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REACTIONS OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DIDEOXY-3-NITRO-α- AND-β-D-*erythro*-HEX-2-ENOPYRANOSIDES WITH PHENYLACETONITRILE: PREPARATION AND STRUCTURAL DETERMINATION OF ADDUCTS AND AN ISOXAZOLE DERIVATIVE*

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ABSTRACT

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside with phenylacetonitrile afforded adducts having the D-*manno* (**2** and **3**) and D-*gluco* configurations (**4** and **5**), the isoxazole **6**, the cyano alkene **7**, and the nitro alcohols **9** and **10**. Similar reaction of the β anomer **11** gave adducts having the D-*gluco* configuration (**12** and **13**) and the nitro alcohol **14**. A mechanism for formation of **6** and tentative assignments of configuration at the phenylacetonitrile substituent of the adducts are described.

INTRODUCTION

As part of current studies on the stereochemistry of nucleophilic addition-reactions to Michael acceptors, we reacted methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside[1,2] (**1**) and its β anomer[3] **11** with active methylene compounds; the former afforded mainly the thermodynamically less-stable mannopyranosides, whereas the latter gave the (more-stable) gluco-pyranosides. Similar stereochemical results were reported by Baer and Hanna[4] in the reactions of 3-nitro sugars with organocopper reagents. In this paper we report the reactions of **1** and **11** with phenylacetonitrile; the isolation and structural determination of adducts (**2–5, 12,** and **13**), and the isoxazole **6**.

RESULTS AND DISCUSSION

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-α-D-*erythro*-hex-2-enopyranoside (**1**) with phenylacetonitrile in tetrahydrofuran in the presence of M sodium hydroxide for 3 h at ~23° afforded as the major products the man-

*Stereochemistry of Nucleophilic Addition Reactions, Part XII. For Part XI, see ref. 1.
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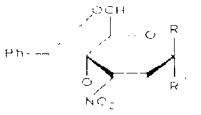
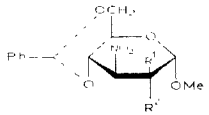
nopyranosides **2** and **3**, which differ in the chirality of the phenylacetonitrile group, together with small amounts of the glucopyranoside **4**, isoxazole **6**, cyano alkene **7**, and nitro alcohols (**9** and **10**). When the reaction time was extended to 30 h, the isoxazole **6** and nitro alcohols (**9** and **10**) became the major products, together with small amounts of the glucopyranosides (**4** and **5**), but the mannopyranosides (**2** and **3**) were barely detectable.

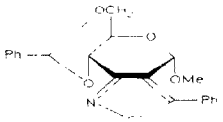
Heterogeneous reaction of **1** with phenylacetonitrile in benzene–0.2M sodium hydroxide in the presence of tributylhexadecylphosphonium bromide as phase-transfer catalyst gave the isoxazole **6**, glucopyranosides (**4** and **5**), and nitro alcohols (**9** and **10**), from which the isoxazole **6** and glucopyranosides **4** and **5** were isolated.



1 R^1 = H, R^2 = OMe
11 R^1 = OMe, R^2 = H



2 R^1 = CHCNPh(*S*), R^2 = H
3 R^1 = CHCNPh(*R*), R^2 = H
4 R^1 = H, R^2 = CHCNPh(*S*)
5 R^1 = H, R^2 = CHCNPh(*R*)
9 R^1 = H, R^2 = OH
10 R^1 = OH, R^2 = H
15 R^1 = CH(CN)$_2$, R^2 = H



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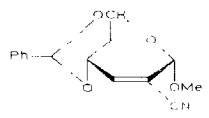

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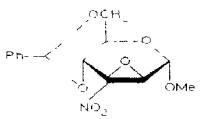

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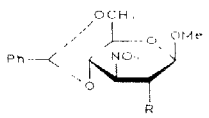


12 R = CHCNPh(*R*)
13 R = CHCNPh(*S*)
14 R = OH

The cyano alkene[5] **7** and nitro alcohols[6] (**9** and **10**) were identical with the respective authentic samples by i.r. and n.m.r. spectroscopy. Structural assignments of the other products were based on elemental analyses and spectral data (i.r. and n.m.r.; see Tables I and II). Assignments of the D-*manno* configuration for **2** and **3** and the D-*gluco* configuration for **4** and **5** were deduced by the coupling constants (Table II). The configurations at the phenylacetonitrile moiety (C-8) were determined as described later.

