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Note

Regiochemistry of epoxide ring opening in methyl 2,3-anhydro-4-azido-4-deoxy-α- and β-L-lyxopyranosides

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Abstract—Methyl 2,3-anhydro-4-*O*-methanesulfonyl-α-D-ribopyranoside (**12**) was prepared through a new six-step sequence starting from D-arabinose. Chemical behaviour of **12** was further studied under solvolytic conditions and in the presence of azide anion as a nucleophile. Factors governing the regiochemistry of epoxide ring opening are briefly discussed.

Keywords: 2,3-Anhydro-ribopyranosides; 2,3-Anhydro-lyxopyranosides; Epoxide ring opening; Regioselectivity; Azido sugars

The epoxide ring opening of anhydroglycosides as versatile intermediates for reactions with a wide range of nucleophiles is a well-established reaction. Factors leading to stereo- and regioselectivity in carbohydrate epoxide ring opening have been frequently investigated.[1,2] Only few examples of nucleophilic ring opening reactions in the series of 2,3-anhydrolyxopyranosides have been reported,[3] including our recent work directed to the conversion of the epoxide **2** to the diazido derivative **3** (Scheme 1), which was used as a model compound in the recent synthesis of (+)-oxybiotin.[4] Thus, the nucleophilic displacement of the mesyloxy group in **1**, with sodium azide in *N*,*N*-dimethylformamide at 140–145 °C, occurred with concomitant regioselective epoxide ring opening in the intermediate **2** to afford the C-3 and C-2 substituted sugars **3** and **4** in the ratio 13:1. In this work, we chose to investigate the similar ring opening reaction of methyl 2,3-anhydro-4-azido-4-deoxy-β-L-lyxopyranoside (**13**, Scheme 2), in order to provide an access to divergent intermediates suitable for preparation of both (+)-oxybiotin and/or the corresponding diamino sugars of potential biological interest. The preparation of the β-L-lyxopyranoside **13** was first attempted starting from 3,4-*O*-isopropylidene-D-arabinose[5] (**5**).

Treatment of **5** with mesyl chloride and triethylamine in dry dichloromethane gave the crystalline glycosyl chloride **6** as the only reaction product. Although compound **6** could be stored at −20 °C for weeks without change, it tended to decompose on prolonged standing at room temperature. Hence, the intermediate **6** was immediately treated with silver oxide in methanol to afford the known[6] α-D-arabinopyranoside **7** (51%) accompanied with a minor amount of the corresponding β-anomer **8** (8%). Hydrolytic removal of the isopropylidene protective group in **7** gave the expected diol **9** (88%). In this way, the intermediate **9** was prepared in an overall yield of 39.5% calculated to the starting compound **5**. However, when the last three-step sequence was carried out without purification of the intermediates **6** and **7**, the desired product **9** was obtained in a considerably higher overall yield (56% from **5**). Treatment of **9** with sodium methoxide in boiling methanol gave the known[6] epoxide **11**, which was subsequently converted to the corresponding 4-*O*-mesyl derivative **12** by treatment with mesyl chloride and triethylamine in dichloromethane (89% from **9**).

