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Stereospecific synthesis of branched-chain sugars by a novel aldol-type cyclocondensation*

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ABSTRACT

A procedure for the preparation of branched-chain sugars having highly functionalised *C*-branches is reported. Reaction of furanos-3-uloses, pyranos-3-uloses, or pyranos-2-uloses with sodium cyanide followed by mesylation of the corresponding cyanohydrin afforded α-mesyloxynitriles which, on treatment with base, underwent aldol-type cyclocondensation to yield furanose-3-spiro-, pyranose-3-spiro-, and pyranose-2-spiro-5′-(4′-amino-1′,2′-oxathiole-2′,2′-dioxide) derivatives. Treatment of the furanose-3-spiro derivatives with methanolic sodium methoxide gave *C*-[(*E*)-1-amino-2-(methoxysulfonyl)vinyl] branched-chain sugars having the same configuration as the starting cyanohydrins.

INTRODUCTION

Sulfonate groups of carbohydrates[1] are good leaving groups which can participate in elimination[2,3] and nucleophilic substitution reactions[4]. However, their utility in S_N2 reactions at sp^3 carbon atoms of sterically crowded substrates is limited[5]. It is difficult to promote the displacement of some secondary sulfonates in the absence of anchimeric assistance[6]. Potentially useful synthons for the preparation of branched-chain sugars[7] are α-mesyloxynitriles (cyanomesylates) which can be easily obtained by reaction of uloses with sodium cyanide followed by mesylation. These sulfonates have been used for the synthesis of rubranitrose, evernitrose, vancosamine, and other components of branched-chain sugar antibiotics[7]. The mesyl group behaves as a good leaving group in intramolecular S_N2 reactions.

We now report a simple method for the stereospecific synthesis of branched-chain sugars having a highly functionalised *C*-branch. In a preliminary account[8], we reported the unexpected behaviour of tertiary cyanomesylates which, under basic conditions, underwent intramolecular aldol-type cyclocondensations to afford *C*-branched spiro derivatives. This new reaction is now reported in detail and extended to other sugar derivatives.

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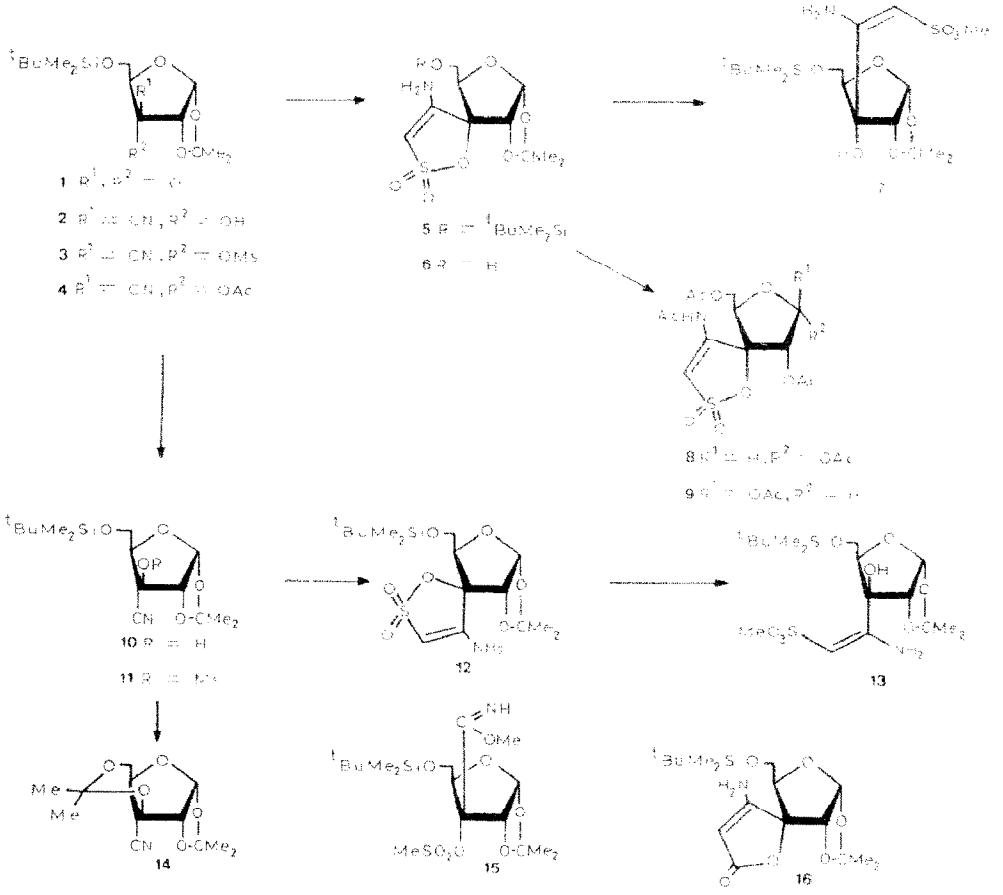
RESULTS AND DISCUSSION

