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Claisen rearrangement of hexenopyranoside allyl ethers: A new approach to α-branched-chain dicarbonyl sugars

Kimiaki Furuichi*, Hiromasa Hashimoto, and Toshio Miwa†
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558 (Japan)

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ABSTRACT

The β-hydroxy phenylselenides prepared by cleavage of 2,3-anhydropyranosides with sodium phenylselenide were quantitatively transformed into the corresponding allyl ethers. Oxidation of the allyl ethers, followed by thermal elimination and rearrangement, gave *C*-allylhexosuloses in good yield. Rearrangement of ethers **10a** and **10c** was especially stereoselective, giving axially oriented *C*-allylhexosulose derivatives, which were readily epimerized to their equatorial isomers in quantitative yield. In the Claisen rearrangement of the crotyl ether **14c**, the chirality of the sugar was transferred to the newly formed asymmetric carbon atom. This procedure provides a convenient method to convert an anhydro sugar into a *C*-allylhexosulose derivative.

INTRODUCTION

Sugars are one of the most important chiral sources for natural product synthesis[1]. Several workers have utilized the Claisen rearrangement as the key step for the introduction of carbon chains into sugar skeletons. Ireland *et al.* explored the Claisen rearrangement of enolates of 4-acyloxyglycals toward the synthesis of many kinds of natural products[2]. The reaction was extended by Curran and Suh to a tandem Claisen reaction of the enolates of 4,5-di-*O*-acylglycals[3]. Likewise, Fraser-Reid *et al.* studied the Claisen rearrangement of the enolates of 2- or 3-(2-acyloxyethylidene)deoxy sugars and succeeded in the synthesis of multiply substituted sugar derivatives[4]. Several years ago, we reported a synthesis of vicinal deoxy-carbonyl sugars by the elimination of β-selenoxy alcohols derived from anhydro sugars[5]. As an extension, starting with an allyl ether leads to unsaturated sugars having an allyloxy function on the alkenic carbon atom, a structure suitable for the Claisen rearrangement. This type of Claisen rearrangement has never been investigated in sugar chemistry and provides new information of both preparative and stereochemical utility.

* To whom correspondence should be addressed.
† Present address: University of Marketing and Distribution Science, Kobe 651-21, Japan.

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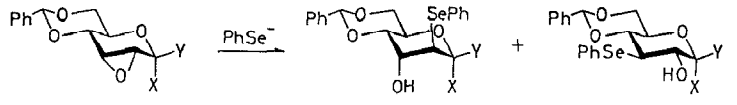
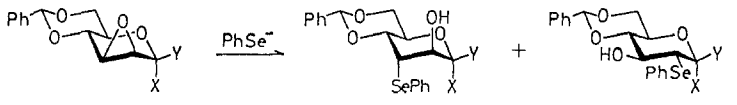
RESULTS AND DISCUSSION

In a previous paper[5], we opened the anhydro sugars with a sodium *o*-nitrophenylselenide–borane complex, prepared from *o*-nitrophenyl selenocyanate and sodium borohydride, in moderate yields. Here, the anhydro sugars (**1a**, **1b**, **2a**, and **2b**) were treated with sodium phenylselenide, a stronger nucleophile, in dimethyl sulfoxide, giving *β*-hydroxy phenylselenyl sugar derivatives (**3a**, **3b**, **5a**, and **5b**) in satisfactory yields, as summarized in Table I. The stereochemistry of reaction, obeying the Fürst–Plattner rule[6], is supported by the smaller coupling constants of the anomeric protons of the major 2,3-diaxial products than those of the corresponding minor 2,3-diequatorial products. The resulting selenides were converted into vicinal deoxy-carbonyl sugars as described before.



1a X = OMe, Y = H **3a** X = OMe, Y = H **4a** X = OMe, Y = H

1b X = H, Y = OMe **3b** X = H, Y = OMe **4b** X = H, Y = OMe



2a X = OMe, Y = H **5a** X = OMe, Y = H **6a** X = OMe, Y = H

2b X = H, Y = OMe **5b** X = H, Y = OMe **6b** X = H, Y = OMe

The *β*-hydroxy phenylselenides were transformed almost quantitatively into the corresponding allyl ethers (**7a**, **7b**, **8a**, and **8b**) by treating them with sodium hydride and allyl bromide in *N*,*N*-dimethylformamide at 0°. Oxidation of these selenides with *m*-chloroperoxybenzoic acid yielded relatively stable selenoxides in quantitative yield.

TABLE I

Reaction of methyl 2,3-anhydro-4,6-*O*-benzylidene-α(or *β*)-D-*allo*(or *manno*)-pyranosides with sodium phenylselenide in dimethyl sulfoxide

Starting material	*Temp. (°C)*	*Min.*	*Compound isolated (Yield, %)*
1a	70	5	**3a** (52), **1a** (44)
1a	90	5	**3a** (69), **4a** (5)
1b	90	5	**3b** (37), **4b** (20), **1b** (39)
1b	90	20	**3b** (73), **4b** (22)
2a	70	5	**5a** (22), **2a** (62)
2a	90	10	**5a** (76), **6a** (trace), **2b** (20)
2b	70	5	**5b** (90), **6b** (4)

TABLE II

Thermolysis of methyl 4,6-*O*-benzylidene-2(or 3)-deoxy-2(or 3)-phenylselenoxyl-α(or β)-D-altropyranosides and their enol ethers in boiling solvent

Starting material	*Solvent*	*Min*	*Product*	*Ratio*	*Yield (%)*
Selenoxide of **7a**	Benzene[a]	50	**9a**		74
8a	Benzene[a]	30	**10a**		87
8b	CH_2Cl_2	240	**10b**		92
8c	Benzene[a]	30	**10c**		91
8d	Benzene[a]	15	**10d**		81
7a	Xylene[a]	20	**11a/12a**[b]		72
7b	Xylene[a]	20	**11b/12b**[b]		85
8a	Xylene[a]	30	**13a/14a**[b]		84
8b	Xylene[a]	20	**13b/14b**[b]		73
9a	Xylene	15	**11a/12a**	2/1	97
10a	Xylene	20	**13a**		99
10b	Xylene	30	**13b/14b**	2/1	95
10c	Xylene	120	**13c**		80
10d	Xylene	120	**13d/14d**	3/1	70

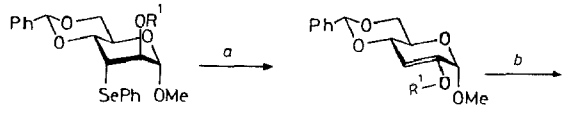
[a] In the presence of triethylamine. [b] Crude products were purified by silica gel chromatography.

The ^{13}C-n.m.r. spectra of these selenoxides showed them to be diastereoisomeric mixtures at the selenium atom.

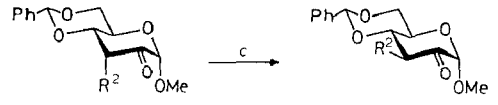
These selenoxides were converted into *C*-allyl compounds in good yields when heated in xylene under reflux in the presence of triethylamine. Under mild conditions, the intermediate enol allyl ethers were isolated, except in one case (**9b**). These enol allyl ethers gave predominantly axial *C*-allyl compounds, as shown in Table II. All of the axial isomers were readily epimerized into their equatorial isomers by treatment with silica gel in benzene.

The selenoxides of **8a**, **8b**, and **7b** have a *syn*-hydrogen atom only on C-2 or C-3, and therefore they should give only one elimination product. On the other hand, that of **7a** has *syn*-hydrogen atoms on both sides of the selenoxide function and could possibly produce two elimination products. In such cases, the fragmentation occurs more easily at the side remote from an electronegative group[7]. In sugar chemistry, the formation of allylic alcohols has been observed in the literature[8]. The two oxygen functions on the anomeric carbon would have a more-powerful effect here than the single hydroxyl group on C-3 in this sense, as previously observed[5].

