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C-Glycosylation of Oxygenated Naphthols with 3-Dimethylamino-2,3,6-trideoxy-L-arabino-hexopyranose and 3-Azido-2,3,6-trideoxy-D-arabino-hexopyranose

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In connection with studies directed towards the synthesis of the pyranonaphthoquinone antibiotic medermycin, *C*-aryl glycosides were prepared by *C*-glycosylation of naphthols with glycosyl donors. Boron trifluoride diethyl etherate proved to be a suitable Lewis acid to promote the *C*-glycosylation, and use of the azido glycosyl donor proved more successful than using the dimethylamino glycosyl donor. 5-Hydroxy-1,4-dimethoxynaphthalene underwent facile *C*-glycosylation with two particular glycosyl donors, whereas 3-bromo-5-hydroxy-1,4-dimethoxynaphthalene was not an effective coupling partner with the same glycosyl donors. These studies indicate that subtle steric and electronic effects need to be considered in order to fine-tune *C*-glycosylations when using highly functionalized glycosyl donors.

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Introduction

Medermycin, an antibiotic isolated from *Streptomyces tanashiensis*,[1] is a unique member of the pyranonaphthoquinone family of antibiotics[2] in that it contains a β-*C*-glycoside linkage to the amino sugar D-angolosamine. Medermycin was found to be identical to an anticancer agent, lactoquinomycin A, that was isolated from the same source by Tanaka et al.[3] ten years later. The point of attachment of the carbohydrate component (D-angolosamine) of medermycin was initially assigned as *ortho* to the hydroxyl group at C8 in structure (1) (see Diagram 1). Subsequent chemical and spectroscopic investigations by Morin and coworkers[4] resulted in temporary revision of the structure of medermycin/lactoquinomycin A to structure (2), where the *C*-glycoside is attached to the kalafungin (3) skeleton at the C10 position* *para* to the hydroxyl group. However, more recently, Wyeth researchers[5] presented sophisticated NMR evidence in support of the original structure for medermycin/lactoquinomycin A (1).

To date, only one lengthy synthesis of medermycin (1) has been reported[6] in which the *C*-glycoside in the pyranonaphthalene skeleton was assembled by addition of a sulfonylphthalide to an enone. The *C*-glycosidic linkage was introduced as a D-olivoside early in the synthetic sequence, before the phthalide annulation step, which rendered it necessary to manipulate the functional groups on the sugar moiety to give the desired D-angolosaminide amino sugar at the conclusion of the synthesis.

Our synthetic effort[7,8] towards medermycin (1) focussed on attachment of a carbohydrate that already bears an amino or azido group to the *ortho* position of a naphthol precursor. We, therefore, herein report our detailed studies on the

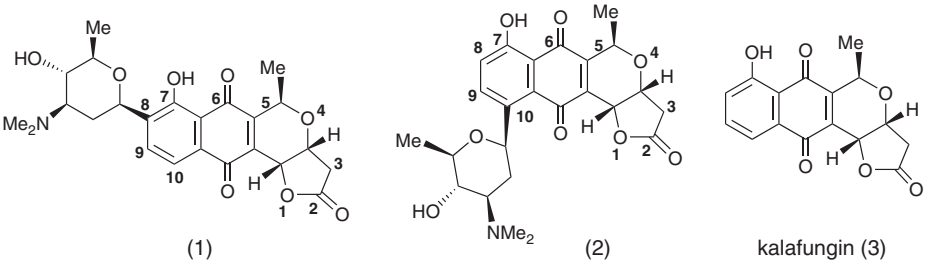

Diagram 1.

* The numbering system of the pyranonaphthoquinone skeleton is used rather than the numbering system used by Morin and coworkers.[4]

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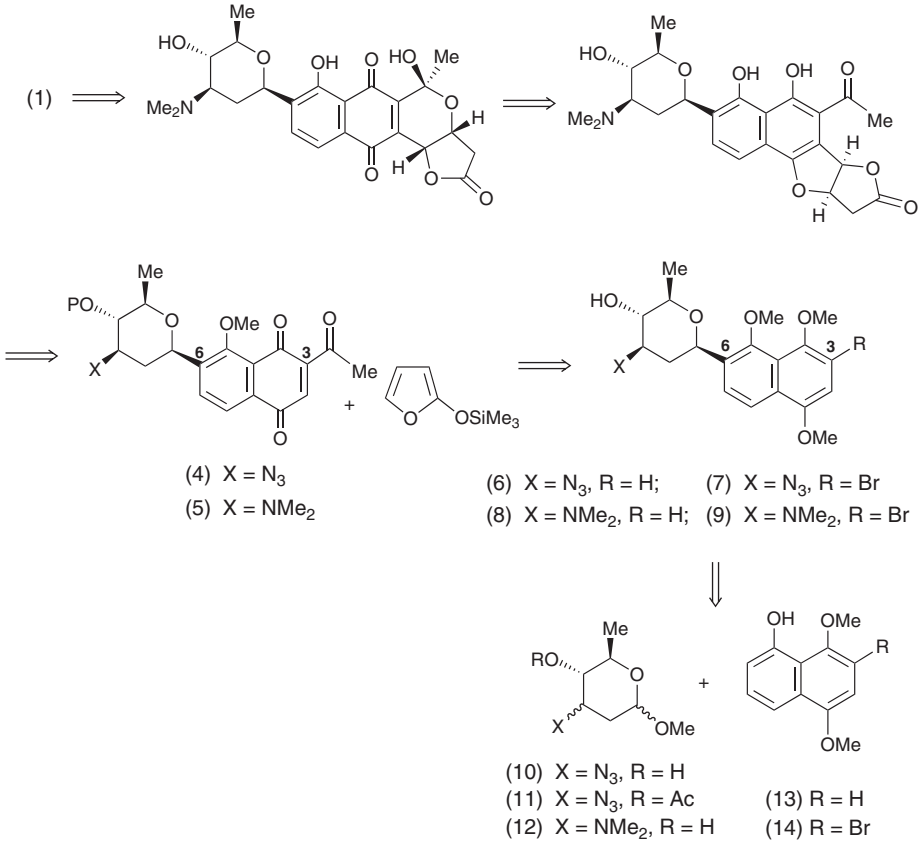
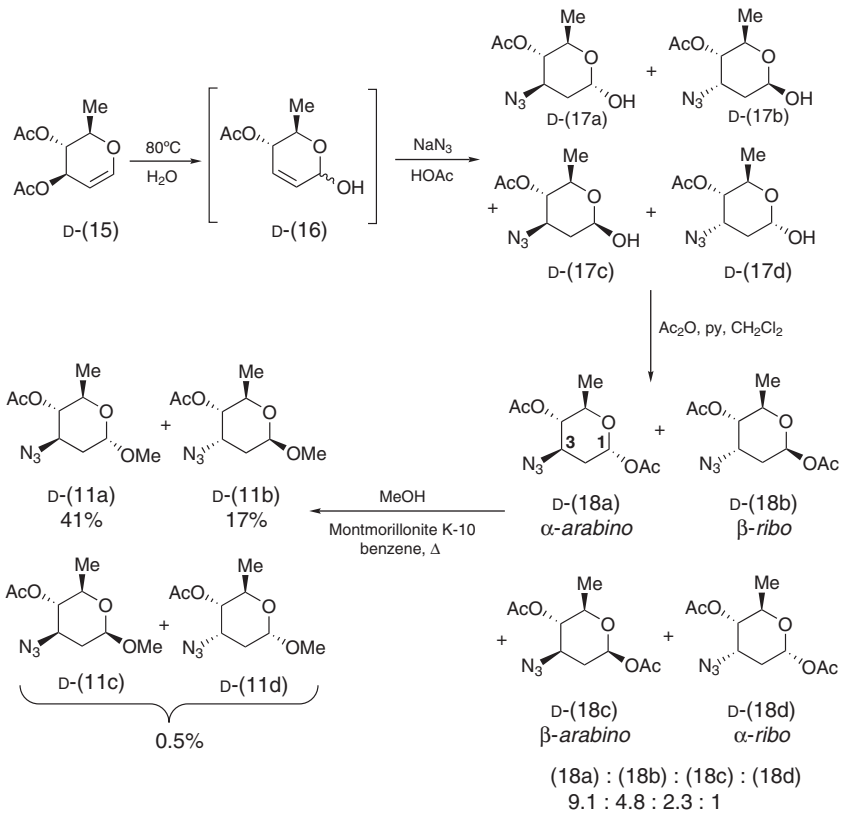


