH=C*H*CH$_3$), 4.75 (d, *J*=11.5 Hz, C*H*$_a$H$_b$Ph), 4.66–4.59 and 4.24–3.19 (m, H-2, H-3, H-4, H-5, both H-6 and CH$_a$*H*$_b$Ph), 2.1 (O*H*), 1.50 (m, OCH=CHC*H*$_3$), 1.57, 1.34 (m, C*Me*$_2$); δ_C (50 MHz) 146.9 (O*C*H=CHCH$_3$), 137.1 (quat. Bn), 113.3 (*C*Me$_2$), 104.2 (C-1), 101.3 (OCH=*C*HCH$_3$), 79.8, 78.0, 77.5, 76.7, 62.0 (C-6), 27.1, 26.8 (C*Me*$_2$), 12.4 (OCH=CH*C*H$_3$); isomer *cis* δ_H (200 MHz) 7.48–7.25 (m, Ph), 6.03 (dq, *J*=6.1, 1.7 Hz, OC*H*=CHCH$_3$), 5.70 (d, *J*=3.6 Hz, H-1), 4.77 (d, *J*=11.5 Hz, C*H*$_a$H$_b$Ph), 4.61–4.51 and 4.24–3.19 (m, H-2, H-3, H-4, H-5, both H-6 and CH$_a$*H*$_b$Ph), 4.34 (m, OCH=C*H*CH$_3$), 2.1 (O*H*), 1.50 (m, OCH=CHC*H*$_3$), 1.57, 1.34 (m, C*Me*$_2$); δ_C (50 MHz) 146.1 (O*C*H=CHCH$_3$), 137.1 (quat. Bn), 113.3 (*C*Me$_2$), 104.2 (C-1), 101.0 (OCH=*C*HCH$_3$), 80.8, 79.2, 77.5, 76.7, 62.3 (C-6), 27.1, 26.8 (C*Me*$_2$), 9.4 (OCH=CH*C*H$_3$); (several signals of the *trans* and *cis* isomers overlapped).

Compound **11b**; colorless oil (46%; *trans*/*cis* ~1:2); R_f (25% AcOEt/hexanes) 0.2; *m*/*z* 373.16340; calcd for $C_{19}H_{26}O_6Na$ (M+Na$^+$): 373.16271; isomer *trans* δ_H (200 MHz) 7.43–7.28 (m, Ph), 6.12 (dq, *J*=12.2, 1.6 Hz, OC*H*=CHCH$_3$), 5.72 (d, *J*=3.6 Hz, H-1), 4.93 (m, OCH=C*H*CH$_3$), 4.75 (d, *J*=11.7 Hz, C*H*$_a$H$_b$Ph), 4.62–4.51 and 4.24–3.60 (m, H-2, H-3, H-4, H-5, both H-6 and CH$_a$*H*$_b$Ph), 2.52 (O*H*), 1.52 (m, OCH=CHC*H*$_3$), 1.57, 1.34 (C*Me*$_2$); δ_C (50 MHz) 146.4 (O*C*H=CHCH$_3$), 136.6 (quat. Bn), 112.8 (*C*Me$_2$), 103.8 (C-1), 100.9 (OCH=*C*HCH$_3$), 79.2, 77.4, 77.8, 76.4, 61.5 (C-6), 26.5, 26.3 (C*Me*$_2$), 11.9 (OCH=CH*C*H$_3$); isomer *cis* δ_H (200 MHz) 7.43–7.28 (m, Ph), 6.02 (dq, *J*=6.2, 1.6 Hz, OC*H*=CHCH$_3$), 5.70 (d, *J*=3.6 Hz, H-1), 4.78 (d, *J*=11.7 Hz, C*H*$_a$H$_b$Ph), 4.92 (m, OCH=C*H*CH$_3$), 4.62–4.51 and 4.24–3.60 (m, H-2, H-3, H-4, H-5, both H-6 and CH$_a$*H*$_b$Ph), 2.47 (O*H*), 1.50 (m, OCH=CHC*H*$_3$), 1.57, 1.34 (C*Me*$_2$); δ_C (50 MHz) 145.6 (O*C*H=CHCH$_3$), 136.6 (quat. Bn), 112.8 (*C*Me$_2$), 103.7 (C-1), 100.6 (OCH=*C*HCH$_3$), 80.2, 78.7, 77.0, 76.1, 61.9 (C-6), 26.5, 26.3 (C*Me*$_2$), 8.9 (OCH=CH*C*H$_3$); (several signals of the *trans* and *cis* isomers overlapped).