When the glucopyranoside **4** was treated with phenylacetonitrile in tetrahydrofuran in the presence of M sodium hydroxide for 30 min at ~23°, a mixture of

TABLE I

CHEMICAL SHIFTS (δ) OF THE PRODUCTS AT 100 MHz IN CHLOROFORM-*d* (Me_4Si AS INTERNAL STANDARD)

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6e*	*PhCH*	*OMe*	*H-8*[a]
2	4.75	2.99	5.22	5.04	~4.0	4.09	4.36	5 77	3.27	3.91
3	4.51	3.25	5.17	4.40	←3.6–4.3→			5.62	3.28	4.07
4	4.27	3.03	5.06		←3.6–4.3→			5.33	3.24	4.04
5	4.36	2.88	5.25		←3.6–4.4→			5.53	3.39	3.98
6	5.66			4.77	4.18	3.94	4.44	5.74	3.63	
12	4.48	2.88	4.85	4.16	3.42	3.80	4.34	5.53	3.48	4.20
13	4.37	2.93	4.92	4.07	3.42	3.81	4.36	5.48	3.63	4.34

[a]Methine proton of the substituent at C-2.

TABLE II

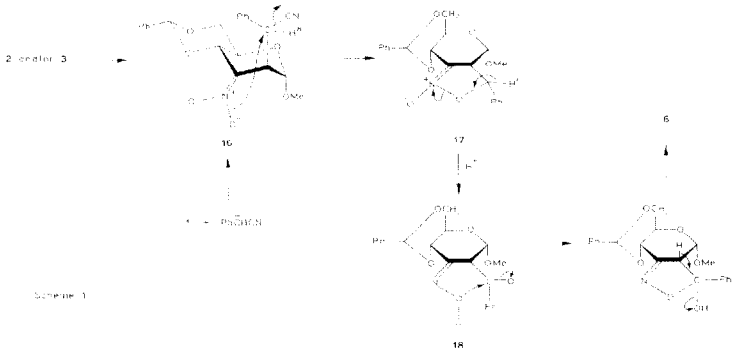
FIRST-ORDER COUPLING-CONSTANTS (Hz) AT 100 MHz IN CHLOROFORM-*d*

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6e}$	$J_{6a,6e}$	$J_{2,8}$
2	~0	5.2	10.4	10.4	9.6	4.1	9.6	3.0
3	~1	5.6	11.0					9.0
4	3.0	11.0	9.6					8.9
5	3.8	11.4	9.5					6.1
6				8.8	9.4	3.8	9.1	
12	8.3	11.4	9.8	9.8	10.4	4.9	10.4	2.7
13	8.3	11.7	9.8	9.8	10.2	4.9	10.2	2.3

4 and **5** in the ratio of 1:2.5, based on the n.m.r. spectrum, was obtained. Similar treatment of **5** also afforded the same results, revealing that compounds **4** and **5** underwent epimerization to give the equilibrium mixture (**4**:**5** = 1:2.5). Even when the reaction time was extended to 30 h, the isoxazole **6** was not detectable (n.m.r. spectroscopy), and the glucopyranosides **4** and **5** (ratio 1:2.5) were recovered as the major products.

Similar treatment of the mannopyranosides **2** or **3** for 30 min yielded a mixture of **2** and **3** in the ratio of 3.5:1 or 2:1, respectively. However, after 30 h, the reaction became complicated, and the isoxazole **6**, mannopyranosides (**2** and **3**), glucopyranosides (**4** and **5**), and a mixture of the nitro alcohols (**9** and **10**) were isolated after column chromatography. Under the same conditions, the isoxazole **6** was recovered in high yield. These results showed that the mannopyranosides were intermediates leading to **6**, but the glucopyranosides were not.

A plausible explanation[7] for the formation of **6** is shown in Scheme 1. One oxygen atom of the nitronate **16** attacks at C-8 to expel the cyano group, yielding the isoxazoline *N*-oxide **17**. Abstraction of the acidic hydrogen atom (H-8) leads to the β-oxyimino-carbonyl derivative **18**, which provides the isoxazole **6** through dehydration. Hydrogen cyanide thus formed undergoes addition to **1**, yielding adducts known to eliminate nitrous acid to provide the cyano alkene **7** under basic



conditions[8]. Inspection of Dreiding models indicated that nucleophilic attack of the oxygen atom at C-8 (phenylacetonitrile group) should be stereochemically favored for the mannopyranosides, but not for the glucopyranosides. Similar results were observed in the reaction of **1** with *S*-ylides[9].