Scheme 1.



Scheme 2.

direct *C*-glycosylation of oxygenated naphthols with azido and dimethylamino glycosyl donors (10), (11), and (12). Several of the *C*-glycosides prepared in the present work are suitable for further elaboration to analogues of medermycin in which the carbohydrate is linked to the C8 position, and a recent synthesis[8] of an azido analogue of medermycin was based on this study.

Results and Discussion

Our synthetic approach to medermycin (1) hinged on the furofuran annulation of azido *C*-glycosyl-3-acetyl-1,4-naphthoquinone (4) or dimethylamino *C*-glycosyl-3-acetyl-1,4-naphthoquinone (5) with 2-trimethylsilyloxyfuran followed by oxidative rearrangement of the resultant adduct (Scheme 1). This strategy has been successfully applied to the synthesis of a 2-deoxyglucosylpyranonaphthoquinone[7] and the spiroacetal-containing pyranonaphthoquinone griseusin A.[9] It was, therefore, envisaged that *C*-glycosylnaphthalenes (6)–(9) would be suitable precursors to the key *C*-glycosylnaphthoquinones (4) and (5), and that they, in turn, would be available by treatment of azido glycosyl donors (10) or (11), or dimethylamino glycosyl donor (12) with naphthols (13) and (14). The bromine substituent at C3 in *C*-glycosylnaphthalenes (7) or (9) is required in order to provide functionality for the introduction of the C3 acetyl group in the *C*-glycosylnaphthoquinones (4) and (5). Our synthetic efforts were initially directed towards establishing an efficient protocol for *C*-glycosylation of naphthols (13) and (14) with a glycosyl donor that could be elaborated to D-angolosamine which is present in medermycin.

Synthesis of the glycosyl donors (10), (11), and (12) was based on existing methodology reported by Monneret and coworkers[10,11] for the L-isomers (Scheme 2). The synthesis could be adapted to both enantiomeric series in that the starting material for the D-series, 3,4-di-*O*-acetyl-D-rhamnal (15), can be prepared from 3,4,6-tri-*O*-acetyl-D-glucal,[12] whereas the L-isomer of this compound, as used by Monneret and coworkers,[10,11] is commercially available. We herein provide full experimental details for the preparation of the D-isomers of the azido glycosyl donors (10) and (11) that have the correct absolute configuration for the synthesis of medermycin.

3,4-Di-*O*-acetyl-D-rhamnal (15) was heated with water to afford pseudo-glycal (16). Subsequent treatment of pseudo-glycal (16) with sodium azide and acetic acid for 24 h gave an inseparable mixture of 3-azidopyranoses (17a)–(17d) in 93% yield, which upon standard acetylation also gave an inseparable mixture of 1-*O*-acetylpyranoses (18a)–(18d) in 95% yield. The ratio of diastereomers (18a) : (18b) : (18c) : (18d) obtained was 9.1 : 4.8 : 2.3 : 1, which thereby established the ratio of D-arabino to D-ribo isomers to be approximately 2 : 1. Conversion of the isomeric mixture of 1-*O*-acetylpyranoses (18) to methyl glycosides (11) was then achieved using montmorillonite K-10 resin and methanol in benzene, which allowed separation of the major α-D-arabino azide (11a) (41% yield) from its β-D-ribo counterpart (11b) (17% yield) by careful flash chromatography. Purification of the β-D-arabino (11c) and α-D-ribo isomer (11d) proved more difficult and they were afforded as an inseparable mixture in 0.5% yield.

Of interest is the low proportion of α-D-ribo isomer (18d) obtained from the initial addition of hydrazoic acid and acetylation of pseudo-glycal (16). This is rationalized by considering that in a chair-like conformation, the C3 and C1 substituents must both assume an axial orientation, which would give rise to severe 1,3-diaxial interactions that oppose the stability offered by the anomeric effect associated with the α-acetoxy group at C1. The overall predominance of the α-D-arabino isomer (18a) is due to the favourable combination of an equatorial substituent at C3 and the stabilizing anomeric effect contributed by the axial C1 acetoxy group (Fig. 1).

Given that 3,4-di-*O*-acetyl-L-rhamnal is more readily available than 3,4-di-*O*-acetyl-D-rhamnal, optimization of the glycosyl donor synthesis and *C*-glycosylation studies was performed on the L-series. To this end, azido glycosyl donor L-(11a) was converted into methyl α-L-angolosaminide, L-(12), in a single step, albeit in 44% yield, by hydrogenation over 10% palladium on charcoal in methanol in the presence of excess formaldehyde. Alternatively, the transformation could be achieved in two steps in higher yield. Thus, hydrogenation of L-(11a) over 10% palladium on charcoal in methanol afforded methyl α-L-acosaminide L-(19) in 86% yield (Scheme 3). The reductive methylation was then conducted using similar conditions except that excess aqueous formaldehyde was also present. After chromatography, L-(12) was obtained in 79% yield. Whereas cleavage of the acetate took only a few hours to go to completion, reductive methylation of the azide group required reaction overnight.