Generally, the Claisen rearrangement proceeds through a chair-like transition state[9]. However, Ireland *et al.* reported that the transition state of the reaction is biased subtly in systems were the allylic double bond is involved in a six-membered ring[10]. In order to clarify the stereochemistry of the present system, the phenylselenyl alcohol **5a** was converted into the corresponding crotyl ether **8c** (*E*:*Z* = 3:1). Oxidation of **8c**, followed by thermal elimination, gave an enol ether **10c**. The Claisen rearrangement of **10c** produced exclusively compound **13c**, having an axial side chain. Treatment of this compound with silica gel led to the equatorial isomer **14c**. The products **13c** and **14c** are



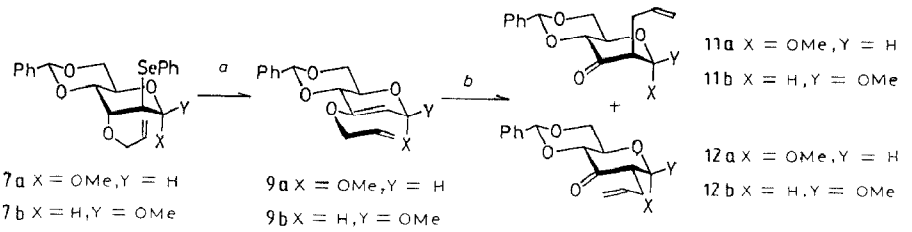
8a $R^1 = CH_2CH{=}CH_2$ 10a $R^1 = CH_2CH{=}CH_2$
8c $R^1 = CH_2CH{=}CHCH_3$ 10c $R^1 = CH_2CH{=}CHCH_3$
8d $R^1 = CH_2CH{=}CMe_2$ 10d $R^1 = CH_2CH{=}CMe_2$



13a $R^2 = CH_2CH{=}CH_2$ 14a $R^2 = CH_2CH{=}CH_2$
13c $R^2 = CH(CH_3)CH{=}CH_2$ 14c $R^2 = CH(CH_3)CH{=}CH_2$
13d $R^2 = CMe_2CH{=}CH_2$ 14d $R^2 = CMe_2CH{=}CH_2$

a 1. MCPBA/CH_2Cl_2, 2. benzene reflux. *b* xylene, reflux.
c SiO_2-benzene

composed of two epimers in the ratio of 3 to 1, reflecting the alkenic composition of the starting crotyl ether.

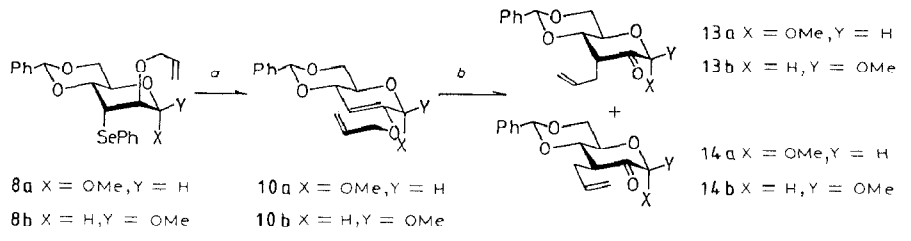


7a X = OMe, Y = H
7b X = H, Y = OMe

9a X = OMe, Y = H
9b X = H, Y = OMe

11a X = OMe, Y = H
11b X = H, Y = OMe

12a X = OMe, Y = H
12b X = H, Y = OMe



8a X = OMe, Y = H
8b X = H, Y = OMe

10a X = OMe, Y = H
10b X = H, Y = OMe

13a X = OMe, Y = H
13b X = H, Y = OMe

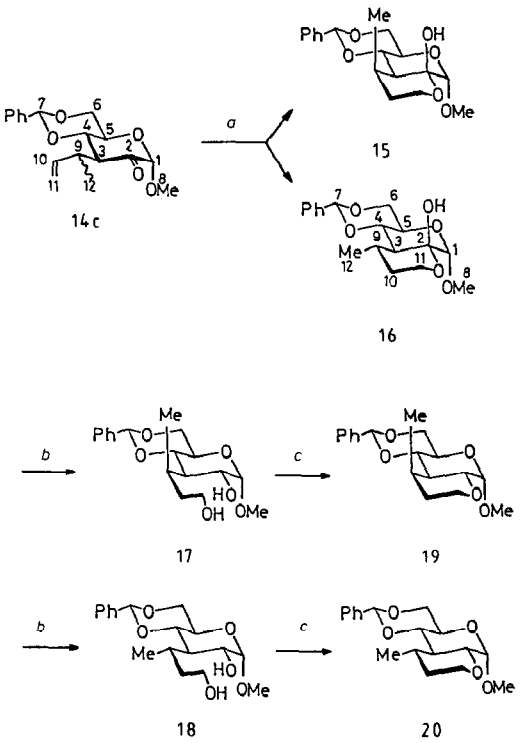
14a X = OMe, Y = H
14b X = H, Y = OMe

a 1. MCPBA, 2. benzene reflux (8b. CH_2Cl_2 reflux)
b xylene, reflux

Hydroboration of the epimeric mixture of **14c** with disiamylborane followed by oxidation gave the cyclic acetals **15** and **16** in 57 and 12% yields, respectively, with simultaneous cyclization. Apparently, the former is derived from the *E*-crotyl ether and the latter from the *Z*-isomer. The reduction of hemiacetals **15** and **16** with sodium borohydride gave glycols **17** and **18**, respectively. Mono-tosylation of these glycols,

followed by treatment with base yielded the tricyclic ethers **19** and **20**. Although the proton n.m.r. spectra of compounds **15** and **19** did not give information about the stereochemistry of the new ether ring, those of compounds **16** (2.28 p.p.m., triplet, J = 9.2 Hz, H-3) and **20** (1.93 p.p.m., quartet, J = 10.0 Hz, H-3) definitely indicated that the new *trans*-fused ring has an equatorial methyl group, as shown in formulas **16** and **20**. Comparison of the carbon-13 n.m.r. spectra (Table III) of compounds **19** and **20** suggested that both of these compounds have the same ring-system, in which the axial methyl group of the former shielded the ring carbon atoms more than did the equatorial methyl group of the latter. Consequently, the minor product has the *S*-configuration at C-9, whereas the major product has *R*-configuration at that carbon atom. These results verified that the Claisen rearangement of this system proceeded through a chair-like transition state. When the allyl group is located in the pyranose ring, the chair-like transition state is unfavorable because of interaction between the vinyl group and the pyranose ring[2,3]; however, the chair-like transition state is more favorable here than the boat-form, as it avoids the eclipsing of the double bonds.

Ireland *et al.* reported that the Claisen rearrangement proceeds so as to favor axial attachment of the side chain[11]. Our main products were likewise those having the side chain in axial orientation. It is very difficult to rationalize why compounds **10a** and **10c** gave only the axial product. Curran and Suh[3] demonstrated that, in the case of



a 1. disyamylborane, 2. H_2O_2–NaOH. *b* $NaBH_4$.
c 1. TsCl–pyridine, 2. NaOMe–MeOH

TABLE III

Assignment of ^{13}C-n.m.r. data of on methyl 3-(or 2)-allyl-4,6-*O*-benzylidenehexopyranosid-2(or 3)-ulose and their derivatives