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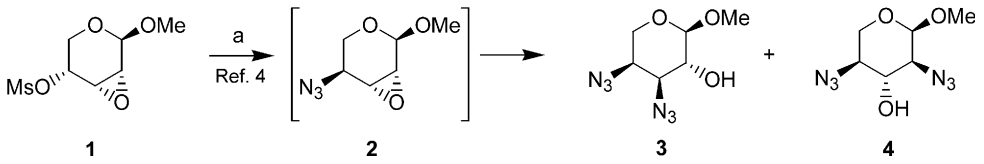
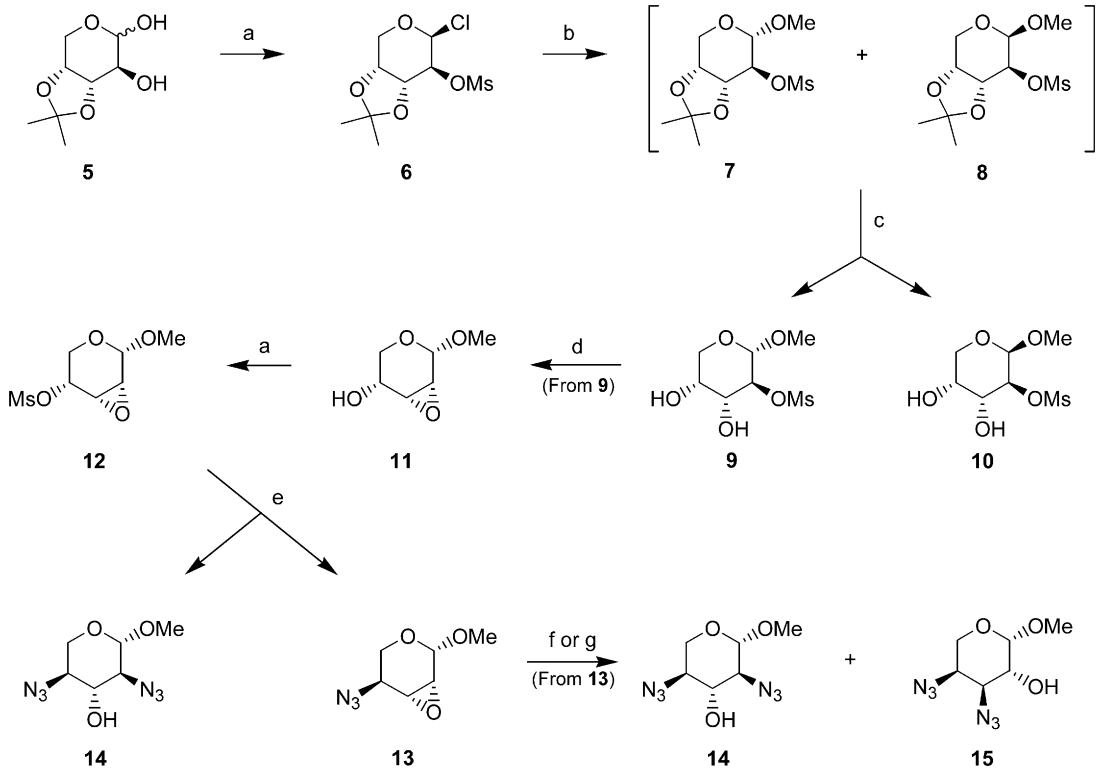


Scheme 1. Reagents and conditions: (a) NaN_3, DMF, 140–145 °C, 3.5 h, 51% of **3**, 4% of **4**.