Initial *C*-glycosylation studies were carried out using the L-series. The naphthols (13)[7] and (14)[13] used in the present study were prepared as described previously and our attention first focussed on the use of the methyl α-L-angolosaminide L-(12) as the glycosyl donor, given the presence of a dimethylamino group on the *C*-glycoside in medermycin. Based on

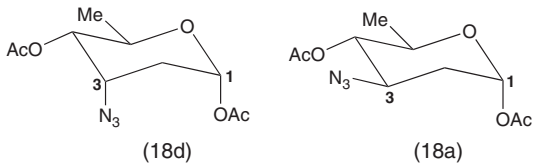
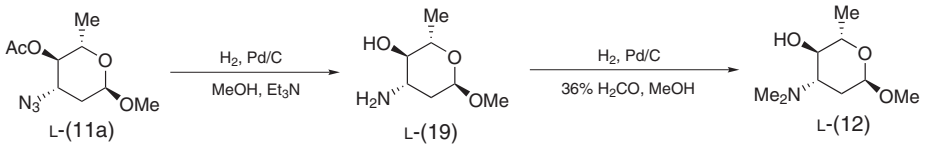
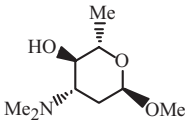
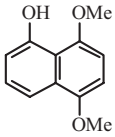
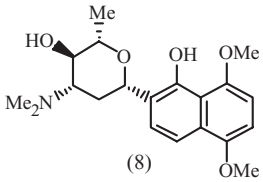
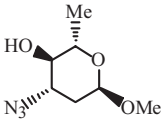
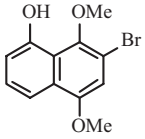
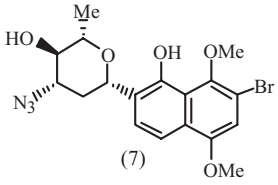
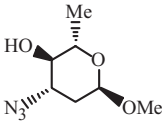
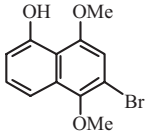
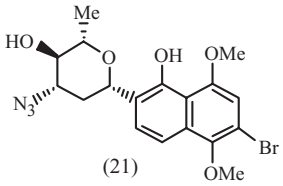
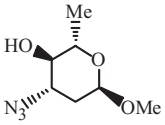
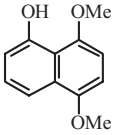
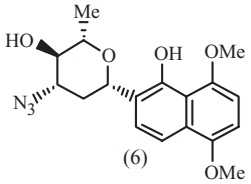
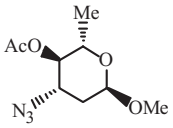
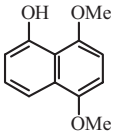
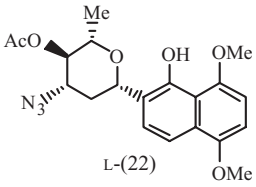
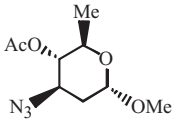
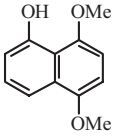
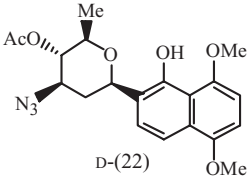


Fig. 1.



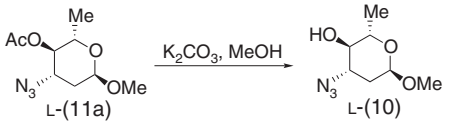
Scheme 3.

Table 1. *C*-Glycosylation of naphthols (13), (14), and (20)

Entry	Glycosyl Donor	Naphthol	Conditions	*C*-Glycoside	
1			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		<5%
2			$BF_3.Et_2O$ (4 eq.)		31%
3			$BF_3.Et_2O$ (6 eq.)		52%
	L-(12)	(13)		(8)	
4			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		<5%
	L-(10)	(14)		(7)	
5			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		34%
	L-(10)	(20)		(21)	
6			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		42%
	L-(10)	(13)		(6)	
7			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		66%
	L-(11a)	(13)		L-(22)	
8			CH_3CN, 0°C $BF_3.Et_2O$ (2 eq.)		60%
	D-(11a)	(13)		D-(22)	

similar studies using 2-deoxy-D-glucosyl donors,[13,14] naphthol (13) was reacted with methyl glycoside L-(12) using boron trifluoride diethyl etherate as the Lewis acid in acetonitrile at 0°C (entries 1–3, Table 1). In this case, it was found that donor L-(12) required six molar equivalents of boron trifluoride etherate to give an optimum yield of 52%. This is possibly due to the Lewis basic dimethylamino and hydroxyl sites on donor L-(12), which can coordinate to the boron trifluoride and, thereby, inhibit formation of the reactive oxonium ion intermediate. Only one *C*-glycoside product was formed and that was established to be the β-*C*-glycoside (8). *O*-Glycoside products were not observed.

In the ^{1}H NMR spectrum for (8), $H2'_{ax}$ resonated as a doublet of doublet of doublets (ddd) at δ 1.49, with large axial–axial couplings to H1′ and H3′ (both 10.8 Hz), and a large geminal coupling to $H2'_{eq}$ (12.5 Hz). The anomeric



Scheme 4.

proton, H1′, resonated as a doublet of doublets at δ 5.02, with coupling constants $J_{1',2'ax}$ 10.8 Hz and $J_{1',2'eq}$ 1.8 Hz. The magnitude of the larger coupling constant is consistent with an axial–axial coupling, thereby supporting the formation of a β-glycoside. The observation of four aromatic hydrogens and a naphthol OH proton at δ 9.76 provided evidence for the formation of a *C*-glycoside rather than an *O*-glycoside.

A setback to the use of *C*-glycoside (8) as a key intermediate in the synthesis of medermycin occurred when attempts to methylate the hydroxyl group resulted in formation of a trimethylammonium salt. This was due to quaternization of the amine function occurring preferentially over methyl ether formation. In order to bypass this problem it was decided to return to the *C*-glycosylation reaction, this time using a donor in which the amine functionality was suitably masked as an azide.

Our attention next turned to the coupling of glycosyl donor L-(10) with 3-bromonaphthol (14) (entry 4, Table 1). Donor L-(10) was readily prepared by deacetylation of the 4-*O*-acetyl sugar L-(11) (Scheme 4). When trimethylsilyl triflate was used as the Lewis acid in dichloromethane no *C*-glycoside was isolated from the reaction despite the use of three molar equivalents of the promoter. Use of boron trifluoride was also disappointing in that the desired *C*-glycoside (7) was only formed in less than 5% yield.

This latter result was in direct contrast to a similar experiment using 2-bromonaphthol (20)[13] in which *C*-glycoside (21) was obtained in 34% yield (entry 5, Table 1). These results reflect those obtained when using a tri-*O*-benzyl-2-deoxy-D-glucosyl donor[13] in that 3-bromonaphthol (14) proved more unreactive towards Lewis acid mediated *C*-glycosylation than 2-bromonaphthol (20). In light of this situation we were forced to carry out the *C*-glycosylation using 5-hydroxy-1,4-dimethoxynaphthalene (13) and to introduce the bromine at C3 on the naphthalene ring after the *C*-glycosylation step.

We can offer some suggestions for the differences in reactivity observed for glycosyl acceptors (13), (14), and (20). Bromine substitution on the aromatic ring is observed to reduce the yield of *C*-glycosylation dramatically for (14) but also for (20). This observation is consistent with the electron-withdrawing nature of this substituent, which deactivates the aromatic ring towards electrophilic substitution. This may be attenuated, in part, for (20) by the ability of the C2 bromine to stabilize the relevant cationic intermediate by resonance, which leads to higher yields for this derivative. The influence of steric effects could also reduce the reactivity of the aromatic coupling partner. In particular, the C3 bromine substituent of (14) would give rise to interactions with the adjacent C4 methoxy group, which in turn, would afford greater *peri*-interactions between this substituent and the C5 hydroxyl that directs the *C*-glycosylation.