Atom	**11a**	**12a**	**11b**	**12b**	**13a**	**14a**	**13b**	**14b**	**13c**	**14c**	**14d**	**15**	**16**	**17**	**18**	**19**	**20**
1	103.3	103.1	102.1	105.4	101.5	100.9	99.9	101.0	100.9	101.0	101.7	101.7	101.3	99.7	99.6	98.2	97.9
2	54.9	53.4	53.5	55.4	199.8	199.6	199.7	198.6	198.9	199.3	200.6	96.4	94.8	68.7	69.0	71.9	78.3
3	200.4	198.3	200.8	198.4	52.5	50.7	51.8	53.6	57.9	55.6	59.8	44.9	46.6	45.5	44.6	39.4	43.7
4	80.8	83.0	79.8	82.4	78.5	80.0	77.8	79.0	77.7	79.1	80.1	76.2	80.4	77.9	77.9	76.9	82.1
5	65.1	66.0	66.6	66.6	59.0	64.2	64.9	69.0	68.9	64.1	65.3	63.9	65.5	63.7	63.5	64.1	64.2
6	69.5	69.5	70.0	69.2	69.3	69.0	69.4	69.3	69.3	69.1	69.3	69.3	69.1	69.3	69.4	69.4	69.5
7	102.2	101.9	101.2	101.7	101.5	101.2	101.4	101.2	101.4	101.0	101.1	101.0	101.1	101.3	101.3	101.5	101.3
8	56.2	55.2	56.2	57.2	56.1	55.6	56.6	56.8	56.3	55.5	55.5	55.2	55.1	55.3	55.2	55.2	55.2
9	35.0	28.2	29.8	28.2	29.7	27.6	30.0	28.8	35.5	32.9	38.7	26.8	28.2	26.1	26.0	23.5	35.1
10	133.6	134.8	134.5	134.9	134.6	134.7	134.4	134.5	114.8	115.2	111.5	29.1	34.7	36.2	39.2	32.0	35.2
11	118.3	117.2	117.6	117.1	117.3	117.3	117.5	117.6	140.6	140.3	146.1	62.5	61.2	61.0	60.7	63.2	68.9
12									17.4	17.3	26.3	21.2	21.6	17.1	14.7	11.8	21.8
13											25.9						
14	136.6	136.6	136.6	136.6	137.0	137.1	137.0	137.0	137.2	137.2	137.3	137.7	137.6	137.5	137.5	137.6	137.7
15	126.3	126.3	126.4	126.3	126.2	126.0	126.1	126.0	125.9	126.0	126.1	125.9	125.9	126.0	125.9	126.1	126.1
16	128.2	128.2	128.2	128.2	128.2	128.3	128.2	128.3	128.2	128.3	128.2	128.2	128.1	128.2	128.2	128.2	128.3
17	129.2	129.2	129.2	129.2	129.2	129.0	129.2	129.1	128.9	129.1	129.0	128.8	128.7	128.9	128.8	128.9	128.9

4,5-diacylglycal enolates, the more crowded is the axial transition state, the faster is the reaction. The faster the Claisen rearrangement, the less products epimerization takes place. In order to provide insight into the reaction, compound **3a** was varied to the corresponding prenyl ether. After oxidation, thermal reaction gave a mixture of **13d** and **14d** in the ratio of 3 to 1. This situation may be attributed to an overcrowded transition state in the rearrangement. Treatment of the mixture with silica gel gave a reversed composition (1:5).

In conclusion, this procedure provides a convenient method for converting an anhydro sugar into a *C*-allylhexosulose derivative, especially one having the side chain axially oriented.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto melting-point apparatus and uncorrected. The following spectrometers were used: i.r.: Jasco A-102; n.m.r.: Jeol FX-100; mass spectra: Jeol D-300. N.m.r. spectra were measured in $CDCl_3$. Chemical shifts in ^{1}H-n.m.r. spectra are reported in p.p.m. downfield from the internal reference (Me_4Si) and those of ^{13}C spectra from the signal of $CDCl_3$ (δ 77.1). I.r. spectra and optical rotations were measured in $CHCl_3$ solution. Elemental analyses were performed by the Microanalytical Laboratory of our Faculty. All solvents were freshly distilled before use. Oxolane was distilled from sodium benzophenone ketyl, Me_2SO, *N,N*-dimethylformamide, and pyridine from BaO, and CH_2Cl_2 and aromatic hydrocarbons from P_2O_5, respectively. All extracts in the preparations were dried over Na_2SO_4 and the solvents removed by rotary evaporation under diminished pressure. Preparative chromatography was carried out on silica gel (Merck, Kieselgel 60, 70–230 mesh ASTM) and eluted with 9:1 (v/v) benzene–EtOAc unless otherwise indicated. Analytical t.l.c. was performed with a 0.25-mm layer of silica gel containing PF_{254} indicator.

Methyl 4,6-O-benzylidene-2-deoxy-2-phenylselenyl-α-D-altropyranoside (**3a**) *and methyl 4,6-O-benzylidene-3-deoxy-3-phenylselenyl-α-D-glucopyranoside* (**4a**). — To a stirred solution of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**1a**) (3.02 g) in Me_2SO (10 mL) was added sodium phenylselenide (2.43 g) and the mixture was heated for 5 min to 90°. After addition of water (100 mL), the mixture was extracted with $CHCl_3$ (5 × 15 mL). The $CHCl_3$ layer was dried and evaporated. Chromatography of the crude product using silica gel (20 g) followed by elution with 19:1 (v/v) benzene–EtOAc gave a major adduct **3a** (69.5% yield) and a minor one **4a** (5.3% yield). Compound **3a** was obtained as crystals from EtOH; m.p. 86–88°, $[\alpha]_D^{17}$ +63.5° (*c* 0.5); ν_{max} 3580, 1578, 1112, 1044, and 698 cm^{-1}; ^{1}H-n.m.r.: δ 3.23 (d, *J* 5.6 Hz, OH), 3.34 (s, 3 H), 3.65 (dd, 1 H, *J* 0.9, 2.6 Hz, H-2), 3.74–4.07 (m, 2 H), 4.12–4.40 (m, 3 H), 5.00 (bs, 1 H, H-1), 5.63 (s, 1 H), 7.20–7.40 (m, 7 H), and 7.40–7.60 (m, 3 H); ^{13}C-n.m.r.: δ 46.9 (d, C-2), 55.5 (q), 58.6 (d, C-5), 69.0 (t, C-6), 69.5 (d, C-3), 76.5 (d, C-4), 101.9 (d, C-1), 102.1 (d), 126.2 (d × 2), 128.2 (d × 2), 128.8 (s), 129.0 (d), 129.4 (d × 2), 133.4 (d × 2), and 137.2 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 56.98; H, 5.24.

Compound **4a** was obtained as crystals from EtOH; m.p. 123–124°, $[\alpha]_D^{28}$ −32.7° (*c* 1.0); ν_{max} 3570, 1580, 1085, 1070, 1050, and 1000 cm^{-1}; ^{1}H-n.m.r.: δ 2.74 (d, *J* 5.6 Hz, OH), 3.10–3.40 (m, 3 H), 3.40 (s, 3 H), 3.40–3.70 (m, 2 H), 3.80 (m, 1 H, H-5), 4.25 (dd, 1 H, *J* 4.4, 9.2 Hz, H-6*e*), 4.79 (d, 1 H, *J* 2.8 Hz, H-1), 5.38 (s, 1 H), 7.20–7.50 (m, 8 H), and 7.60–7.70 (m, 2 H); ^{13}C-n.m.r.: δ 47.8 (d, C-3), 55.2 (q), 64.6 (d, C-5), 68.9 (t, C-6), 69.7 (d, C-2), 78.1 (d, C-4), 99.3 (d, C-1), 101.6 (d), 125.1 (s), 126.2 (d × 2), 128.2 (d × 2), 128.5 (d), 128.9 (d × 3), and 137.1 (d × 2, s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 57.13; H, 5.22.