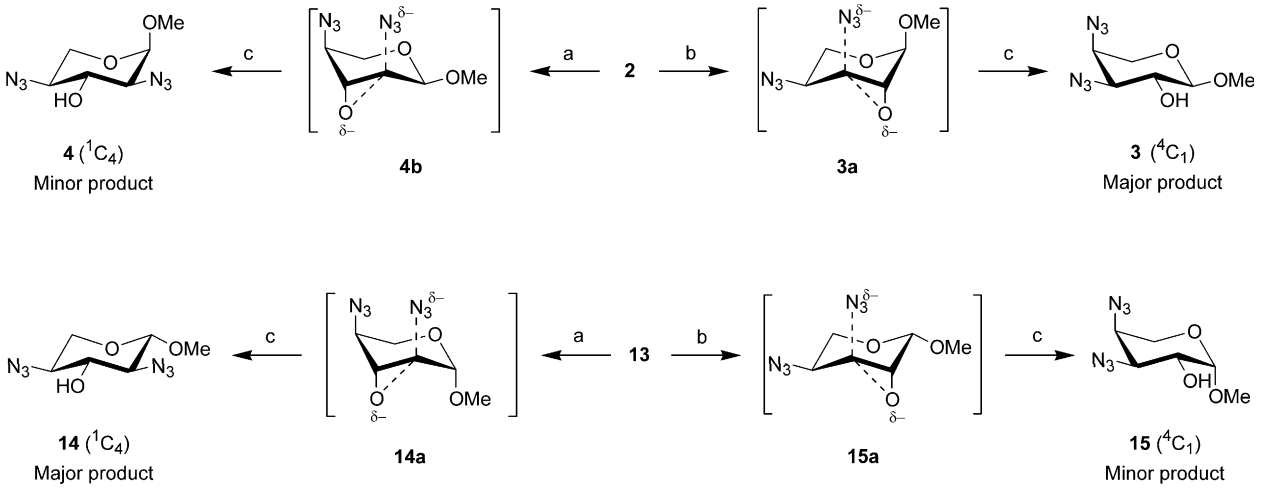


Scheme 2. Reagents and conditions: (a) MsCl, Et_3N, CH_2Cl_2, −10 °C, 1 h for **5**, 88% of **6**, 1.5 h for **11**, 93% of **12**; (b) Ag_2O, MeOH, 0 °C, 0.5 h, then rt, 20 h, 51% of **7**, 8% of **8**; (c) 9:1 TFA–H_2O, rt, 0.5 h, 88%; (d) NaOMe, MeOH, 55–60 °C, 1 h, 96%; (e) NaN_3, DMF, 95 °C, 1 h, 32% of **13**, 16% of **14**; (f) NaN_3, DMF, 105 °C, 21 h, 48% of **14**, 8% of **15**; (g) Me_3SiN_3, $BF_3{\cdot}OEt_2$, CH_2Cl_2, rt, 23 h, 40% of **14**, 8% of **15**.

We further investigated the possibility of conversion of the new methyl 2,3-anhydro-4-*O*-mesyl-α-D-ribopyranoside (**12**) into the corresponding 4-azido-4-deoxy-β-L-lyxopyranoside **13**. However, the reaction of the α-anomer **12**, under the same conditions as for methyl 2,3-anhydro-4-*O*-mesyl-β-D-ribopyranoside,[4] was not so straightforward and afforded a mixture of several products with the expected 4-azido derivative **13** (32%)[†] being a dominant component. A minor amount of the 2,4-diazido derivative **14** (16%) was also isolated from the reaction mixture, thus indicating that the nucleophilic displacement of the mesyloxy group in **12** has occurred with concomitant regioselective epoxide ring opening in the intermediate **13**. Indeed, when the last reaction was carried out at 105 °C for 21 h, the 2,4-disubstituted product **14** was isolated in 48% yield along with a minor quantity of the 3,4-diazido derivative **15** (15%). In the next step, we have focused on the ring opening of epoxide **13** by $Me_3SiN_3/BF_3{\cdot}OEt_2$. This reagent system sometimes gives a different regioselectivity with respect to NaN_3 in DMF, as observed recently in the ring opening reaction of benzyl 2-acetamido-3,4-anhydro-2,6-dideoxy-α-L-talopyranoside.[7] However, the reaction of **13** with $Me_3SiN_3/BF_3{\cdot}OEt_2$, in CH_2Cl_2 (rt, 23 h), also afforded the 2,4-diazido sugar **14** as a major product (40%), whereas its 3,4-regioisomer **15** was again isolated as a minor reaction product (8%).

Obviously, the epoxide ring opening in both **2** and **13** occurs according to Fürst–Plattner rule, to afford predominantly the *trans*-diaxial products **3** and **14**. These reactions show the same regiochemistry as the ring opening in methyl 2,3-anhydro-4-azido-4-deoxy-pentopyranosides with sodium hydroxide earlier observed by Dick and Jones.[8] The major reaction products **3** and

[†] An attempted preparation of **13** *via* the triflic analogue of **12** failed, since the corresponding triflic ester rapidly decomposes at room temperature turning into a variety of products.



Scheme 3. Regiochemistry of epoxide ring opening in α- (**2**) and β-anomer **13**: (a) nucleophilic attack at C-2 from an axial direction; (b) axially directed attack at C-3; (c) formation of *trans*-diaxial products followed by conformational interconversion.

14 might be formed via the chair-like transition states **3a** and **14a** (Scheme 3) that are obviously more favourable than **4b** and **15a** (that lead towards the minor regioisomers **4** and **15**), presumably due to the anomeric effect caused by the equatorially oriented C-1 methoxy groups.[1b,9]