Our efforts were next focussed on the *C*-glycosylation of naphthol (13) with azido glycosyl donor L-(10) to afford *C*-glycoside (6) in 42% yield using boron trifluoride etherate (2.0 equiv.) in acetonitrile at 0°C (entry 6, Table 1). In this case, increasing the ratio of Lewis acid did not improve the yield. The yield of *C*-glycoside L-(22) improved to 66% when azido glycosyl donor L-(11), in which the hydroxyl group was protected as an acetate, was used (entry 7, Table 1). Protection of the azido glycosyl donor L-(10) as the acetate derivative L-(11) may improve the yield obtained in the *C*-glycosylation because by masking the secondary hydroxyl group, unproductive oligomerization of the glycosyl donor is prevented.

For the purpose of synthesizing medermycin, use of the correct azido *C*-glycosyl donor D-(11) was also investigated. This reaction was conducted on a larger scale (0.5–1.5 g) using two equivalents of boron trifluoride diethyl etherate and consistently gave yields of *C*-glycoside D-(22) in the range 59–62% (entry 8, Table 1). The material obtained was spectroscopically identical to the L-isomer L-(22) and exhibited an optical rotation of $[\alpha]_D^{22}$ +70.0°. The ^{1}H NMR spectrum for D-(22) was consistent with the proposed structure, featuring expected signals arising from both the azido sugar and the naphthalene moieties. A three-proton singlet at δ 2.16 was assigned to the 4′-*O*-acetyl protons, and a three-proton doublet at δ 1.29 was assigned to the C6′ methyl protons. The axial proton $H2'_{ax}$ gave rise to a doublet of doublet of doublets at δ 1.71, with large axial–axial couplings, both 11.3 Hz, to H1′ and H3′. The geminal coupling constant $J_{2'ax,2'eq}$ was 13.1 Hz. The equatorial proton $H2'_{eq}$, at δ 2.46, also resonated as a doublet of doublet of doublets but with small equatorial–axial coupling constants to H3′ and H1′ (4.9 and 1.9 Hz, respectively). The anomeric proton appeared as a doublet of doublets at δ 5.06 with coupling constants of 11.3 and 1.9 Hz. The larger coupling constant corresponds to an axial–axial relationship between H1′ and $H2'_{ax}$ and is, therefore, consistent with the formation of a β-glycoside. In the naphthol portion of the molecule, H7 and H8 resonated as doublets at δ 7.74 and 7.56, respectively, with a coupling constant of $J_{7,8}$ 8.7 Hz. A singlet at δ 9.79 was assigned to the naphthol OH proton and an OH stretch at 3356 cm^{-1} was present in the infrared spectrum. A very strong band was also observed at 2096 cm^{-1}, which confirmed the presence of an azide functional group.

In summary, an effective method for the key *C*-glycosylation of azido glycosyl donor D-(11) with naphthol (13) has been developed. The final *C*-glycoside thus obtained, D-(22), does require further functionalization at C3 in order for the synthetic strategy proposed in Scheme 1 to be pursued, however, prior functionalization of the naphthol with a bromine substituent at C3 afforded poorer yields in the key *C*-glycosylation step. Use of an azido glycosyl donor was also more successful than using a dimethylamino glycosyl donor.

Experimental

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured using a PolAAR 2001

polarimeter at room temperature in the indicated solvent. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier-transform infrared spectrophotometer as thin films or Nujol mulls between sodium chloride plates. Proton (^{1}H) NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker DRX 400 (400 MHz) spectrometer at ambient temperature. Carbon NMR spectra were recorded on a Bruker AC 200 (50.3 MHz) or a Bruker DRX 400 (100.5 MHz) spectrometer at ambient temperature with complete proton decoupling. Low-resolution mass spectra were recorded on a VG70-250S, a VG70-s.d. or a AEI model MS902 double focussing magnetic sector mass spectrometer operating with an ionization potential of 70 eV (EI, DEI, CI and DCI). High-resolution mass spectra were recorded at a nominal resolution of 5000 or 10 000 as appropriate. Major fragments are given as percentages relative to the base peak and are assigned where possible. Ionization methods employed were either electron impact or chemical ionization (CI) with ammonia or methane as reagent gas. Flash chromatography was performed using Merck Kieselgel 60 or Riedel-de-Haen Kieselgel S silica gel (both 230–400 mesh) with the solvents indicated. Compounds were visualized under ultraviolet light or by staining with iodine or vanillin in methanolic sulfuric acid. Acetonitrile was distilled from calcium hydride before use.

4-O-*Acetyl-3-azido-2,3,6-trideoxy-D-hexopyranoses (17a)–(17d)*[10]

To 3,4-di-*O*-acetyl-D-rhamnal (15)[12] (5.00 g, 23.3 mmol) was added water (35 mL) and the mixture was stirred at 80°C for 2 h. The reaction mixture was allowed to cool to room temperature then glacial acetic acid (5.20 mL) and sodium azide (2.44 g, 37.3 mmol) were added in single portions. The reaction mixture quickly turned yellow and was stirred at room temperature overnight. The mixture was then poured into saturated aqueous sodium bicarbonate solution (50 mL) and stirred until bubbling ceased. The product was extracted into ethyl acetate (3 × 50 mL) and the combined organic phases were dried over anhydrous sodium sulfate. Filtration and concentration under vacuum gave *4*-O-*acetyl-3-azido-2,3,6-trideoxy-D-hexopyranoses (17a)–(17d)* (4.67 g, 93%) as a yellow syrup that was not purified further. ν_{max} (film)/cm^{-1} 3360, 2104, 1743. δ_H[†] (400 MHz; $CDCl_3$) 5.26 (br d, $J_{1,2ax}$ 3.1, H1$_{\alpha\text{-}arabino}$), 5.07 (br m, H1$_{\alpha\text{-}ribo}$), 4.98 (dd, $J_{1,2eq}$ 2.0 and $J_{1,2ax}$ 9.2, H1$_{\beta\text{-}ribo}$), 4.79 (dd, $J_{1,2eq}$ 1.9 and $J_{1,2ax}$ 9.5, H1$_{\beta\text{-}arabino}$), 4.63 (dd, $J_{4,3}$ 3.3 and $J_{4,5}$ 9.6, H4$_{\alpha\text{-}ribo}$), 4.59 (dd, $J_{4,3}$ 9.7 and $J_{4,5}$ 9.7, H4$_{\alpha\text{-}arabino}$ and H4$_{\beta\text{-}arabino}$), 4.58 (dd, $J_{4,3}$ 3.6 and $J_{4,5}$ 9.7, H4$_{\beta\text{-}ribo}$), 4.27–3.31 (m, H3 and H5), 3.21 (br s, OH), 2.24 (ddd, $J_{2eq,1}$ 2.0, $J_{2eq,2ax}$ 13.0 and $J_{2eq,3}$ 4.8, H2$_{eq\ \beta\text{-}arabino}$), 2.12 (ddd, $J_{2eq,1}$ 1.2, $J_{2eq,2ax}$ 13.2 and $J_{2eq,3}$ 4.9, H2$_{eq\ \alpha\text{-}arabino}$), 2.10 (s, OAc$_{\alpha\text{-}ribo}$), 2.08 (s, OAc$_{\beta\text{-}arabino}$), 2.06 (s, OAc$_{\alpha\text{-}arabino}$), 2.06 (s, OAc$_{\beta\text{-}ribo}$), 1.93–2.05 (m, H2$_{eq\ \alpha\text{-}ribo}$ and H2$_{eq\ \beta\text{-}ribo}$), 1.47–1.74 (m, H2$_{ax}$), 1.15 (d, $J_{6,5}$ 6.2, H6$_{\beta\text{-}ribo}$), 1.15 (d, $J_{6,5}$ 6.2, H6$_{\beta\text{-}arabino}$ and H6$_{\alpha\text{-}ribo}$), 1.08 (d, $J_{6,5}$ 6.4 Hz, H6$_{\alpha\text{-}arabino}$).