In order to confirm such a stereochemical requirement for the formation of the isoxazole derivative, a similar reaction of the β anomer **11** was examined. As expected[3,4], the nucleophile approaches exclusively from the equatorial side of **11** to give the glucopyranosides **12** and **13**, together with the nitro alcohol **14**. No evidence was obtained for formation of the isoxazole corresponding to **6**. When either compound **12** or **13** was treated with phenylacetonitrile in the presence of M sodium hydroxide, a mixture of **12** and **13** in the ratio of 1:1.2 was obtained, indicating that the thermodynamic stabilities of these two compounds were nearly equal.

The chirality at the phenylacetonitrile moiety was tentatively assigned as follows. In the α-D-mannopyranoside derivatives, it is expected that the least bulky hydrogen atom (H-8) should point toward the most-crowded ring, as shown in conformation I in Fig. 1, and the $J_{2,8}$ value is large. In fact, the $J_{2,8}$ values of most 2-*C*-substituted derivatives, such as the 2-*C*-diacetylmethyl derivative, are[1,2] in the range 6.0–10.6 Hz, whereas the 2-*C*-dicyanomethyl derivative **15** has a small $J_{2,8}$ value (3.8 Hz)[1], indicating that the linear cyano group points toward the ring instead of H-8 (conformation II). The α-D-mannopyranoside having the (*S*) configuration, should, therefore, exist mostly, in conformation III, in which the unfavorable 1,3-diaxial interaction is minimized. On the other hand, the C-8 epimer may exist in conformation IV and/or V*. Appearance of the H-8 signals in **2** and **3** as doublets having splittings of 3.0 and 9.0 Hz suggests that compound **2** has the (*S*) and **3** the (*R*) configuration, respectively, and that compound **3** exists, at least

*The remaining gauche conformation should be the least stable, because the bulky phenyl group points toward the ring in this conformation.

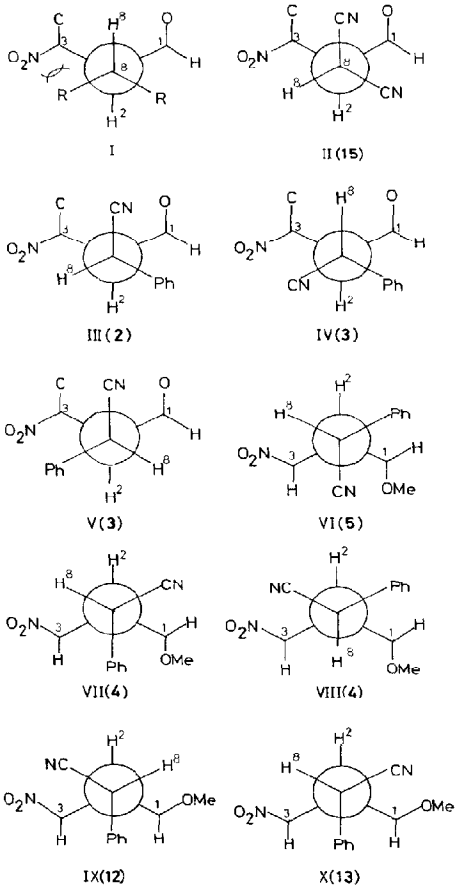


Fig. 1. "Newman" projections of compounds (**2–5, 12, 13,** and **15**), showing projections along C-8–C-2.

mainly, in conformation IV. This is reasonable, because 1,3-diaxial interaction (including steric and electrostatic repulsion) between the nitro and phenyl groups [symbolized as (NO_2,Ph)] should be more serious than (NO_2,CN). Conformation III is undoubtedly more stable than IV, because the latter has (NO_2,CN), but the former has no such unfavorable interaction. This is in good agreement with the ex-

perimental result that compound **2** is thermodynamically more stable than **3**. The chemical shift of H-4 also supports the foregoing assignment. The H-4 signals of **2** (δ 5.04) and the dicyanomethyl derivative **15** (δ 4.73) (exceptionally, the cyano group of both compounds points toward the ring) resonate at lower field than those of **3** (δ 4.40) and other 2-*C*-branched derivatives obtained by Michael addition to **1** (in the range δ 4.43–4.50), because of the deshielding effect of the cyano group[10].