The stereochemistry of ring-opened products was resolved by a careful examination of their ^{1}H NMR spectra, especially the coupling constants between the relevant protons. To determine the stereochemistry of the major product **3** in the α-series, the coupling constants $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ were used. $J_{1,2}$ has a value of 7.2 Hz, suggesting a diaxial arrangement of H-l and H-2. Both H-2 and H-3 are double doublets with vicinal couplings of 7.2, 9.8 and 9.8, 3.8 Hz, respectively. Thus, therefore, $J_{2,3}$ is 9.8 Hz and $J_{3,4}$ is 3.8 Hz. The first value immediately leads to the conclusion that both H-2 and H-3 are axially positioned and that H-3 and H-4 bear an axial–equatorial relationship. All these observations can be accounted for satisfactorily only when **3** is an α-L-arabinopyranoside derivative in the $^4C_1$ conformation. Likewise, in the minor product **4**, the coupling constants of significance are $J_{1,2}$ = 3.5, $J_{2,3}$ = 10.1 and $J_{3,4}$ = 8.9 Hz. Once again, these values clearly prove that H-2, H-3 and H-4 are all axially oriented, and that H-1 and H-2 are in an equatorial–axial relationship. This is possible only if **4** is of the α-L-*xylo* configuration. The major conformer of **4**, compatible with the observed coupling constants, is thus $^1C_4$. The anomeric proton signal in the spectrum of **4** is shifted downfield (δ 4.78 ppm) with respect to the H-1 signal in the spectrum of **3** (δ 4.13 ppm). These data additionally prove that the anomeric proton in **3** occupies an axial position, opposite to the regioisomer **4** whose H-1 is equatorially oriented.

^{1}H NMR spectrum of the major product in β-series (**14**) shows the following coupling constants: $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.4 and $J_{3,4}$ = 8.9 Hz. These values clearly prove that H-1, H-2, H-3 and H-4 are all axially oriented, and are consistent with the β-L-*xylo* configuration. The major conformer of **14**, compatible with the observed vicinal couplings, is thus $^1C_4$. The following coupling constants were used to determine the stereochemistry of the minor product in β-series (**15**): $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.0 and $J_{3,4}$ = 3.5 Hz. The first two values clearly prove that H-2 and H-3 are both axially oriented, and that H-1 and H-2 are in an equatorial–axial relationship. Finally, the coupling constant $J_{3,4}$ = 3.5 Hz is consistent with an axial–equatorial arrangement of H-3 and H-4. This is possible only if **15** is of the β-L-*arabino* configuration. The predominant conformer of **15**, compatible with the observed coupling constants, is thus $^4C_1$. As in the case of **3** and **4**, positions of the anomeric proton signals in the corresponding ^{1}H NMR spectra additionally proved that both the products **14** and **15** preferentially occupy $^1C_4$ and $^4C_1$ conformations, respectively. Namely, the anomeric proton of **14** appears in the spectrum at significantly higher field (δ 4.14 ppm) with respect to H-1 of **15** (δ 4.78 ppm). These data are consistent with an axial position of H-1 in **14**, as well as an equatorial orientation of H-1 in **15**.

In summary, it has been confirmed that the regiochemistry of epoxide ring opening in methyl 2,3-anhydro-4-azido-4-deoxy-α- and β-L-lyxopyranosides **2** and **13** with azide anion does depend upon their anomeric configuration. Thus, the α-anomer **2** under solvolytic conditions and in the presence of azide anion as a nucleophile predominantly gave the C-3 substituted sugar **3**, the similar ring opening reaction of β-anomer **13** afforded the C-2 substituted derivative **14** as the main reaction product. In addition, both diazido derivatives **3** and **14** represent suitable intermediates for preparation of the corresponding amino sugars of potential biological importance, while the regioisomer **3** represents, a

postulated intermediate in an alternative approach to (+)-oxybiotin, a biologically active analogue of natural biotin.

1. Experimental

1.1. General methods

Melting points were determined on a Büchi 510 apparatus and were not corrected. Optical rotations were measured on a Polamat A (Zeiss, Jena) polarimeter. IR spectra were recorded with a Specord 75 IR spectrophotometer. NMR spectra were recorded on a Bruker AC 250 E instrument and chemical shifts are expressed in ppm downfield from tetramethylsilane. The NMR data are presented in Tables 1–3. Low resolution mass spectra were recorded on Finnigan-MAT 8230 (CI) and VG AutoSpec (FAB) mass spectrometers. High resolution mass spectra were taken on a Micromass LCT KA111 spectrometer. TLC was performed on DC Alufolien Kieselgel 60 F_{254} (E. Merck). Flash column chromatography was performed using ICN silica 32–63. All organic extracts were dried with anhydrous Na_2SO_4. Organic solutions were concentrated in a rotary evaporator under diminished pressure at a bath temperature below 35 °C.