1,4-Di-O-*acetyl-3-azido-2,3,6-trideoxy-D-hexopyranoses (18a)–(18d)*[10]

To a stirred, ice-cooled solution of pyranoses (17a)–(17d) (4.33 g, 20.1 mmol) in anhydrous pyridine (40 mL) under an atmosphere of nitrogen were added acetic anhydride (15 mL, 150 mmol) and a catalytic quantity of 4-dimethylaminopyridine. The reaction mixture was then allowed to warm to room temperature and was stirred under nitrogen overnight. The mixture was then cooled to 0°C with an ice-bath, and water (25 mL) was added with stirring. The mixture was poured into a conical flask then saturated aqueous sodium bicarbonate solution (50 mL) and dichloromethane (50 mL) were added with vigorous stirring. When bubbling had ceased, the phases were separated and the organic phase was treated with further portions of saturated aqueous sodium bicarbonate solution (2 × 50 mL) before being dried over anhydrous sodium sulfate and concentrated under vacuum. Residual pyridine was removed by heating under high vacuum to afford a mixture of *1,4-di*-O-*acetyl-3-azido-2,3,6-trideoxy-D-hexopyranoses (18a)–(18d)* (4.94 g, 95%) as a pale-yellow syrup which was not purified further. The ratio (18a) : (18b) : (18c) : (18d) was determined to be 9.1 : 4.8 : 2.3 : 1 by ^{1}H NMR analysis. ν_{max} (film)/cm^{-1} 2100, 1745. δ_H[‡] (200 MHz; $CDCl_3$) 6.16 (br d, $J_{1,2ax}$ 2.6, H1$_{\alpha\text{-}arabino}$), 6.05 (app br s, H1$_{\alpha\text{-}ribo}$), 5.94 (dd, $J_{1,2eq}$ 2.6 and $J_{1,2ax}$ 8.9, H1$_{\beta\text{-}ribo}$), 5.73 (dd, $J_{1,2eq}$ 2.3 and $J_{1,2ax}$ 10.1, H1$_{\beta\text{-}arabino}$), 4.64–4.72 (m, H4), 3.49–4.24 (m, H3 and H5), 1.71–2.22 (m, H2$_{eq}$ and H2$_{ax}$), 2.06–2.14 (m, OAc × 2), 1.23 (d, J 6.3, H6$_{\beta\text{-}ribo}$), 1.21 (d, $J_{6,5}$ 6.2, H6$_{\beta\text{-}arabino}$), 1.16 (d, $J_{6,5}$ 6.2, H6$_{\alpha\text{-}arabino}$).

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-D-hexopyranosides (11a)–(11d)*[10]

To a solution of 1-*O*-acetyl-D-azidopyranoses (18a)–(18d) (1.93 g, 7.50 mmol) in dry benzene (60 mL) under an atmosphere of nitrogen was added montmorillonite K-10 (9.04 g) and dry methanol (1.6 mL, 39.6 mmol). The mixture was stirred vigorously and heated under reflux overnight. The mixture was then allowed to cool to room temperature and was filtered through a pad of celite, washing with ethyl acetate (100 mL). The solution was concentrated under vacuum and the residue was purified by flash column chromatography (hexanes/ethyl acetate, 92 : 8) to afford the following:

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-α-D-arabino-hexopyranoside (11a)*. Clear oil (705 mg, 41%), $[\alpha]_D^{22}$ + 168.9° (*c* 1.2 in CH_2Cl_2) (lit.[10] $[\alpha]_D^{22}$ −171° (*c* 1 in $CHCl_3$) for L-isomer). ν_{max} (film)/cm^{-1} 2099, 1748. δ_H (400 MHz; $CDCl_3$) 4.73 (1 H, d, $J_{1,2ax}$ 3.3, H1), 4.65 (1 H, dd, $J_{4,5} = J_{4,3}$ 9.7, H4), 3.71–3.87 (2 H, m, H3 and H5), 3.32 (3 H, s, OMe), 2.14 (1 H, ddd, $J_{2eq,1}$ 1.0, $J_{2eq,2ax}$ 13.1 and $J_{2eq,3}$ 5.1, H2$_{eq}$), 2.11 (3 H, s, OAc), 1.71 (1 H, ddd, $J_{2ax,1}$ 3.4 and $J_{2ax,2eq} = J_{2ax,3}$ 13.1, H2$_{ax}$), 1.15 (3 H, d, $J_{6,5}$ 6.3, H6). δ_C (100 MHz; $CDCl_3$) 170.7, 98.0, 76.2, 66.4, 58.4, 55.4, 35.8, 21.5, 18.1. The ^{1}H NMR data were in agreement with the data reported for the L-isomer.[10]

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-β-D-ribo-hexopyranoside (11b)*. Clear oil (299 mg, 17%), $[\alpha]_D^{22}$ +42.2° (*c* 1.0 in CH_2Cl_2) (lit.[10] $[\alpha]_D{}^{22}$ −41° (*c* 1 in $CHCl_3$) for L-isomer). δ_H (400 MHz; $CDCl_3$) 4.65 (1 H, dd, $J_{4,3}$ 3.4 and $J_{4,5}$ 9.1, H4), 4.62 (1 H, dd, $J_{1,2eq}$ 2.0 and $J_{1,2ax}$ 8.9, H1), 4.10–4.19 (1 H, m, H3), 3.92–3.97 (1 H, m, H5), 3.47 (3 H, s, OMe), 2.13 (3 H, s, OAc), 2.05 (1 H, ddd, $J_{2eq,1}$ 2.0, $J_{2eq,3}$ 3.8 and $J_{2eq,2ax}$ 13.8, H2$_{eq}$), 1.80 (1 H, ddd, $J_{2ax,1}$ 8.9, $J_{2ax,3}$ 3.4 and $J_{2ax,2eq}$ 13.8, H2$_{ax}$), 1.24 (3 H, d, $J_{6,5}$ 6.3, H6). The ^{1}H NMR data were in agreement with the data reported for the L-isomer.[10]