If 1,3-diaxial interactions involving a hydrogen atom may be ignored, the sequence, (NO_2,Ph) > (NO_2,CN) > (CN,O) could be deduced by the foregoing conformational preference. The α-D-glucopyranoside having the (*R*) configuration should then exist mainly in conformation VI, as the other conformations have more serious interactions, for example, (NO_2,Ph). On the other hand, the C-8 epimer may assume conformation VII and/or VIII. Compound **4**, having a larger $J_{2,8}$ value (8.9 Hz), may be assigned as having the (*S*) configuration, existing mainly in conformation VIII, and compound **5** ($J_{2,8}$ 6.1 Hz) as having the (*R*) configuration. These assignments are supported by the chemical-shift values; H-3 and the methoxyl group of **5** resonate at lower field than those of **4**, whereas the H-2 signal of **5** appeared at higher field than that of **4**, owing to the deshielding effect of the cyano group. As apparent from the foregoing sequence, conformer VI should be more stable than conformer VIII, that is, compound **5** should be more stable than **4**; in fact the equilibrium mixture consisted of **4** and **5** in the ratio of 1:2.5.

Although the $J_{2,8}$ values and the thermodynamic stabilities of the β-D-glucopyranosides **12** and **13** were nearly equal, tentative assignments of the configuration at C-8 were performed as follows. As compound **4** exists mainly in conformation VIII, but not in conformation VII, destabilization by (Ph,OMe) might exceed that of (NO_2,CN). The most stable conformations, therefore, for the β-D-glucopyranosides having the (*R*) and (*S*) configurations should be IX and X, respectively. The methoxyl signal of **13** appears at lower field than that of **12**, suggesting that compound **12** has the (*R*) and **13** the (*S*) configuration, respectively. In the α-D-mannopyranosides (**2**, $[\alpha]_D^{22}$ −22.7°; **3**, $[\alpha]_D^{22}$ +13.3°) and also the α-D-glucopyranosides (**4**, $[\alpha]_D^{22}$ +21.2°; **5**, $[\alpha]_D^{22}$ +42.4°), the compound having the (*R*) configuration was more dextrorotatory than the corresponding compound having the (*S*) configuration. Therefore, the same trend may be expected in the β-D-glucopyranosides[11]. Compound **12** ($[\alpha]_D^{22}$ −18.1°), being more dextrorotatory than **13** ($[\alpha]_D^{22}$ −46.0°), seems to have the (*R*) configuration; this conclusion is in agreement with the speculation made on the basis of chemical-shift values.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries and are uncorrected. I.r. spectra were recorded for potassium bromide discs, and n.m.r. spectra were determined in chloroform-*d* with tetramethylsilane as internal standard with a JNM-PS-100 (JEOL) spectrometer. Solutions were evaporated under diminished pressure. Column chromatography was conducted on silica gel

(C-300, Wakogel, Japan). T.l.c. was performed with Merck (Darmstadt) silica gel GF 254. In this section the catalyst refers to tributylhexadecylphosphonium bromide.

Reaction of **1** *with phenylacetonitrile in a homogeneous system.* — To a solution of **1** (ref. 12, 293 mg, 1 mmol) and phenylacetonitrile (150 mg, 1.28 mmol) in tetrahydrofuran (5 mL) was added M sodium hydroxide (1 mL) at ~23°. The mixture was stirred for 3 h at that temperature and then deionized with cation-exchange resin (Amberlite IR-120, H^+). After removal of the resin, the mixture was evaporated to a syrup, the n.m.r. spectrum of which showed the presence of **2** as the major product, together with small proportions of other products. The syrup was chromatographed successively with benzene, benzene–ethyl acetate (20:1 and 10:1, v/v), and benzene-ethanol (10:1, v/v) as eluant. The first fraction was a mixture (92 mg) of phenylacetonitrile containing a small amount (~15 mg) of the cyano alkene **7** (ref. 5) and **2**. The second was 127.5 mg of **2** (103 mg, after recrystallization from 2-propanol); m.p. 171–171.5°, $[\alpha]_D^{22}$ −22.7° (*c* 0.53, chloroform); ν_{max} 2230 (CN) and 1558 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found : C, 64.65; H, 5.51; N, 6.78.

The third (40 mg) was a mixture of **4, 6,** and **7** in the ratio of ~1.2:1:3. The fourth (91 mg) was fairly pure **3** (46 mg after crystallization from ethanol); m.p. 205.5–206° (dec.), $[\alpha]_D^{22}$ +13.3° (*c* 0.4, chloroform); ν_{max} 2240 (CN), 1565, and 1550 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found : C, 64.09; H, 5.51; N, 6.77.

The fifth (40 mg) was a mixture of the nitro alcohols **9** and **10**, as judged from the n.m.r. and i.r. spectra[6].