*Methyl 4,6-O-benzylidene-2-deoxy-2-phenylselenyl-β-*D*-altropyranoside* (**3b**) *and methyl 4,6-O-benzylidene-3-deoxy-3-phenylselenyl-β-*D*-glucopyranoside* (**4b**). — Compound **1b** gave **3b** (73% yield) and **4b** (22% yield) as described for **3a** and **4a**. Compound **3b** was obtained as crystals from EtOH; m.p. 109–110°, $[\alpha]_D^{22}$ +3.8° (*c* 1.0); ν_{max} 3580, 1580, 1100, 1090, and 1015 cm^{-1}; ^{1}H-n.m.r.: δ 2.38 (s, OH), 3.56 (s, 3 H), 3.63 (dd, 1 H, *J* 2.2, 3.2 Hz, H-2), 3.80–4.50 (m, 5 H), 4.98 (d, 1 H, *J* 2.2 Hz, H-1), 5.61 (s, 1 H), 7.20–7.40 (m, 8 H), and 7.50–7.60 (m, 2 H); ^{13}C-n.m.r.: δ 49.9 (d, C-2), 57.1 (q), 64.4 (d, C-5), 68.9 (t, C-6), 70.4 (d, C-4), 76.8 (d, C-4), 99.9 (d, C-1), 101.9 (d), 126.1 (d × 2), 127.5 (d), 128.1 (d × 2), 129.1 (d × 3), 129.2 (s), 133.9 (d × 2), and 137.0 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 56.88; H, 5.24.

Compound **4b** was obtained as crystals from EtOH; m.p. 112–114°, $[\alpha]_D^{18}$ +163.0° (*c* 1.0); ν_{max} 3580, 3510, 1580, 1095, and 1090 cm^{-1}; ^{1}H-n.m.r.: δ 2.97 (s, OH), 3.10–3.40 (m, 3 H), 3.56 (s, 3 H), 3.50–3.66 (m, 2 H), 4.30 (m, 1 H, H-6*e*), 4.36 (d, 1 H, *J* 6.4 Hz, H-1), 5.39 (s, 1 H), 7.20–7.50 (m, 8 H), and 7.55–7.65 (m, 2 H); ^{13}C-n.m.r.: δ 49.2 (d, C-3), 57.2 (q), 68.5 (t, C-6), 69.8 (d, C-5), 71.2 (d, C-2), 77.5 (d, C-4), 101.4 (d, C-1), 105.2 (d), 124.8 (s), 125.9 (d × 2), 128.1 (d × 2), 128.6 (d), 128.8 (d), 128.9 (d × 2), and 137.1 (d × 2, s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 56.88; H, 5.20.

*Methyl 4,6-O-benzylidene-3-deoxy-3-phenylselenyl-α-*D*-altropyranoside* (**5a**) *and methyl 4,6-O-benzylidene-2-deoxy-2-phenylselenyl-α-*D*-glucopyranoside* (**6a**). — Compound **2a** gave **5a** (76% yield) and **6a** (in traces) as indicated for **3a** and **4a**. Compound **5a** formed crystals from EtOH; m.p. 156.5–157.5°, $[\alpha]_D^{14}$ −50.7° (*c* 0.5); ν_{max} 3600, 1580, 1110, 1050, 1030, and 1020 cm^{-1}; ^{1}H-n.m.r.: δ 2.40 (d, *J* 6.4 Hz, OH), 3.21 (s, 3 H), 3.70–4.00 (m, 2 H), 4.20–4.40 (m, 4 H), 4.61 (bs, 1 H, H-1), 5.61 (s, 1 H), 7.10–7.30 (m, 8 H), and 7.55–7.66 (m, 2 H); ^{13}C-n.m.r.: δ 47.1 (d, C-3), 54.9 (q), 60.9 (d, C-5), 68.9 (t, C-6), 72.7 (d, C-2), 75.3 (d, C-4), 100.7 (d, C-1), 101.5 (d), 126.2 (d × 2), 127.0 (d), 128.0 (d × 2), 128.6 (d × 2), 128.8 (d), 132.4 (s), 133.9 (d × 2), and 137.2 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 57.07; H, 5.25.

Compound **6a** formed crystals from EtOH; m.p. 134–135°, $[\alpha]_D^{15}$ +24.8° (*c* 0.25); ν_{max} 3590, 1580, 1130, 1120, 1090, and 1080 cm^{-1}; ^{1}H-n.m.r.: δ 2.68 (bs, OH), 3.19 (dd, 1 H, *J* 3.5, 10.7 Hz, H-2), 3.41 (s, 3 H), 3.55 (t, 1 H, *J* 9.0 Hz, H-4), 3.72 (t, 1 H, *J* 9.3 Hz, H-6*a*), 3.92 (dd, 1 H, *J* 4.1, 9.3 Hz, H-5), 4.14 (dd, 1 H, *J* 9.3, 10.8 Hz, H-3), 4.30 (m, 1 H, H-6*e*), 4.93 (d, 1 H, *J* 3.4 Hz, H-1), 5.55 (s, 1 H), 7.20–7.50 (m, 8 H), and 7.60–7.70 (m, 2 H); ^{13}C-n.m.r.: δ 52.0 (d, C-2), 55.9 (q), 63.1 (d, C-5), 69.1 (t, C-6), 70.7 (d, C-3), 83.0 (d,

C-4), 101.7 (d, C-1), 102.2 (d), 126.4 (d × 2), 127.7 (d), 128.4 (d × 2), 129.2 (d × 3), 130.0 (s), 134.1 (d × 2), and 137.2 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 56.89; H, 5.20.

*Methyl 4,6-O-benzylidene-3-deoxy-3-phenylselenyl-β-*D*-altropyranoside* (**5b**) *and methyl 4,6-O-benzylidene-2-deoxy-2-phenylselenyl-β-*D*-glucopyranoside* (**6b**). — Compound **2b** gave **5b** (90% yield) and **6b** (4% yield) as described for **3a** and **4a**. Compound **5b** formed crystals from EtOH; m.p. 151–152°, $[\alpha]_D^{25}$ −64.4° (*c* 1.0); ν_{max} 3570, 1580, 1100, 1090, and 1000 cm^{-1}; ^{1}H-n.m.r.: δ 2.66 (s, OH), 3.56 (s, 3 H), 3.80–4.00 (m, 4 H), 4.20–4.40 (m, 2 H), 4.93 (s, 1 H, H-1), 5.60 (s, 1 H), 7.20–7.50 (m, 8 H), and 7.50–7.60 (m, 2 H); ^{13}C-n.m.r.: δ 46.7 (d, C-3), 56.8 (q), 66.4 (d, C-4), 68.8 (t, C-6), 71.7 (d, C-2), 75.3 (d, C-5), 98.9 (d, C-1), 101.7 (d), 126.2 (d × 2), 127.6 (d), 128.1 (d × 2), 128.9 (d), 129.1 (d × 2, s), 134.1 (d × 2), and 137.3 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 57.00; H, 5.29.

Compound **6b** gave crystals from EtOH; m.p. 39–41°, $[\alpha]_D^{25}$ +37.0° (*c* 1.0); ν_{max} 3590, 3530, 1575, 1120, 1095, 1080, and 980 cm^{-1}; ^{1}H-n.m.r.: δ 2.98 (s, OH), 3.00 (m, 1 H), H-2), 3.30 (m, 1 H, H-5), 3.55 (s, 3 H), 3.50–3.90 (m, 3 H), 4.31 (m, 1 H, H-6*e*), 4.32 (d, 1 H, *J* 8.0 Hz, H-1), 5.54 (s, 1 H), 7.20–7.50 (m, 8 H), and 7.60–7.70 (m, 2 H); ^{13}C-n.m.r.: δ 51.8 (d, C-2), 57.4 (q), 66.0 (d, C-5), 68.6 (t, C-6), 70.5 (d, C-3), 81.8 (d, C-4), 101.9 (d), 103.6 (d, C-1), 125.5 (s), 126.3 (d × 2), 128.3 (d × 2), 128.8 (d), 129.2 (d × 3), 136.7 (d × 2), and 137.0 (s).

Anal. Calc. for $C_{20}H_{22}O_5Se$: C, 57.01; H, 5.27. Found: C, 56.84; H, 5.55.