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-β-D-arabino-hexopyranoside (11c) and methyl 4*-O-*acetyl-3-azido-2,3,6-trideoxy-α-D-ribo-hexopyranoside (11d)*. Yellow oil (8 mg, 0.5%) identified on the basis of data extracted from the ^{1}H NMR spectrum. For β-D-arabino isomer (11c): δ_H (400 MHz; $CDCl_3$) 4.63 (1 H, dd, $J_{4,5}$ $J_{4,3}$ 9.4, H4), 4.40 (1 H, dd, $J_{1,2eq}$ 1.9 and $J_{1,2ax}$ 9.4, H1), 3.40–3.62 (2 H, m, H3 and H5), 3.50 (3 H, s, OMe), 2.20 (1 H, ddd, $J_{2eq,1}$ 1.9, $J_{2eq,3}$ 5.0, and $J_{2eq,2ax}$ 12.8, H2$_{eq}$), 2.13 (3 H, s, OMe), 1.63 (1 H, ddd, $J_{2ax,1}$ 9.4 and $J_{2ax,3} = J_{2ax,2eq}$ 12.8, H2$_{ax}$), 1.22 (3 H, d, $J_{6,5}$ 6.2, H6). For α-D-ribo isomer (11d): δ_H (400 MHz; $CDCl_3$) 4.60–4.66 (2 H, m, H1 and H4), 4.05–4.17 (2 H, m, H3 and H5), 3.35 (3 H, s, OMe), 2.13 (3 H, s, OAc), 1.94–2.07 (2 H, m, H2), 1.17 (3 H, d, $J_{6,5}$ 6.5, H6).

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-L-hexopyranosides L-(11a) and L-(11b)*[10]

The above procedure was repeated using 1-*O*-acetyl-L-azidopyranoses L-(18a)–(18d) (4.94 g, 19.2 mmol), which had been prepared from 3,4-di-*O*-acetyl-L-rhamnal, to afford the following:

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(11a)*. Clear oil (1.80 g, 41%), $[\alpha]_D^{22}$ −172.2° (*c* 2.1 in CH_2Cl_2) [lit.[10] $[\alpha]_D^{22}$ −171° (*c* 1 in $CHCl_3$)].

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-β-L-ribo-hexopyranoside L-(11b)*. Clear oil (614 mg, 14%), $[\alpha]_D^{22}$ −40.3° (*c* 0.8 in CH_2Cl_2) [lit.[10] $[\alpha]_D^{22}$ −41° (*c* 1 in $CHCl_3$)].

Methyl 4-O-*acetyl-3-azido-2,3,6-trideoxy-β-L-arabino-hexopyranoside L-(11c) and methyl 4*-O-*acetyl-3-azido-2,3,6-trideoxy-α-L-ribo-hexopyranoside L-(11d)*. Yellow oil (58 mg, 1.3%).

[†] Due to the extensive overlapping of signals in the ^{1}H NMR spectrum, integrations of the individual resonances for the four diastereomers are not reported.
[‡] Only selected data is reported due to extensive overlap of signals. Signals for the minor α-ribo isomer (18d) were partially obscured.

Methyl 3-azido-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(10)[10]

Methyl 4-*O*-acetyl-3-azido-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(11a) (260 mg, 1.14 mmol) in methanol (10 mL) was treated with potassium carbonate (500 mg) and the mixture was stirred at room temperature for 16 h. Neutralization with Amberlite IR-115 resin (H^+) followed by evaporation under reduced pressure and flash chromatography afforded *methyl 3-azido-2,3,6-trideoxy-α-arabino-hexopyranoside L-(10)* as a syrup, $[\alpha]_D^{22}$ −122.1° (*c* 1.2 in $CHCl_3$) [lit.[10] $[\alpha]_D^{25}$ −125.0° (*c* 0.86 in $CHCl_3$)]. The ^1H NMR data were in agreement with the literature.[10]

Methyl 3-amino-2,3,6-trideoxy-α-L-arabino-hexopyranoside (Methyl α-L-acosaminide) L-(19)[10]

To a solution of methyl pyranoside L-(11a) (260 mg, 1.14 mmol) in methanol (10 mL) was added triethylamine (0.2 mL) and 10% palladium on charcoal (262 mg). The vessel was evacuated using a water aspirator and hydrogen was introduced from a balloon. This sequence was repeated twice more before the reaction mixture was allowed to stir for 2 h under an atmosphere of hydrogen. The reaction slurry was filtered through celite, washed with methanol (50 mL), and the pale solution was concentrated under vacuum. Purification through a small plug of silica and trituration of the residue with diethyl ether gave *methyl 3-amino-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(19)* (156 mg, 86%) as a white solid, mp 130–131°C (lit.[10] mp 132°C), $[\alpha]_D^{22}$ −134.3° (*c* 2.2 in MeOH) [lit.[10] $[\alpha]_D^{22}$ −135.0° (*c* 0.5 in MeOH)]. δ_H (200 MHz; $CDCl_3$) 4.67 (1 H, d, $J_{1,2ax}$ 2.8, H1), 3.59 (1 H, dq, $J_{5,4}$ 9.1 and $J_{5,6}$ 6.0, H5), 3.31 (3 H, s, OMe), 2.91–3.07 (1 H, m, H3), 2.88 (1 H, dd, $J_{4,3} = J_{4,5}$ 9.1, H4), 2.72 (3 H, app s, OH and NH_2), 1.94–2.02 (1 H, m, $H2_{eq}$), 1.58 (1 H, ddd, $J_{2ax,1}$ 2.8 and $J_{2ax,2eq} = J_{2ax,3}$ 12.5, $H2_{ax}$), 1.26 (3 H, d, $J_{6,5}$ 6.0, H6). The ^1H NMR data were in agreement with the literature.[10]

Methyl 3-dimethylamino-2,3,6-trideoxy-α-L-arabino-hexopyranoside (Methyl α-L-angolosaminide) L-(12)[15]

From azido sugar L-(11a). To a solution of methyl pyranoside L-(11a) (1.08 g, 4.72 mmol) in methanol (100 mL) was added formaldehyde (36% aqueous solution, 6.50 mL, 86.7 mmol) and 10% palladium on charcoal (0.9 g). The vessel was evacuated using a water aspirator and hydrogen was introduced from a balloon. The reaction mixture was allowed to stir overnight under an atmosphere of hydrogen. Workup as described above followed by purification of the residue by flash column chromatography (dichloromethane/methanol, 4 : 1) gave *methyl 3-dimethylamino-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(12)* (396 mg, 44%) as a pale-yellow syrup, $[\alpha]_D^{22}$ −86.1° (*c* 1.2 in MeOH) (lit.[15] $[\alpha]_D^{22}$ +87.0° (*c* 1.8 in MeOH) for D-isomer). ν_{max} (film)/cm^{-1} 3461. δ_H (200 MHz; $CDCl_3$) 4.80 (1 H, d, $J_{1,2ax}$ 3.1, H1), 3.85 (1 H, s, OH), 3.64 (1 H, dq, $J_{5,4}$ 9.8 and $J_{5,6}$ 6.1, H5), 3.32 (3 H, s, OMe), 3.12 (1 H, dd, $J_{4,3} = J_{4,5}$ 9.8, H4), 2.91 (1 H, ddd, $J_{3,2eq}$ 3.6, $J_{3,2ax}$ 12.5 and $J_{3,4}$ 9.8, H3), 2.29 (6 H, s, NMe_2), 1.85 (1 H, dd, $J_{2eq,3}$ 3.6 and $J_{2eq,2ax}$ 12.5, $H2_{eq}$), 1.58 (1 H, ddd, $J_{2ax,1}$ 3.5 and $J_{2ax,2eq} = J_{2ax,3}$ 12.5, $H2_{ax}$), 1.30 (3 H, d, $J_{6,5}$ 6.1, H6). The ^1H NMR data were in agreement with the literature.[15]