1.1.1. Methyl 3,4-*O*-isopropylidene-2-*O*-methanesulfonyl-α-D-arabinopyranoside (7). To a stirred and cooled (−10 °C) soln of **5**[5] (1.15 g, 6.05 mmol) in a mixture of dry CH_2Cl_2 (12 mL) and Et_3N (2.53 mL, 18.15 mmol) was added dropwise a soln of MsCl (1.17 mL, 15.12 mmol) in CH_2Cl_2 (3.5 mL). The mixture was stirred for 1 h at −10 °C, then diluted with CH_2Cl_2 (20 mL) and washed successively with cold (+4 °C) aq 5% HCl (2 × 40 mL) and 1% $NaHCO_3$ (20 mL). Organic phase was dried and evaporated to a pale yellow solid. Flash column chromatography (CH_2Cl_2) gave pure **6** (1.52 g, 88%). Recrystallization from CH_2Cl_2–hexane gave colourless crystals, mp 130 °C (decomposition), $[\alpha]_D^{23}$ −202.9 (*c* 1.0, $CHCl_3$), R_f 0.40 (CH_2Cl_2); lit.[4] mp 129–131 °C (decomposition), $[\alpha]_D^{23}$ −205.3 (*c* 1.0, $CHCl_3$). To a stirred and cooled (0 °C) soln of **6** (2.20 g, 7.67 mmol) in abs MeOH (20 mL) was added Ag_2O (1.90 g, 8.20 mmol). The suspension was stirred at 0 °C for 30 min, then allowed to warm to room temperature and then stirred for the next 20 h. The reaction mixture was diluted with EtOAc, filtered through a Celite pad and evaporated. Flash column chromatography (1:1 benzene–EtOAc) of the residue first gave pure β-anomer **8** (0.171 g, 8%), which upon crystallization from CH_2Cl_2–hexane gave colourless needles, mp 138 °C, $[\alpha]_D^{23}$ −191.5 (*c* 0.5, $CHCl_3$), R_f 0.29 (CH_2Cl_2); lit.[6] mp 138–139 °C, $[\alpha]_D^{23}$ −187 (*c* 1.1, $CHCl_3$). IR (KBr): ν_{max} 1400–1370 (as.

Table 1. ^{1}H NMR resonances in compounds **7**–**15** (in $CDCl_3$)

Compound	Chemical shifts (ppm)						
	H-1	H-2	H-3	H-4	H-5a	H-5b	Other signals
7	4.24 (d)	4.45 (t)	4.19 (t)	4.26 (m)	3.79 (dd)	4.16 (dd)	1.34 and 1.53 (CMe_2), 3.10 ($MeSO_2$), 3.47 (OMe)
8	4.85 (d)	4.60 (dd)	4.35 (dd)	4.28 (dd)	3.93 (dd)	4.02 (d)	1.37 and 1.58 (CMe_2), 3.16 ($MeSO_2$), 3.43 (OMe)
9[a]	4.46–4.57[b]	4.46–4.57[b]	3.87–4.01[b]	4.06 (br s)	3.71 (d)	3.87–4.01[b]	3.30 ($MeSO_2$), 3.60 (OMe)
10	4.95 (d)	4.78 (dd)	4.06[b]	4.06[b]	3.75 (dd)	3.86[b]	3.15 ($MeSO_2$), 3.60 (OMe), 3.86[b] (OH), 4.06[b] (OH)
11	4.79 (d)	3.06–3.67[b]	3.06–3.67[b]	4.04 (m)	3.06–3.67[b]	3.06–3.67[b]	2.67 (OH), 3.43 (OMe)
12	4.83 (d)	3.55 (dd)	3.59 (dd)	5.03 (ddd)	3.62 (dd)	3.77 (dd)	3.10 ($MeSO_2$), 3.44 (OMe)
13	4.95 (d)	3.40–3.46[b]	3.40–3.46[b]	3.55–3.65[b]	3.55–3.65[b]	4.00 (dd)	3.47 (OMe)
14	4.14 (d)	3.29 (dd)	3.40 (ddd)	3.56 (ddd)	3.15 (dd)	4.01 (dd)	3.56 (OMe)
15	4.78 (d)	3.97 (ddd)	3.75–3.88[b]	3.75–3.88[b]	3.69 (dd)	3.75–3.88[b]	2.31 (OH), 3.46 (OMe)

[a] In D_2O.
[b] Group of signals.