*Methyl 3-O-allyl-4,6-O-benzylidene-2-deoxy-2-phenylselenyl-α-*D*-altropyranoside* (**7a**). — To a solution of NaH (2 mg, 50% oil-suspension) in *N,N*-dimethylformamide was added compound **3a** (100 mg) at 0° and the mixture was stirred for 30 min. Allyl bromide (0.03 mL) was added and, after 20 min, water (100 mL) was added and extracted with $CHCl_3$ (3 × 10 mL). The $CHCl_3$ layer was dried. Evaporation of the solvent gave **7a** as a syrup (quantitative yield); $[\alpha]_D^{26}$ +68.8° (*c* 1.0); ν_{max} 1620, 1578, 1126, 1112, 1082, 1042, 1004, and 970 cm^{-1}; ^{1}H-n.m.r.: δ 3.41 (s, 3 H), 3.63–3.92 (m, 3 H), 4.08–4.43 (m, 5 H), 4.98 (s, 1 H, H-1), 5.00–5.20 (m, 2 H), 5.62 (s, 1 H), 5.83 (ddt, 1 H, *J* 5.6, 10.0, 17.2 Hz), 7.20–7.40 (m, 6 H), and 7.40–7.60 (m, 4 H); ^{13}C-n.m.r.: δ 46.2 (d, C-2), 55.5 (q), 58.5 (d, C-5), 69.3 (t, C-6), 71.8 (t), 74.8 (d, C-3), 76.8 (d, C-4), 101.5 (d, C-1), 102.1 (d), 116.8 (t), 126.2 (d × 2), 128.1 (d × 2, d), 128.9 (d), 129.3 (d × 2, s), 134.0 (d × 2), 134.8 (d), and 137.6 (s); m.s. calc. for $C_{23}H_{26}O_5{}^{78}Se$: 460.0954. Found: 460.0956.

*Methyl 3-O-allyl-4,6-O-benzylidene-2-deoxy-2-phenylselenyl-β-*D*-altropyranoside* (**7b**). — Compound **7b** was obtained quantitatively from **3b** as described for **7a**. Compound **7b** formed crystals from EtOH; m.p. 104–105°, $[\alpha]_D^{26}$ −10.0° (*c* 1.0); ν_{max} 1640, 1604, 1578, 1104, 1090, and 1010 cm^{-1}; ^{1}H-n.m.r.: δ 3.55 (s, 3 H), 3.65 (dd, 1 H, *J* 2.2, 3.2 Hz, H-2), 3.80–4.00 (m, 7 H), 4.97 (bs, 1 H, H-1), 4.95–5.30 (m, 2 H), 5.54 (s, 1 H), 5.77 (m, 1 H), 7.20–7.50 (m, 8 H), and 7.60–7.70 (m, 2 H); ^{13}C-n.m.r.: δ 49.5 (d, C-2), 57.0 (q), 64.7 (d, C-5), 69.1 (t, C-6), 72.0 (t), 76.8 (d, C-3), 77.3 (d, C-4), 100.1 (d, C-1), 102.1 (d), 116.8 (t), 126.2 (d × 2), 127.6 (d), 128.1 (d × 2), 128.9 (d), 129.1 (d × 2), 129.3 (s), 134.2 (d × 2), 134.5 (d), and 137.6 (s).

Anal. Calc. for $C_{23}H_{26}O_5Se$: C, 59.87; H, 5.68. Found: C, 59.87; H, 5.68.

Methyl 2-O-allyl-4,6-O-benzylidene-3-deoxy-3-phenylselenyl-α-D-altropyranoside (**8a**). — Compound **8a** was prepared quantitatively from **5a** as described for **3a** as a syrup; $[\alpha]_D^{26}$ −8.6° (*c* 1.4); ν_{max} 1620, 1578, 1144, 1086, and 1044 cm^{-1}; ^{1}H-n.m.r.: δ 3.45 (s, 3 H), 3.80–3.90 (m, 2 H), 4.10–4.40 (m, 6 H), 4.71 (s, 1 H, H-1), 5.15–5.50 (m, 2 H), 5.67 (s, 1 H), 5.95 (ddt, 1 H, *J* 5.6, 9.3, 17.2 Hz), 7.10–7.40 (m, 8 H), and 7.60–7.70 (m, 2 H); ^{13}C-n.m.r.: δ 44.4 (d, C-3), 54.7 (q), 60.8 (d, C-5), 68.9 (t, C-6), 71.2 (t), 75.6 (d, C-4), 79.3 (d, C-2), 99.2 (d, C-1), 101.4 (d), 118.0 (t), 126.2 (d × 2), 127.0 (d), 127.9 (d × 2), 128.6 (d × 2), 128.7 (d), 132.3 (s), 133.9 (d), 134.1 (d × 2), and 137.4 (s); m.s. calc. for $C_{23}H_{26}O_5{}^{78}Se$: 460.0954. Found: 460.0959.

Methyl 2-O-allyl-4,6-O-benzylidene-3-deoxy-3-phenylselenyl-β-D-altropyranoside (**8b**). — Compound **8b** was produced quantitatively from **5b** as indicated for **7a** as a syrup; $[\alpha]_D^{27}$ −53.1° (*c* 1.4); ν_{max} 1602, 1576, 1102, 1092, 1050, and 1002 cm^{-1}; ^{1}H-n.m.r.: δ 3.51 (s, 3 H), 3.68 (dd, 1 H, *J* 2.9, 1.0 Hz, H-3), 3.82–4.10 (m, 5 H), 4.18 (m, 1 H), 4.31 (m, 1 H, H-6*e*), 4.93 (s, 1 H, H-1), 4.90–5.40 (m, 2 H), 5.58 (s, 1 H), 5.78 (ddt, 1 H, *J* 5.8, 10.0, 18.0 Hz), 7.20–7.50 (m, 8 H), and 7.50–7.60 (m, 2 H); ^{13}C-n.m.r.: δ 46.2 (d, C-3), 57.2 (q), 66.6 (d, C-5), 68.9 (t, C-6), 72.5 (t), 75.9 (d, C-4), 77.4 (d, C-2), 99.9 (d, C-1), 101.7 (d), 117.8 (t), 126.2 (d × 2), 127.8 (d), 128.2 (d × 2), 128.7 (s), 128.9 (d), 129.1 (d × 2), 134.3 (d), 134.7 (d × 2), and 137.3 (s); m.s. calc. for $C_{23}H_{26}O_5{}^{78}Se$: 460.0954. Found: 460.0938.

Methyl 4,6-O-benzylidene-2-O-[2-buten-1-yl]-3-deoxy-3-phenylselenyl-α-D-altropyranoside (**8c**). — Compound **8c** was prepared quantitatively from **5a** using crotyl bromide (*E*:*Z* = 3:1) as the alkylating reagent as described for **7a** as a syrup (*E*:*Z* = 3:1); ^{1}H-n.m.r.: *E*; δ 1.70 (d, 9/4 H, *J* 5.1 Hz, 3.42 (s, 3 H), 4.00 (m, 2 H), 4.05–4.40 (m, 6 H), 4.66 (s, 1 H, H-1), 5.65 (s, 1 H), 5.60–5.75 (m, 2 H), 7.10–7.20 (m, 3 H), 7.33 (bs, 5 H), and 7.60–7.70 (m, 2 H); *Z*; δ 1.61 (d, 3/4 H, *J* 7.3 Hz; ^{13}C-n.m.r.: *E*; δ 17.8 (q), 44.7 (d, C-3), 54.8 (q), 60.8 (d, C-5), 69.0 (t, C-6), 71.1 (t), 75.7 (d, C-4), 79.0 (d, C-2), 99.6 (d, C-1), 101.5 (d), 126.3 (d × 2), 126.9 (d), 127.1 (d), 128.1 (d × 2), 128.6 (d × 2), 128.8 (d), 130.8 (d), 132.6 (s), 134.2 (d × 2), and 137.6 (s); *Z*; δ 29.7 (q) and 75.3 (t).