From acosaminide L-(19). To a solution of methyl pyranoside L-(19) (199 mg, 1.23 mmol) in methanol (30 mL) was added formaldehyde (36% aqueous solution, 1.50 mL, 20.0 mol) and 10% palladium on charcoal (285 mg). The reaction mixture was allowed to stir overnight under an atmosphere of hydrogen. Workup as described above followed by purification of the residue by flash column chromatography (dichloromethane/methanol, 4 : 1) gave *methyl 3-dimethylamino-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(12)* (185 mg, 79%) as a pale syrup, which was identical to the material prepared above.

6-(3′-Dimethylamino-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene (8)

To a stirred solution of methyl α-L-angolosaminide L-(12) (53 mg, 0.280 mmol) and naphthol (13)[7] (48 mg, 0.24 mmol) in dry acetonitrile at 0°C under an atmosphere of nitrogen was added dropwise boron trifluoride diethyl etherate (178 μL, 1.40 mmol). The mixture was stirred for 2 h then quenched with saturated sodium hydrogen carbonate solution (3 mL), diluted with ethyl acetate (5 mL), stirred an additional 10 min and then extracted with ethyl acetate (3 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous sodium sulphate, and concentrated under vacuum. Purification by flash column chromatography (dichloromethane/methanol, 4 : 1) gave *6-(3′-dimethylamino-2′,3′,6′-trideoxy-β-L-arabino- hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene (8)* (44 mg, 52%) as a pale foam, $[\alpha]_D^{22}$ −35.2° (*c* 0.9 in CH_2Cl_2) (Found: $[M+H]^{+\bullet}$, 362.1978. $C_{20}H_{28}NO_5$ requires $[M+H]^{+\bullet}$, 362.1967). ν_{max} (film)/cm^{-1} 3355, 2937, 1614, 1517, 1454, 1391, 1251, 1097. δ_H (400 MHz; $CDCl_3$) 9.76 (1 H, s, ArOH), 7.73 (1 H, d, $J_{7,8}$ 8.7, H7), 7.59 (1 H, d, $J_{8,7}$ 8.7, H8), 6.66 (1 H, d, $J_{2,3}$ 8.4, H2), 6.60 (1 H, d, $J_{3,2}$ 8.4, H3), 5.02 (1 H, dd, $J_{1',2'ax}$ 10.8 and $J_{1',2'eq}$ 1.8, H1′), 3.99 (3 H, s, OMe), 3.96 (3 H, s, OMe), 3.54–3.58 (1 H, m, H5′), 3.45 (1 H, br s, OH), 3.25 (1 H, dd, $J_{4',5'} = J_{4',3'}$ 9.6, H4′), 2.81–2.88 (1 H, m, H3′), 2.38 (6 H, s, NMe_2), 2.17 (1 H, br d, $J_{2'eq,2'ax}$ 12.5, $H2'_{eq}$), 1.49 (1 H, ddd, $J_{2'ax,1'} = J_{2'ax,3'}$ 10.8 and $J_{2'ax,2'eq}$ 12.5, $H2'_{ax}$), 1.44 (3 H, d, $J_{6',5'}$ 6.1, H6′). δ_C (100 MHz; $CDCl_3$) 151.0, 150.8, 150.4, 128.2, 125.3, 124.6, 115.9, 113.8, 104.5, 103.6, 78.1, 73.3, 72.3, 68.4, 57.1, 56.4, 40.9, 28.9, 19.4. Mass spectrum (CI) *m*/*z* 362 (100%, $[M+H]^{+\bullet}$), 311 (17), 132 (49).

6-(4′-O-Acetyl-3′-azido-2′,3′,6′-trideoxy-β-D-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene D-(22)

A solution of methyl 4-*O*-acetyl-3-azido-2,3,6-trideoxy-α-D-arabino-hexopyranoside D-(11) (1.36 g, 5.93 mmol) and naphthol (13)[7] (1.00 g, 4.90 mmol) was stirred in dry acetonitrile (30 mL) at 0°C under an atmosphere of nitrogen. Boron trifluoride diethyl etherate (1.3 mL, 10.2 mmol) was added dropwise. The mixture was stirred for 2 h then quenched with water (10 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic phases were washed with water (50 mL), dried over anhydrous sodium sulphate, and concentrated under vacuum. Purification by flash column chromatography (hexanes/ethyl acetate, 4 : 1) gave *6-(4′-O-acetyl-3′-azido-2′,3′,6′-trideoxy-β-D-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene D-(22)* (1.19 g, 60%) as a pale foam, $[\alpha]_D^{22}$+70.0° (*c* 0.6 in CH_2Cl_2) (Found: C, 59.6; H, 5.7; N, 10.6%. $C_{20}H_{23}N_3O_6$ requires C, 59.8; H, 5.8; N, 10.5%). ν_{max} (film)/cm^{-1} 3356, 2936, 2096, 1744, 1614, 1518, 1390, 1251, 1055. δ_H (400 MHz; $CDCl_3$) 9.79 (1 H, s, OH), 7.74 (1 H, d, $J_{7,8}$ 8.7, H7), 7.56 (1 H, d, $J_{8,7}$ 8.7, H8), 6.69 (1 H, d, $J_{2,3}$ 8.4, H2), 6.63 (1 H, d, $J_{3,2}$ 8.4, H3), 5.06 (1 H, dd, $J_{1',2'ax}$ 11.3 and $J_{1',2'eq}$ 1.9, H1′), 4.80 (1 H, dd, $J_{4',3'} = J_{4',5'}$ 9.5, H4′), 4.02 (3 H, s, OMe), 3.93 (3 H, s, OMe), 3.62–3.78 (2 H, m, H3′ and H5′), 2.46 (1 H, ddd, $J_{2'eq,1'}$ 1.9, $J_{2'eq,2'ax}$ 13.1 and $J_{2'eq,3'}$ 4.9, $H2'_{eq}$), 2.16 (3 H, s, OAc), 1.71 (1 H, ddd, $J_{2'ax,1'} = J_{2'ax,3'}$ 11.3 and $J_{2'ax,2'eq}$ 13.1, $H2'_{ax}$), 1.29 (3 H, d, $J_{6',5'}$ 6.2, H6′). δ_H (100 MHz; $CDCl_3$) 170.3, 150.3, 150.1, 149.9, 127.7, 124.4, 122.5, 115.1, 113.3, 103.8, 103.0, 75.6, 74.8, 71.9, 61.7, 56.5, 55.8, 36.9, 21.0, 18.0. Mass spectrum (EI) *m*/*z* 401 (55%, $M^{+\bullet}$), 256 (15), 255 (11), 241 (23), 230 (52), 218 (34), 215 (26), 43 (100).