Compound **10c**; colorless oil (38%; *trans*/*cis* ~1:2); R_f (25% AcOEt/hexanes) 0.4; *m*/*z* 325.16232; calcd for $C_{15}H_{26}O_6Na$ (M+Na$^+$): 325.16271; isomer *trans* δ_H (200 MHz) 6.17 (dq, *J*=11.4, 1.6 Hz, OC*H*=CHCH$_3$), 5.00 (m, OCH=C*H*CH$_3$), 4.20–3.74 (m, H-2, H-3, H-4, H-5, both H-1 and both H-6), 1.52 (m, CH=CHC*H*$_3$), 1.40, 1.39, 1.38, 1.33 (2×C*Me*$_2$); δ_C (50 MHz) 146.6 (O*C*H=CHCH$_3$), 109.7 (double, 2×*C*Me$_2$), 101.1 (OCH=*C*HCH$_3$), 80.8, 79.1, 77.6, and 76.7, 67.9 and 62.6 (C-1, C-6), 27.0, 26.4, 25.1 (double) (2×C*Me*$_2$), 12.1 (OCH=CHC*H*$_3$); isomer *cis* δ_H (200 MHz) 6.06 (dq, *J*=6.1, 1.6 Hz, OC*H*=CHCH$_3$), 4.40 (m, OCH=C*H*CH$_3$), 4.20–3.74 (m, H-2, H-3, H-4, H-5, both H-1 and both H-6), 1.61 (m, CH=CHC*H*$_3$), 1.42, 1.40, 1.36, 1.33 (2×C*Me*$_2$); δ_C (50 MHz) 145.7 (O*C*H=CHCH$_3$), 109.6 (double, 2×*C*Me$_2$), 101.3 (OCH=*C*HCH$_3$), 80.9, 80.2, 77.3, and 76.6, 67.9 and 63.1 (C-1, C-6), 27.1, 26.4 (double), 25.1 (2×C*Me*$_2$), 9.3 (OCH=CHC*H*$_3$); (several signals of the *trans* and *cis* isomers overlapped).

Compound **11c**; colorless oil (62%; *trans*/*cis* ~2:3); R_f (25% AcOEt/hexanes) 0.4; *m*/*z* 325.16203; calcd for $C_{15}H_{26}O_6Na$ (M+Na$^+$): 325. 16271; isomer *trans* δ_H (200 MHz) 6.27 (dq, *J*=12.6, 1.6 Hz, OC*H*=CHCH$_3$), 4.82 (m, OCH=C*H*CH$_3$), 4.21–3.70 (m, H-2, H-3, H-4, H-5, both H-1 and both H-6), 2.45 (O*H*), 1.55 (m, OCH=CHC*H*$_3$), 1.42 (double), 1.38, 1.34 (2×C*Me*$_2$); δ_C (50 MHz) 146.1, (O*C*H=CHCH$_3$), 109.6 and 109.5 (2×*C*Me$_2$), 101.6 (OCH=*C*HCH$_3$), 79.9, 77.0, 68.8, and 68.5, 70.4 and 67.6 (C-1, C-6), 27.0, 26.7, 26.5, 25.1 (2×C*Me*$_2$), 9.0 (OCH=CH*C*H$_3$); isomer *cis* δ_H (200 MHz) 5.99 (dq,*J*=6.1, 1.7 Hz, OC*H*=CHCH$_3$), 4.44 (m, OCH=C*H*CH$_3$), 4.21–3.70 (m, H-2, H-3, H-4, H-5, both H-1 and both H-6), 2.50 (O*H*), 1.55 (m, OCH=CHC*H*$_3$), 1.42 (double), 1.38, 1.34 (2×C*Me*$_2$); δ_C (50 MHz) 145.4 (O*C*H=CHCH$_3$), 109.6 and 109.5 (2×*C*Me$_2$), 98.5 (OCH=*C*HCH$_3$),79.7, 77.0, 68.8, and 68.5, 73.4 and 67.6 (C-1, C-6), 27.0, 26.7, 26.5, 25.1 (2×C*Me*$_2$), 12.3 (OCH=CH*C*H$_3$); (several signals of the *trans* and *cis* isomers overlapped).

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