Table 2. ^{1}H vicinal couplings in compounds **7**–**15** (in $CDCl_3$)

Compound	Coupling constants (Hz)						
	1,2	2,3	3,4	4,5a	4,5b	5a,5b	Other coupling constants
7	7.6	7.6	6.0	3.1	2.5	13.4	
8	3.4	7.7	5.4	2.5	0	3.4	
9[a]			3.5	<1	1.9	13.0	
10	3.6	9.3	<1	1.6		12.6	
11	3.4						$J_{4,OH}$ = 8.7 Hz
12	2.8	4.2	1.7	6.0	9.8	10.8	
13	2.8			1.7	2.0	12.4	
14	7.5	9.4	8.9	10.7	5.3	11.8	
15	3.6	10.0	3.5	2.3		12.7	$J_{2,OH}$ = 10.1 Hz

[a] In D_2O.

Table 3. ^{13}C NMR data of compounds **7**–**15** (in $CDCl_3$)

Compound	Chemical shifts (ppm)						
	C-1	C-2	C-3	C-4	C-5	OMe	Other signals
7	100.41	82.04	76.37	73.40	62.71	56.36	25.93 and 27.49 (CMe_2), 38.91 ($MeSO_2$), 110.69 (CMe_2)
8	97.97	79.50	73.08	73.92	58.21	55.83	26.07 and 27.95 (CMe_2), 38.57 ($MeSO_2$), 109.67 (CMe_2)
9[a]	104.30	84.17	73.01	71.53	69.10	59.98	41.25 ($MeSO_2$)
10	100.54	80.92	72.12	69.08	65.37	57.96	40.43 ($MeSO_2$)
11	94.55	54.77[b]	53.28[b]	64.59	60.36	55.85	
12	93.87	54.83	50.38	72.16	56.55	55.95	38.72 ($MeSO_2$)
13	94.41	51.13	49.75	53.81	58.99	55.82	
14	103.51	66.08	74.09	60.84	63.76	57.15	
15	99.04	68.59	61.72[b]	60.18	60.20[b]	55.70	

[a] In D_2O.
[b] Assignation might be reversed.

SO_2), 1190 (sym. SO_2). FAB MS: *m/z* 304 (M^+−H+Na), 283 (M^++H), 251 (M^+−OMe). Pure α-anomer **7** (1.10 g, 51%), was then eluted, which crystallized from CH_2Cl_2–hexane as colourless needless, mp 143–144 °C, $[\alpha]_D^{23}$ −34.0 (*c* 0.5, $CHCl_3$), R_f 0.26 (CH_2Cl_2); lit.[6] mp 144–145 °C, $[\alpha]_D^{23}$ −33.1 (*c* 0.5, $CHCl_3$). IR (KBr): ν_{max} 1360 (as. SO_2), 1200–1180 (sym. SO_2). NOE-contact: H-1 and H-3.

1.1.2. Methyl 2-*O*-methanesulfonyl-α-D-arabinopyranoside (9). *Procedure A*. A soln of **7** (0.96 g, 3.39 mmol) in aq 90% TFA (10 mL) was stirred for 0.5 h at room temperature. The mixture was evaporated by co-distillation with toluene (3 × 20 mL) to a yellow syrup. Flash column chromatography (EtOAc) of the residue gave pure **9** (0.724 g, 88%), which crystallized from EtOAc–hexane.