Methyl 4,6-O-benzylidene-3-deoxy-2-O-[3-methyl-2-buten-1-yl]-3-phenylselenyl-α-D-altropyranoside (**8d**). — Compound **8d** was obtained quantitatively by the alkylation of **5a** with 1-bromo-3-methyl-2-butene as crystals from EtOH; m.p. 54–55°, $[\alpha]_D^{13}$ +7.2° (*c* 1.1); ν_{max} 1664, 1572, 1106, 1078, 1060, 1040, and 1018 cm^{-1}; ^{1}H-n.m.r.: δ 1.68 (s, 3 H), 1.77 (s, 3 H), 3.47 (s, 3 H), 3.70–4.40 (m, 8 H), 4.72 (s, 1 H, H-1), 5.38 (m, 1 H), 5.69 (s, 1 H), 7.10–7.40 (m, 8 H), and 7.55–7.75 (m, 2 H); ^{13}C-n.m.r.: δ 18.1 (q), 25.8 (q), 44.7 (d, C-3), 54.8 (q), 60.8 (d, C-5), 66.5 (t), 69.0 (t, C-6), 75.0 (d, C-4), 79.0 (d, C-2), 99.6 (d, C-1), 101.4 (d), 120.5 (d), 126.2 (d × 2), 127.0 (d), 128.0 (d × 2), 128.6 (d × 2), 128.8 (d), 132.6 (s), 134.1 (d × 2), 137.5 (s), and 138.1 (s).

Anal. Calc. for $C_{25}H_{30}O_5Se$: C, 61.35; H, 5.94. Found: C, 61.35; H, 6.15.

*Methyl 3-O-allyl-4,6-O-benzylidene-2-deoxy-α-D-*erythro*-hex-2-enopyranoside* (**9a**). — To a solution of **7a** (95 mg) in CH_2Cl_2 (3 mL) was added *m*-chloroperoxybenzoic acid (50 mg) at 0–5° and the mixture was stirred for 10 min. The mixture was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$ and brine, and dried. After evaporation of the solvent, the residue was dissolved in benzene (15 mL) and Et_3N (0.2 mL) and refluxed for 50 min. After concentration, the crude product was chromatographed to

give **9a** (74% yield) as crystals from hexane; m.p. 100–104°, $[\alpha]_D^{27}$ +79.8° (*c* 0.3); ν_{max} 1654, 1128, 1090, 1050, and 956 cm^{-1}; ^{1}H-n.m.r.: δ 3.40 (s, 3 H), 3.79 (t, 1 H, *J* 8.3 Hz, H-6*a*), 4.02 (dd, 1 H, *J* 4.0, 8.9 Hz, H-5), 4.15–4.38 (m, 4 H), 4.66 (dd, 1 H, *J* 1.3, 3.1 Hz, H-2), 5.02 (d, 1 H, *J* 2.9 Hz, H-1), 5.21 (ddd, 1 H, *J* 1.6, 2.9, 10.1 Hz), 5.39 (ddd, 1 H, *J* 1.5, 3.1, 17.3 Hz), 5.55 (s, 1 H), 5.96 (m, 1 H), 7.20–7.40 (m, 3 H), and 7.40–7.55 (m, 2 H); ^{13}C-n.m.r.: δ 55.5 (q), 63.6 (d, C-5), 68.4 (t), 69.1 (t, C-6), 75.0 (d, C-4), 95.4 (d, C-2), 97.3 (d, C-1), 102.2 (d), 117.9 (t), 126.3 (d × 2), 128.1 (d × 2), 128.9 (d), 132.3 (d), 137.2 (s), and 154.3 (s, C-3).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.16; H, 6.37.

*Methyl 2-*C*-allyl-4,6-*O*-benzylidene-α-*D*-*arabino*-* (**11a**) *and* α-D-*hexopyranosid-3-ulose* (**12a**). — A solution of **9a** (80 mg) in xylene (10 mL) was refluxed for 20 min. After evaporation of the solvent, the residue (2:1 mixture of **11a** and **12a** based on ^{13}C-n.m.r.) was dissolved in benzene and the solution was stirred with silica gel (0.5 g) for 2 days at a room temperature and filtered. Evaporation of the solvent gave **12a** as crystals (97% yield, from EtOH); m.p. 161–162°, $[\alpha]_D^{29}$ +83.8° (*c* 0.6); ^{1}H-n.m.r.: δ 2.25 (m, 1 H), 2.50 (m, 1 H), 2.73 (m, 1 H, H-2), 3.36 (s, 3 H), 3.80–4.45 (m, 4 H), 5.00 (d, 1 H, *J* 4.0 Hz), 5.00–5.25 (m, 2 H), 5.57 (s, 1 H), 5.77 (dddd, 1 H, *J* 5.6, 8.2, 9.8, 17.2 Hz), and 7.30–7.60 (m, 5 H).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.79; H, 6.60.

*Methyl 2-*C*-allyl-4,6-*O*-benzylidene-β-*D*-*arabino*- (**11b**) *and* -D-*ribo*-hexopyranosid-3-ulose* (**12b**). — Oxidation of **7b** followed by elimination, as described for **9a**, did not give **9b**, but directly led to a 2:1 mixture of **11b** and **12b**. Treatment of the mixture with silica gel gave **12b** (92% yield) as crystals from EtOH; m.p. 187–188°, $[\alpha]_D^{28}$ −16.4° (*c* 0.5); ν_{max} 1735, 1635, 1607, 1119, 1101, 1095, and 999 cm^{-1}; ^{1}H-n.m.r.: δ 2.40–2.60 (m, 2 H), 2.55 (m, 1 H, H-2), 3.56 (s, 3 H), 3.58 (dt, 1 H, *J* 4.8, 11.1 Hz, H-5), 3.90 (t, 1 H, *J* 10.5 Hz, H-6*a*), 4.30 (dd, 1 H, *J* 1.5, 11.0 Hz, H-4), 4.45 (d, 1 H, *J* 7.5 Hz, H-1), 4.47 (dd, 1 H, *J* 4.6, 10.3 Hz, H-6*e*), 4.95–5.20 (m, 2 H), 5.57 (s, 1 H), 5.87 (m, 1 H), 7.20–7.45 (m, 3 H), and 7.45–7.60 (m, 2 H).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.07; H, 6.62.

*Methyl 2-*O*-allyl-4,6-*O*-benzylidene-3-deoxy-α-*D*-*erythro*-hex-2-enopyranoside* (**10a**). — Compound **8a** was transformed as described for **7a** into compound **10a** (87% yield, from EtOH); m.p. 112–113°, $[\alpha]_D^{31}$ +41.7° (*c* 0.8); ν_{max} 1661, 1101, 1062, 1029, 999, and 971 cm^{-1}; ^{1}H-n.m.r.: δ 3.48 (s, 3 H), 3.90–4.10 (m, 2 H), 4.10–4.30 (m, 3 H), 4.28 (m, 1 H, H-6*e*), 4.77 (s, 1 H, H-1), 4.99 (bs, 1 H, H-3), 5.10–5.40 (m, 2 H), 5.56 (s, 1 H), 5.91 (ddt, 1 H, *J* 5.4, 10.0, 17.1 Hz), and 7.30–7.50 (m, 5 H); ^{13}C-n.m.r.: δ 56.1 (q), 65.0 (d, C-5), 68.5 (t), 69.0 (t, C-6), 76.0 (d, C-4), 96.6 (d, C-1), 97.9 (d, C-3), 101.9 (d), 118.1 (t), 126.2 (d × 2), 128.2 (d × 2), 129.0 (d), 132.3 (d), 137.4 (s), and 152.6 (s, C-2).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.86; H, 6.56.

*Methyl 3-*C*-allyl-4,6-*O*-benzylidene-α-*D*-ribo-hexopyranosid-2-ulose* (**13a**). — Compound **13a** was obtained from **10a** as indicated for **12a** as a syrup (99% yield); $[\alpha]_D^{28}$ + 52.0° (*c* 1.8); ν_{max} 1720, 1638, 1108, and 1102 cm^{-1}; ^{1}H-n.m.r.: δ 2.75 (m, 2 H), 3.00 (m, 1 H, H-3), 3.46 (s, 3 H), 3.74–3.98 (m, 2 H), 4.14–4.45 (m, 2 H), 4.56 (s, 1 H, H-1), 4.56–5.14 (m, 2 H), 5.54 (s, 1 H), 5.64 (m, 1 H), and 7.25–7.55 (m, 5 H).