Similar treatment of **1** (147 mg, 0.5 mmol) with phenylacetonitrile (65.8 mg, 0.51 mmol) for 30 h at ~23° afforded a crystalline residue. Recrystallization from ethanol gave 30 mg of **6**; m.p. 187–189° (dec.), $[\alpha]_D^{22}$ +120° (*c* 1, chloroform); ν_{max} 1625 cm^{-1} (C=N); *m/z* 365 (M^+), 334 ($M^+ - OMe$).

Anal. Calc. for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found : C, 69.03; H, 5.35; N, 3.71.

The mother liquor was evaporated and the residue was similarly chromatographed. Each fraction containing products was examined by n.m.r. spectroscopy and approximate yields were calculated by integration of signals of the benzylidene methine and methoxyl groups; **4**, 2; **5**, 8.8; **6**, 31.7; **7**, 2.2; **9**, 26; and **10**, 3.2%.

To a solution of **1** (14.7 mg, 0.05 mmol) and phenylacetonitrile (7.5 mg, 0.064 mmol) in tetrahydrofuran (0.75 mL) was added M sodium hydroxide (0.05 mL) at ~23°. The mixture was stirred for 30 min and processing as already described gave a residue, the n.m.r. spectrum of which showed it to be a mixture of **1, 2, 3,** and **9** in the ratio of ~3.5:3:1:1.

When commercially available 1,4-dioxane or tetrahydrofuran was used

directly without pretreatment with lithium aluminium hydride, the nitro epoxide **8**, identical with an authentic sample[13], became the major product.

Reaction of **1** *with phenylacetonitrile in a heterogeneous system.* — To a solution of **1** (147 mg, 0.5 mmol) and phenylacetonitrile (65.8 mg, 0.51 mmol) in benzene (20 mL) in the presence of the catalyst (30 mg) was added 0.2M sodium hydroxide (5 mL) at ~24°. The mixture was stirred for 7 h and then diluted with benzene. The organic layer was washed with water and evaporated to a syrup, which was similarly chromatographed. The yields of the products were similarly calculated on the basis of the n.m.r. spectra: **1**, 3.3; **2** and **3** not detected; **4**, 4.8; **5**, 12.4; **6**, 25.6; **9**, 22.9; and **10**, 5.8%. Compound **4** (6 mg) was isolated by recrystallization from ethanol; m.p. 191–191.5°, $[\alpha]_D^{22}$ +21.2° (*c* 0.87, chloroform); ν_{max} 2230 (CN) and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.32; H, 5.56; N, 6.87.

Compound **5** was recrystallized from ethanol to give 15 mg of **5**, m.p. 166–167°, $[\alpha]_D^{22}$ +42.4° (*c* 0.5, chloroform); ν_{max} 2230 (CN) and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found : C, 64.20; H, 5.49; N, 6.84.

*Methyl 4,6-O-benzylidene-2,3-dideoxy-2-C-(1-cyano-1-phenyl)methyl-3-nitro-β-*D*-glucopyranosides* (**12** and **13**). — To a solution of **11** (ref. 14, 147 mg, 0.5 mmol) and phenylacetonitrile (65.8 mg, 0.51 mmol) in tetrahydrofuran (22 mL) was added M sodium hydroxide (1 mL). The mixture was stirred for 2 h at ~24° and then deionized with cation-exchange resin. After removal of the resin, the filtrate was evaporated to a syrup. Addition of ethanol afforded crystals, which were recrystallized from ethanol to give 14 mg (6.8%) of **12**; m.p. 203–204°, $[\alpha]_D^{22}$ −18.1° (*c* 1, chloroform); ν_{max} 2230 (CN) and 1550 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.31; H, 5.50; N, 6.75.

The mother liquor was concentrated and chromatographed, eluting successively with benzene and benzene–ethyl acetate (10:1, v/v). The first fraction (24 mg), being pure **13**, was recrystallized from ethanol to afford 20 mg (11.7%) of **13**; m.p. 164–165.5°, $[\alpha]_D^{22}$ −46.0° (*c* 1, chloroform); ν_{max} 2240 (CN) and 1560 cm^{-1} (NO_2).

Anal. Calc. for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.21; H, 5.49; N, 6.76.

The second fraction (29.5 mg) was a mixture of **12** and **13** in 1:2 ratio as judged from n.m.r. spectroscopy. The third (27.5 mg) was a mixture of **12** and **13** in the ratio of 1.2:1. The last fraction (60 mg) was the nitro alcohol **14**, identical (i.r. and n.m.r. spectra) with an authentic sample[14].