Reaction of 5-*O*-(*tert*-butyldimethylsilyl)-1,2-*O*-isopropylidene-α-D-*erythro*-pentofuranosid-3-ulose[9] (**1**) with sodium cyanide and sodium hydrogencarbonate in ether–water (2:1) at room temperature afforded the cyanohydrin **2** (94%). Compound **2** was epimerised to the thermodynamically more stable cyanohydrin **10** (89%) by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile.



The absolute configuration at C-3 of the epimeric cyanohydrins **2** and **10** was determined as follows. Removal of the 5-*O*-*tert*-butyldimethylsilyl group of **10** with methanolic 0.1M hydrogen chloride followed by reaction of the resulting 3,5-diol with acetone, *p*-toluenesulfonic acid, and triethyl orthoformate, gave the 3,5-*O*-isopropylidene derivative **14** (61%). Similar treatment of **2** did not afford any isopropylidene derivative. The *trans* relationship of HO-3 and $HOCH_2$-5 in the kinetic product **2** accords with the approach of the cyanide ion from the sterically less-hindered β-face of the ulose **1**, opposite to the 1,2-*O*-isopropylidene group.

Reaction of **2** and **10** with mesyl chloride in pyridine gave the respective α-mesyloxynitriles **3** (80%) and **11** (71%), treatment of which with DBU afforded the spiro derivatives **5** (76%) and **12** (71%), respectively. The formation of **5** and **12** can be explained by abstraction of a proton from the mesylate group, followed by nucleophilic attack of the resulting carbanion at the nitrile carbon atom. The imine formed initially undergoes base-catalysed tautomerism to the enamine. The unusual intramolecular aldol-type cyclocondensations **3** → **5** and **11** → **12** can also be effected with other base/solvent systems such as sodium hydroxide in acetonitrile and sodium hydride in dimethoxyethane. The use of a more nucleophilic base, such as sodium methoxide in methanol, afforded the α-mesyloxyiminoether **15** (61%) by nucleophilic attack at the CN group, and the formation of **5** was not detected. In these reactions, neither elimination nor substitution of the tertiary 3-*O*-mesyl group was observed. This finding contrasts with those for 3-sulfonates of furanoses[2,3] and pyranoses[10] which afford, by a *trans* elimination, 2,3- and 3,4-unsaturated sugars[2,3,10], as well as nucleophilic substitution products[4,11]. Based on these precedents, the basic treatment of **3** and **11** should result in *trans* elimination of MsO-3 and H-2 and H-4, respectively. However, this MsO-3 is a very poor leaving group and did not behave as expected. This behaviour was also found for a variety of secondary sulfonyloxy groups of carbohydrates[5].

The spirocyclic sulfonate group was relatively stable under acidic conditions. Thus, treatment of **5** with methanolic 0.1M hydrogen chloride removed the silyl group and gave **6** (86%). Acetylation of **6** followed by treatment with aqueous trifluoroacetic acid removed the 1,2-*O*-isopropylidene group to give an α,β-mixture that was characterised as the α- (**8**) and β-tetra-acetate (**9**).

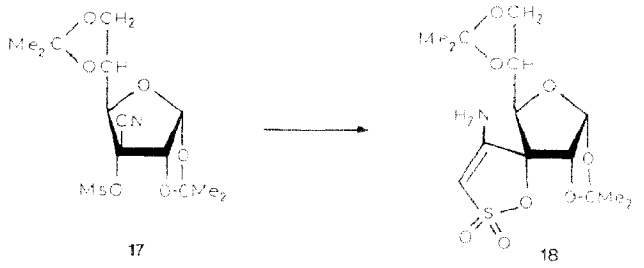
The spiro derivatives **5** and **12** were stable under the basic non-nucleophilic conditions used in their preparation. However, treatment of **5** and **12** with a nucleophilic base, such as methanolic sodium methoxide, afforded the 3-*C*-branched-chain sugars **7** (70%) and **13** (64%), respectively. Thus, the sequences **2** → **7** and **10** → **13** result in the transformation of a cyanide group of a cyanohydrin into a highly functionalised *E*-aminovinylsulfonate derivative with retention of the configuration at the carbon atom α to the cyano group.