Procedure B. To a cooled (−10 °C) and stirred soln of **5** (5.00 g, 26.29 mmol) in dry CH_2Cl_2 (50 mL) and dry Et_3N (14.38 mL, 103.17 mmol), was added a cooled (−10 °C) soln of MsCl (6.11 mL, 78.78 mmol) in dry CH_2Cl_2 (12 mL). The mixture was stirred at −10 °C for 0.5 h, then diluted with CH_2Cl_2 (20 mL) and washed successively with aq 5% HCl (2 × 100 mL) and 1% $NaHCO_3$ (50 mL). The organic soln was dried and evaporated, and the remaining crude **6** was dissolved in abs MeOH (50 mL) and cooled to 0 °C. To the soln was added Ag_2O (6.05 g, 26.11 mmol), the resulting suspension was stirred at 0 °C for 0.5 h, and then at room temperature for 1 h. The reaction mixture was diluted with EtOAc, filtered through a Celite pad and evaporated to a yellow syrup. The residue was dissolved in aq 90% TFA (40 mL) and stirred for 0.5 h at room temperature. The mixture was evaporated by co-distillation with toluene (5 × 30 mL) to a yellow oil. Flash column chromatography (4:1 light petroleum–EtOAc) of the residue first gave pure β-anomer **10** (0.212 g, 3%), which crystallized from a mixture of EtOAc–hexane in the form of colourless crystals, mp 88–90 °C, $[\alpha]_D^{23}$ −168 (*c* 0.8, $CHCl_3$), R_f 0.11 (Et_2O); lit.[6] mp 69–70 °C, $[\alpha]_D^{23}$ −153 (*c* 0.8, $CHCl_3$); lit.[10] (for L-isomer) mp 86 °C, $[\alpha]_D^{23}$ +163 (*c* 1.0, $CHCl_3$). IR (KBr): ν_{max} 3530–3350 (OH), 1370 (as. SO_2), 1190 (sym. SO_2). FAB MS: *m/z* 265 (M^++Na), 243 (M^++H), 211 (M^+−OMe). Further elution gave pure **9** (3.57 g, 56%), which crystallized from EtOAc–hexane as colourless needles, mp 115–116 °C, $[\alpha]_D^{23}$ −16.0 (*c* 0.5, H_2O), R_f 0.25 (EtOAc); lit.[6] mp 115–116 °C, $[\alpha]_D^{23}$ −12.2 (*c* 0.4, MeOH). IR (KBr): ν_{max} 3420 (OH), 1360–1340 (as. SO_2), 1190–1180 (sym. SO_2).

1.1.3. Methyl 2,3-anhydro-α-D-ribopyranoside (11). To a soln of **9** (2.94 g, 12.14 mmol) in anhydrous MeOH (30 mL) was added 1 M NaOMe in MeOH (24.3 mL, 24.3 mmol). The mixture was stirred at 55–60 °C for 1 h and then evaporated. Flash column chromatography (Et_2O) of the residue gave pure **11** (1.71 g, 96%) that crystallized from CH_2Cl_2–light petroleum in the form of colourless silky crystals, mp 85 °C, $[\alpha]_D^{23}$ +148.9 (*c* 0.5, $CHCl_3$), R_f 0.26 (Et_2O); lit.[6] mp 83.5 °C, $[\alpha]_D^{23}$ +165.0 (*c* 0.2, $CHCl_3$). IR (KBr): ν_{max} 3420–3350 (OH).

1.1.4. Methyl 2,3-anhydro-4-*O*-methanesulfonyl-α-D-ribopyranoside (12). To a stirred and cooled soln (−10 °C) of **11** (0.82 g, 5.65 mmol) in dry CH_2Cl_2 (10 mL) was added Et_3N (1.55 mL, 11.12 mmol) and a cooled (−10 °C) soln of MsCl (0.53 mL, 6.83 mmol) in dry CH_2Cl_2 (5 mL). Stirring was continued for 1.5 h at −10 °C and the mixture diluted with CH_2Cl_2 (10 mL), washed successively with aq 5% HCl (2 × 25 mL) and 1% $NaHCO_3$ (20 mL). The organic soln was dried and evaporated to yellow syrup. Flash column chromatography (3:2 light petroleum–EtOAc) of the residue gave pure **12** (1.177 g, 93%) as a solid, which upon crystallization from CH_2Cl_2–hexane gave colourless needles, mp 115 °C, $[\alpha]_D^{23}$ = +142.6 (*c* 0.5, $CHCl_3$), R_f 0.39 (Et_2O). IR (KBr): ν_{max} 1360 (as. SO_2), 1190 (sym. SO_2). FAB MS: *m/z* 247 (M^++Na), 225 (M^++H). Anal. Calcd for $C_7H_{12}O_6S$: C, 37.49; H, 5.39; S, 14.30. Found: C, 37.57; H, 5.43; S, 14.10.