*Methyl 3-C-allyl-4,6-O-benzylidene-α-D-*arabino*-hexopyranosid-2-ulose* (**14a**). — Silica gel treatment of **13a**, as described for **12a**, gave **14a** as crystals from EtOH; m.p. 100–101°, $[\alpha]_D^{28}$ +57.8° (*c* 0.6); ν_{max} 1735, 1637, 1103, 1087, 1051, and 993 cm^{-1}; ^{1}H-n.m.r.: δ 2.50–2.60 (m, 2 H), 3.10 (ddd, 1 H, *J* 4.1, 6.0, 11.5 Hz, H-3), 3.47 (s, 3 H), 3.45–3.70 (m, 2 H), 4.10–4.50 (m, 2 H), 4.59 (s, 1 H, H-1), 5.00–5.20 (m, 2 H), 5.48 (s, 1 H), 5.87 (dddd, 1 H, *J* 6.6, 7.2, 9.9, 17.2 Hz), and 7.30–7.55 (m, 5 H).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.93; H, 6.66.

*Methyl 2-O-allyl-4,6-O-benzylidene-3-deoxy-β-D-*erythro*-hex-2-enopyranoside* (**10b**). — Oxidative elimination of **8b**, as indicated for **9a**, gave **10b** (92% yield) as a syrup; $[\alpha]_D^{29}$ −12.4° (*c* 1.0); ν_{max} 1656, 1088, 1074, and 996 cm^{-1}; ^{1}H-n.m.r.: δ 3.43 (s, 3 H), 3.64 (dd, 1 H, *J* 5.0, 9.0 Hz, H-4), 3.84 (t, 1 H, *J* 10.0 Hz, H-6*a*), 4.20–4.55 (m, 4 H), 5.10 (bs, 1 H, H-1), 5.24 (s, 1 H, H-3), 5.20–5.50 (m, 2 H), 5.57 (s, 1 H), 5.96 (m, 1 H), and 7.25–7.60 (m, 5 H); ^{13}C-n.m.r.: δ 54.4 (q), 68.7 (t × 2), 70.3 (d, C-4), 74.8 (d, C-5), 98.2 (d, C-3), 99.8 (d, C-1), 101.5 (d), 117.9 (t), 126.1 (d × 2), 128.2 (d × 2), 128.9 (d), 132.2 (d), 137.2 (s), and 151.7 (s, C-2).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.16; H, 6.37.

*Methyl 3-C-allyl-4,6-O-benzylidene-β-D-*ribo- (**13b**) *and* -D-arabino-*hexopyranosid-3-ulose* (**14b**). — Claisen rearrangement of **10b**, as described for **11a** and **12a**, gave a 2:1 mixture of **13b** and **14b**. Treatment of the mixture with silica gel gave **14b** (71% yield) as crystals from EtOH; m.p. 121–122°, $[\alpha]_D^{26}$ −44.1° (*c* 1.3); ν_{max} 1741, 1635, 1089, 1077, 1025, and 997 cm^{-1}; ^{1}H-n.m.r.: δ 2.50–2.70 (m, 2 H), 2.80 (m, 1 H, H-3), 3.57 (s, 3 H), 3.70–3.90 (m, 3 H), 4.45 (m, 1 H, H-6*e*), 4.57 (s, 1 H, H-1), 5.00–5.25 (m, 2 H), 5.52 (s, 1 H), 5.86 (m, 1 H), and 7.30–7.60 (m, 5 H).

Anal. Calc. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.01; H, 6.61.

*Methyl 4,6-O-benzylidene-2-O-[2-buten-1-yl]-3-deoxy-α-D-*erythro*-hex-2-enopyranoside* (**10c**). — Oxidative elimination of **8c**, as described for **9a**, gave **10c** (91% yield) as a syrup; ν_{max} 1128, 1090, 1050, and 956 cm^{-1}; ^{1}H-n.m.r.: *E*; δ 1.70 (d, 9/4 H, *J* 5.0 Hz), 3.54 (s, 3 H), 3.70–4.15 (m, 2 H), 4.30–4.50 (m, 4 H), 4.79 (s, 1 H, H-1), 5.02 (d, 1 H, *J* 1.0 Hz, H-3), 5.60 (s, 1 H), 5.50–5.90 (m, 2 H), and 7.30–7.60 (m, 5 H); *Z*; δ 1.67 (d, 3/4 H, *J* 5.4 Hz); ^{13}C-n.m.r.: *E*; δ 17.8 (q), 56.1 (q), 65.0 (d, C-5), 68.6 (t), 69.1 (t, C-6), 76.1 (d, C-4), 96.7 (d, C-1), 97.7 (d, C-3), 101.9 (d), 125.3 (d), 126.4 (d × 2), 128.3 (d × 2), 129.1 (d), 131.2 (d), 137.5 (s), and 158.2 (s, C-2); *Z*; 13.3 (q), 63.7 (t), 124.9 (d), and 128.6 (d).

*Methyl 4,6-O-benzylidene-3-C-[1-methyl-2-propenyl]-α-D-*ribo- (**13c**) *and [1-methyl-2-propenyl]-α-D-*arabino-*hexopyranosid-2-ulose* (**14c**). — Thermal rearrangement of **10c**, as described for **11a** and **12a**, gave an epimeric mixture of **13c** on the side-chain methyl group; ^{1}H-n.m.r.: δ 1.10 (d, 3/4 H, *J* 7.0 Hz), 1.23 (d, 9/4 H, *J* 7.0 Hz), 2.80–3.20 (m, 2 H), 3.48 (s, 3 H), 3.60–4.05 (m, 2 H), 4.30–4.70 (m, 2 H), 4.50 (s, 1 H, H-1), 4.80–5.20 (m, 2 H), 5.48 (s, 1 H), 5.78 (m, 1 H), and 7.20–7.50 (m, 5 H). Silica gel treatment of the mixture gave **14c** as crystals from EtOH; m.p. 67–68°, $[\alpha]_D^{30}$ +65.3° (*c* 1.0); ν_{max} 1730 cm^{-1}; ^{1}H-n.m.r.: δ 1.20 (d, 3 H, *J* 7.1 Hz), 3.05 (d, 1 H, *J* 10.7 Hz, H-3), 3.47 (s, 3 H), 3.70–3.90 (m, 2 H), 4.00–4.30 (m, 3 H), 4.54 (s, 1/4 H, H-1), 4.56 (s, 3/4 H, H-1), 4.80–5.10 (m, 2 H), 5.50 (s, 1 H), 5.90 (m, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calc. for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.81; H, 6.95.

Methyl 4,6-O-benzylidene-3-C-[1,1-dimethyl-2-propenyl]-α-D-ribo- (**13d**) *and D-arabino-hexopyranosid-2-ulose* (**14d**). — Compound **8d** was converted into a mixture of **13d** and **14d** as described for **11a** and **12a**, which was further treated with silica gel to give **13d** and **14d** (1:5) as crystals (69% yield, from EtOH); m.p. 161–162°, $[\alpha]_D^{13}$ +83.8° (*c* 0.6); ν_{max} 1730, 1635, 1097, 1077, 1045, and 993 cm^{-1}; ^{1}H-n.m.r.: 1.24 (s, 5 H), 1.29 (s, 1 H), 3.01 (d, 1 H, *J* 10.0 Hz, H-3), 3.46 (s, 3 H), 3.50–4.05 (m, 2 H), 4.15 (m, 1 H, H-5), 4.37 (dd, 1 H, *J* 4.3, 9.6 Hz, H-6*e*), 4.53 (s, 1 H, H-1), 4.90–5.10 (m, 2 H), 5.45 (s, 1/6 H), 5.50 (s, 5/6 H), 6.08 (dd, 1 H, *J* 10.5, 17.6 Hz), and 7.30–7.55 (m, 5 H).