Similar treatment of **11** (147 mg) with phenylacetonitrile for 30 h afforded only the nitro alcohol **14** (47 mg, 30%).

Epimerization of **2** *and* **3**. — To a solution of **2** (20.5 mg, 0.05 mmol) and phenylacetonitrile (7.5 mg, 0.05 mmol) in tetrahydrofuran (0.75 mL) was added M

sodium hydroxide (0.05 mL) at ~24°. The mixture was stirred for 30 min and then processing similar to that described for the preparation of **2** and **3** afforded a residue, consisting of **2** and **3**, in the ratio of 3.5:1 as judged from n.m.r. spectroscopy.

To the residue was added phenylacetonitrile (7.5 mg), M sodium hydroxide (0.05 mL), and tetrahydrofuran (0.75 mL). The mixture was stirred for 2.75 h, giving a 3:1 mixture of **2** and **3**, together with small proportions of the isoxazole **6** and the glucopyranoside **5** (≤10%), as judged from n.m.r. spectroscopy.

Similar treatment of **3** (20.5 mg) for 30 min afforded a mixture of **2** and **3** in the ratio of 2:1.

To a solution of **2** (83 mg, 0.2 mmol) in tetrahydrofuran (3 mL) was added M sodium hydroxide at ~24°. The mixture was stirred for 30 h at that temperature and then deionized with cation-exchange resin. After removal of the resin, the filtrate was evaporated to a syrup that was chromatographed, eluting successively with benzene and benzene–ethyl acetate (10:1, v/v). The first fraction (22 mg) was a mixture of **2, 5,** and **6** in the ratio of ~3:1:5.5, from which 11 mg of **6** was isolated as the first crop by recrystallization from ethanol and 8 mg of **2** as the second crop from 2-propanol. The second fraction (29.3 mg) was a mixture of **5** and **6** in the ratio of 1:3.4, from which 20 mg of **6** was crystallized from ethanol. The third and fourth fractions were almost pure **3** (10 mg) and **4** (4 mg), respectively. The last one (11.1 mg) was a mixture of the nitro alcohols **9** and **10** (7:1).

Epimerization of **4** *and* **5**. — To a solution of **4** (9 mg, 0.02 mmol) and phenylacetonitrile (3.3 mg, 0.03 mmol) in tetrahydrofuran (0.3 mL) was added M sodium hydroxide (0.02 mL) at ~23°. The mixture was stirred for 30 min and then processed as already described to provide a 1:2.5 mixture of **4** and **5**.

Similar treatment of **5** (17 mg, 0.04 mmol) also yielded a mixture of **4** and **5** in the ratio of 1:2.5. These two mixtures were combined and deionized with cation-exchange resin. After removal of the resin, the filtrate was evaporated. To the residue was added phenylacetonitrile (6.6 mg), tetrahydrofuran (0.6 mL), and M sodium hydroxide (0.04 mL) at ~23°. After stirring for 30 h, the mixture was similarly processed to give a syrup, the n.m.r. spectrum of which showed it to consist of **4** and **5** in the ratio of 1:2.5. The syrup was chromatographed with benzene as eluant to give 11 mg of **5** as a fast-moving component and 5 mg of **4** as a slower-moving component.

Treatment of **6** *with phenylacetonitrile*. — To a solution of the isoxazole **6** (36.5 mg, 0.1 mmol) and phenylacetonitrile (12.9 mg, 0.11 mmol) in tetrahydrofuran (4.4 mL) was added M sodium hydroxide (0.2 mL). The mixture was stirred for 30 h and then treated as already described to give a residue, the n.m.r. spectrum of which showed it to be almost pure **6**. Recrystallization from ethanol gave 32 mg of **6** (87.7% recovery).

Epimerization of **12** *and* **13**. — To a solution of **12** (13 mg, 0.032 mmol) and phenylacetonitrile (4.8 mg, 0.041 mmol) in tetrahydrofuran (0.4 mL) was added M sodium hydroxide (0.03 mL). After stirring for 2 h, the mixture was treated simi-

larly to give a residue, whose n.m.r. spectrum showed the presence of **12** and **13** in the ratio of 1:1.2.

Similar treatment of **13** (13 mg) also afforded a mixture of **12** and **13**, in the ratio of 1:1.2.

The combined, crude mixture obtained (25 mg) was similarly treated for 37 h to give 9 mg of a mixture of **12** and **13** (1:1.2).

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