6-(4′-O-Acetyl-3′-azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene L-(22)

The above experiment was repeated in the L-enantiomeric series by reacting glycosyl donor L-(11) (136 mg, 0.592 mmol) with naphthol (13) (100 mg, 0.490 mmol) and boron trifluoride diethyl etherate (125 μL, 0.99 mmol) in acetonitrile (3 mL) to afford, after work up and chromatography, L-(22) (130 mg, 66%) as a colourless foam, $[\alpha]_D^{22}$ −74.4° (*c* 0.48 in CH_2Cl_2). This material was spectroscopically identical to D-(22) prepared above.

6-(3′-Azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-3-bromo-5-hydroxy-1,4-dimethoxynaphthalene (7)

A mixture of 3-bromo-5-hydroxy-1,4-dimethoxynaphthalene (14)[13] (63 mg, 0.22 mmol) and methyl 2,3,6-trideoxy-3-azido-α-L-arabino-hexopyranoside L-(10) (45 mg, 0.24 mmol) was evacuated on a high vacuum line for 3–4 h. Dry distilled acetonitrile (1 mL) was added by cannula and the solution was cooled to 0°C. Distilled boron trifluoride diethyl etherate (54 μL, 0.44 mmol) was added dropwise with

a dry microsyringe. An initial red coloration was observed which turned to brown within five minutes. After stirring at this temperature for 15 min no further change was observed by TLC and the reaction mixture was poured into water (1 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure to give the crude product as a brown oil. Purification by flash chromatography using hexane/ethyl acetate (4 : 1) as eluent afforded *6-(3′-azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-3-bromo-5-hydroxy-1,4-dimethoxynaphthalene (7)* (ca. 5 mg, 5%) as a colourless oil (Found: $M^{+\bullet}$, 439.0559 and 437.0581. $C_{18}H_{20}BrN_3O_5$ requires $M^{+\bullet}$, 439.0566 and 437.0586). ν_{max} (film)/cm^{-1} 3251, 2092, 1392, 1248. δ_H (200 MHz; $CDCl_3$) 9.73 (1 H, s, OH), 7.72 (1 H, d, $J_{7,8}$ 8.8, H7), 7.58 (1 H, d, $J_{8,7}$ 8.8, H8), 6.83 (1 H, s, H2), 5.08 (1 H, dd, $J_{1',2'ax}$ 9.3 and $J_{1',2'eq}$ 1.9, H1′), 4.00 (3 H, s, OMe), 3.95 (3 H, s, OMe), 3.52–3.62 (2 H, m, H4′ and H5′), 3.25 (1 H, m, H3′), 2.48 (1 H, m, $H2'_{eq}$), 1.57–1.75 (1 H, m, $H2'_{ax}$), 1.42 (3 H, d, $J_{6',5'}$ 6.1, H6′).

6-(3′-Azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-2-bromo-5-hydroxy-1,4-dimethoxynaphthalene (21)

Using the procedure described above for *C*-glycoside (22), 2-bromo-5-hydroxy-1,4-dimethoxynaphthalene (20)[13] (43 mg, 0.15 mmol) and methyl 3-azido-2,3,6-trideoxy-α-L-arabino-hexopyranoside L-(10) (35 mg, 0.19 mmol) were reacted with boron trifluoride diethyl etherate (38 μL, 0.30 mmol) in acetonitrile (1 mL) to give the *6-(3′-azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-2-bromo-5-hydroxy-1,4-dimethoxynaphthalene (21)* (22 mg, 34%) as a pale-yellow oil (Found: $M^{+\bullet}$, 439.0553 and 437.0579. $C_{18}H_{20}BrN_3O_5$ requires $M^{+\bullet}$, 439.0566 and 437.0586). ν_{max} (film)/cm^{-1} 3245, 2095, 1395, 1246. δ_H (200 MHz; $CDCl_3$) 9.51 (1 H, s, OH), 7.64 (1 H, d, $J_{7,8}$ 8.8, H7), 7.58 (1 H, d, $J_{8,7}$ 8.8, H8), 6.86 (1 H, s, H3), 5.02 (1 H, dd, $J_{1',2'ax}$ 11.1 and $J_{1',2'eq}$ 1.9, H1′), 4.05 (3 H, s, OMe), 3.90 (3 H, s, OMe), 3.25–3.72 (3 H, m, H3′, H4′ and H5′), 2.41 (1 H, m, $H2'_{eq}$), 1.57–1.75 (1 H, m, $H2'_{ax}$), 1.41 (3 H, d, $J_{6',5'}$ 6.2, H6′).

6-(3′-Azido-2′,3′,6′-trideoxy-β-L-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene (6)

Using the procedure described above for *C*-glycoside (22), 5-hydroxy-1,4-dimethoxynaphthalene (13)[7] (30 mg, 0.15 mmol) and methyl 3-azido-2,3,6-trideoxy-β-L-arabino-hexopyranoside L-(10) (33 mg, 0.18 mmol) were reacted with boron trifluoride diethyl etherate (38 μL, 0.30 mmol) in acetonitrile (1 mL) to give *6-(3′-azido-2′,3′,6′-trideoxy-α-L-arabino-hexopyranosyl)-5-hydroxy-1,4-dimethoxynaphthalene (6)* (22 mg, 42%) as a colourless gum (Found: $M^{+\bullet}$, 359.1476. $C_{18}H_{21}N_3O_5$ requires $M^{+\bullet}$, 359.1481). ν_{max} (film)/cm^{-1} 3363, 2097, 1390, 1249. δ_H (400 MHz; $CDCl_3$) 9.79 (1 H, s, OH), 7.73 (1 H, d, $J_{7,8}$ 8.7, H7), 7.56 (1 H, d, $J_{8,7}$ 8.7, H8), 6.62 (1 H, d, $J_{2,3}$ 8.4, H3), 6.68 (1 H, d, $J_{2,3}$ 8.4, H2), 5.05 (1 H, dd, $J_{1',2'ax}$ 11.2 and $J_{1',2'eq}$ 2.0, H1′), 4.02 (3 H, s, OMe), 3.93 (3 H, s, OMe), 3.54–3.58 (2 H, m, H4′ and H5′), 3.26 (1H, m, H3′), 2.44 (1 H, m, $H2'_{eq}$), 2.30 (1 H, br s, 4′-OH), 1.63–1.72 (1 H, m, $H2'_{ax}$), 1.42 (3 H, d, $J_{6',5'}$ 6.0, H6′). δ_C (100 MHz; $CDCl_3$) 150.3, 150.1, 149.9, 127.6, 124.5, 122.9, 115.2, 113.2, 103.8, 103.0, 76.4, 76.0, 71.8, 64.6, 56.4, 55.8, 36.6, 18.3.

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