Anal. Calc. for $C_{19}H_{24}O_5$: C, 68.65; H, 7.25. Found: C, 68.55; H, 7.20.

*Methyl 4,6-O-benzylidene-3-C-[(1R)- (***15***) and (1S)-1-methyl-3-hydroxypropyl]-α-D-arabino-hexopyranosid-2-ulose* (**16**). — To a solution of **14c** (663 mg) in oxolane (6 mL) was added a 1.5M solution (2 mL) of disiamylborane in oxolane and the mixture was stirred for 1 h at room temperature. An aqueous solution (1.5 mL) of NaOH (2M) and 30% aqueous H_2O_2 (1.5 mL) were added successively to the mixture. After 1.5 h of stirring at 35°, oxolane was evaporated and the residue was extracted with CH_2Cl_2 (3 × 15 mL) and the extracts were washed with brine and dried. After evaporation of the solvent, the residue was chromatographed to give **15** (399 mg, 57% yield) and **16** (84 mg, 12% yield). Compound **15** had m.p. 155–156° from benzene; $[\alpha]_D^{25}$ +37.6° (*c* 1.0); ν_{max} 3570, 3400, 1090, 1054, and 1008 cm^{-1}; ^{1}H-n.m.r.: δ 1.16 (d, 3 H, *J* 7.1 Hz), 1.40 (m, 1 H), 1.83 (m, 1 H), 2.09 (dd, 1 H, *J* 3.4, 10.0 Hz, H-3), 2.43 (m, 1 H), 2.85 (bs, OH), 3.45 (s, 3 H), 4.29 (s, 1 H, H-1), 3.80–4.30 (m, 6 H), 5.56 (s, 1 H), and 7.30–7.40 (m, 5 H).

Anal. Calc. for $C_{18}H_{24}O_6$: C, 64.24; H, 7.19. Found: C, 64.37; H, 7.21.

Compound **16** had m.p. 151–152° from benzene; $[\alpha]_D^{25}$ +52.4° (*c* 1.0); ν_{max} 3600, 1130, 1100, 1090, and 1080 cm^{-1}; ^{1}H-n.m.r.: δ 1.22 (d, 3 H, *J* 6.1 Hz), 1.30–1.60 (m, 2 H), 2.28 (t, 1 H, *J* 9.2 Hz, H-3), 2.45 (m, 1 H), 3.39 (s, 3 H), 3.60–4.50 (m, 7 H), 4.67 (s, 1 H, H-1), 5.69 (s, 1 H), 7.20–7.50 (m, 3 H), and 7.55–7.75 (m, 2 H).

Anal. Calc. for $C_{18}H_{24}O_6$: C, 64.24; H, 7.19. Found: C, 64.43; H, 7.24.

Methyl 4,6-O-benzylidene-3-C-[(1R)-1-methyl-3-hydroxypropyl]-α-D-glucopyranoside (**17**). — To an ice-cooled solution of **15** (81 mg) in MeOH (5 mL) and water (1.5 mL) was added $NaBH_4$ (10 mg). The mixture was stirred for 1 h at 0° and then 3 h at room temperature. After evaporation of the solvent, the residue was extracted with $CHCl_3$ (3 × 10 mL). The extracts were dried and removed from the solvent. The residue was recrystallized from benzene to give **17**; m.p. 150–151°, $[\alpha]_D^{25}$ +72.9° (*c* 1.0); ν_{max} 3700, 3575, and 1055 cm^{-1}; ^{1}H-n.m.r.: δ 1.07 (d, 3 H, *J* 7 Hz), 1.40–1.90 (m, 2 H), 2.00–2.50 (m, 2 H, 2 OH), 3.35 (m, 1 H), 3.45 (s, 3 H), 3.50–3.95 (m, 5 H), 4.27 (m, 1 H, H-6*e*), 4.66 (d, 1 H, *J* 3.7 Hz, H-1), 5.47 (s, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calc. for $C_{18}H_{26}O_6$: C, 63.88; H, 7.74. Found: C, 63.98; H, 7.74.

Methyl 4,6-O-benzylidene-3-C-[(1S)-1-methyl-3-hydroxypropyl]-α-D-glucopyranoside (**18**). — Compound **16** was reduced as described for **15** to give **18** as crystals from benzene; m.p. 118–119°, $[\alpha]_D^{23}$ +80.2° (*c* 1.0); ν_{max} 3600 and 1060 cm^{-1}; ^{1}H-n.m.r.: δ 1.02 (d, 3 H, *J* 6.9 Hz), 1.60–1.90 (m, 2 H), 1.95–2.50 (m, 2 H, 2 OH), 3.43 (s, 3 H), 3.45–3.90 (m, 6 H), 4.24 (m, 1 H, H-6*e*), 4.67 (d, 1 H, *J* 3.4 Hz, H-1), 5.46 (s, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calc. for $C_{18}H_{26}O_6$: C, 63.88; H, 7.74. Found: C, 63.90; H, 7.74.

(2R,4aR,6S,6aR,10R,10aS,10bS)-6-Methoxy-10-methyl-2-phenyl-perhydro-8H-pyrano[3',2':4,5]pyrano[3,2-d]-1,3-dioxin (**19**). — To a solution of the diol **17** (138 mg) in pyridine (1 mL) was added a solution of TsCl (95 mg) in pyridine (1 mL) at −15° and kept for 1 h at the temperature. Thereafter the mixture was stirred at room temperature overnight and diluted with $CHCl_3$, washed with aq. $NaHCO_3$ and brine, and dried. After evaporation of the solvent at room temperature, the residue (292 mg) chromatographed. Ditosylate, monotosylate, and **19** were isolated in 16, 30, and 12% yields, respectively. To a solution of the monotosylate (60 mg) in methanol was added Bu'OK (20 mg), and the mixture was stirred for 2 h at room temperature. After addition of NH_4Cl solution, MeOH was removed. The residue was extracted with $CHCl_3$ (3 × 10 mL). The extracts were washed with brine, dried, and removed from the solvent. The residue was recrystallized from hexane to give **19** (31 mg, 79% yield); m.p. 137–138°, $[\alpha]_D^{17}$ +25.4° (*c* 1.0); ν_{max} 1090, 1045, and 985 m^{-1}; ^{1}H-n.m.r.: δ 1.09 (d, 3 H, *J* 6.8 Hz), 1.38 (m, 1 H), 1.95 (m, 1 H), 2.10–2.50 (m, 2 H), 3.30 (m, 1 H, H-4), 3.46 (s, 3 H), 3.40–3.60 (m, 2 H), 3.60–4.00 (m, 3 H), 4.20 (m, 1 H, H-6*e*), 4.70 (d, 1 H, *J* 3.7 Hz, H-1), 5.48 (s, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calc. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.53; H, 7.55.

(2R,4aR,6S,6aR,10S,10aS,10bS)-6-Methoxy-10-methyl-2-phenyl-perhydro-8H-pyrano[3',2':4,5]pyrano[3,2-d]-1,3-dioxin (**20**). — A similar process for **18** gave **20** (60% yield, from hexane); m.p. 94–95°, $[\alpha]_D^{17}$ +38.6° (*c* 0.35); ν_{max} 1100, 1070, and 995 cm^{-1}; ^{1}H-n.m.r.: δ 1.18 (d, 3 H, *J* 5.1 Hz), 1.30–1.70 (m, 3 H), 1.93 (q, 1 H, *J* 10.0 Hz, H-3), 3.27 (dd, 1 H, *J* 3.2, 9.9 Hz, H-2), 3.46 (s, 3 H), 3.30–4.30 (m, 6 H), 4.70 (d, 1 H, *J* 3.3 Hz, H-1), 5.52 (s, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calc. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.77; H, 7.54.

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