1.1.5. Methyl 2,3-anhydro-4-azido-4-deoxy-β-L-lyxopyranoside (13) and methyl 2,4-diazido-2,4-dideoxy-β-L-xylopyranoside (14). To a soln of **12** (0.117 g, 0.52 mmol) in dry DMF (7 mL) was added NaN_3

(0.30 g, 4.62 mmol). The mixture was stirred at 95 °C for 1 h, then evaporated and extracted with EtOAc (20 mL). The organic phase was filtered, washed with water (2 × 10 mL), dried and evaporated. The residue was purified by flash chromatography (4:1 light petroleum–EtOAc) to give pure **13** (0.029 g, 32%) as a colourless oil, $[\alpha]_D^{23}$ +50.1 (*c* 0.9, $CHCl_3$), $R_f = 0.55$ (CH_2Cl_2); lit.[11] (for D-isomer): $[\alpha]_D^{23}$ −54 (*c* 0.4, $CHCl_3$). IR (film): ν_{max} 2120 (N_3). CI MS: *m/z* 215 ($M^+ + C_4H_{10} - N$), 200 ($M^+ + C_4H_{10} - H - N_2$), 172 ($M^+ + H$). HR MS (ES+): *m/z* 194.0545 ($M^+ + Na$). Calcd for $C_6H_9N_3O_3Na$: 194.0542. Further elution of the column gave **14** (0.065 g, 16%) that crystallized from CH_2Cl_2–hexane as colourless crystals, mp 72–73 °C, $[\alpha]_D^{23}$ +13.5 (*c* 0.6, $CHCl_3$), R_f 0.26 (CH_2Cl_2); lit.[12] (for D-isomer): mp 72–73 °C, $[\alpha]_D^{23}$ −18.4 (*c* 1.0, $CHCl_3$). IR (KBr): ν_{max} 3290 (OH), 2150–2130 (N_3). CI MS: *m/z* 215 ($M^+ + H$). Anal. Calcd for $C_6H_{10}N_6O_3$: C, 33.65; H, 4.71; N, 39.24. Found: C, 33.74; H, 4.76; N, 39.48.

1.1.6. Methyl 2,4-diazido-2,4-dideoxy-β-L-xylopyranoside (14) and methyl 3,4-diazido-3,4-dideoxy-β-L-arabinopyranoside (15). *Procedure A.* A suspension of **12** (0.448 g, 2.00 mmol) and NaN_3 (1.30 g, 20.00 mmol) in dry DMF (10 mL) was stirred at 85–90 °C for 4 h, and then at 100–105 °C for 20 h. The mixture was evaporated and the residue extracted with EtOAc (30 mL) and filtered. The organic soln was washed with water (2 × 15 mL), dried and evaporated. Flash column chromatography (3:2 light petroleum–EtOAc) of the residue gave two fractions. The first fraction contained pure **14** (0.206 g, 48%), which crystallized from CH_2Cl_2–hexane as colourless crystals. Pure **15** (0.064 g, 15%) was then eluted, which crystallized from CH_2Cl_2–hexane as colourless needless.

Procedure B. A soln of **13** (0.147 g, 0.86 mmol) in CH_2Cl_2 (1 mL) was treated with Me_3SiN_3 (0.35 mL, 3.81 mmol), then with $BF_3{\cdot}OEt_2$ (0.1 mL, 0.49 mmol) and the mixture was stirred for 23 h. After neutralization with triethylamine (0.05 mL), the solvent was evaporated. The residue was chromatographed on a column of flash silica (7:3 hexane–Et_2O) to give two fractions. The first fraction contained pure **14** (0.074 g, 40%), which crystallized from CH_2Cl_2–hexane as colourless crystals. Pure **15** (0.014 g, 8%) was then eluted, which crystallized from CH_2Cl_2–hexane as colourless needless, mp 111–112 °C, $[\alpha]_D^{23}$ +217.0 (*c* 0.8, $CHCl_3$), R_f 0.71 (Et_2O); lit.[12] (for D-isomer) mp 107–109 °C, $[\alpha]_D^{23}$ −220.0 (*c* 1.0, $CHCl_3$). IR (KBr): ν_{max} 3440 (OH), 2130–2100 (N_3); CI MS: *m/z* 215 ($M^+ + H$). Anal. Calcd for $C_6H_{10}N_6O_3$: C, 33.65; H, 4.71; N, 39.40. Found: C, 33.64; H, 5.06; N, 39.54.

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