The structures of the new compounds were established from their analytical and spectroscopic data. The ^{1}H-n.m.r. spectra of the spiro derivatives **5** and **12** contained no signal for a mesylate group, but there were two new singlets (4.74 and 5.57 p.p.m. for **5**, 4.67 and 5.41 p.p.m. for **12**). The highfield signals disappeared on rapid exchange with D_2O and were assigned to the NH_2 group. The downfield singlets that disappeared on slow exchange with D_2O were assigned to H-3'*. The slow exchange could be due to an imine–enamine tautomeric equilibrium.

The ^{1}H-n.m.r. spectra of the branched-chain derivatives **7** and **13** contained singlets at 3.75 and 3.76 p.p.m., respectively, for a $MeOSO_2$ group, and the ^{13}C-n.m.r. spectra contained corresponding signals at 54.75 and 54.80 p.p.m., respectively. The i.r. spectra and elemental analyses were in agreement with the proposed structures.

* Although the oxathiole ring has priority over the tetrahydrofuran or tetrahydropyran, primes have been used in the numbering of the oxathiole ring in order to keep the same numbering system for the furanose and pyranose rings.

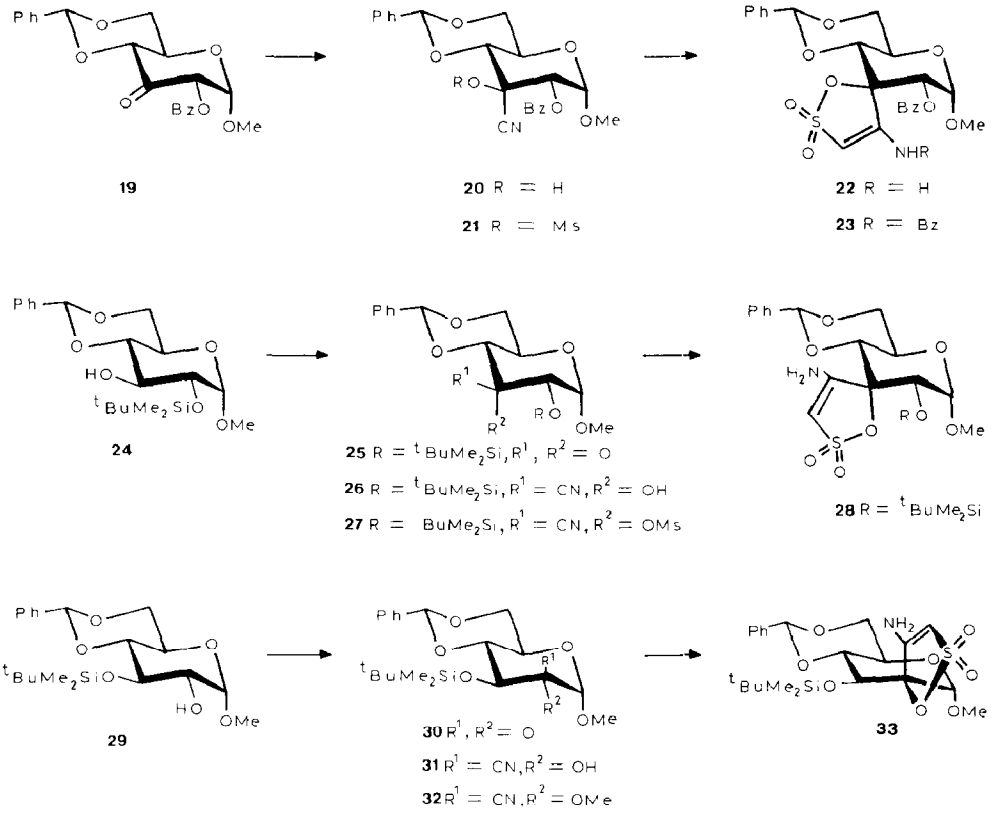
This new reaction was also applied to 3-*C*-cyano-1,2:5,6-di-*O*-isopropylidene-3-*O*-mesyl-α-D-allofuranose[15] (**17**). Treatment of **17** with DBU in acetonitrile effected the aldol-type cyclocondensation reaction to afford the spiro derivative **18** (66%). The ^{1}H-n.m.r. spectrum of **18** contained two new singlets at 6.43 and 5.63 p.p.m. assigned to NH_2 and H-3', respectively.



Finally, the reaction was applied to the α-mesyloxynitriles obtained from hexopyranosid-3- (**19**[13]), and -2-uloses (**25** and **30**). The uloses **25** (77%) and **30** (82%) were obtained by reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with *tert*-butyldimethylsilyl chloride in pyridine followed by oxidation of the products, **24** and **29**, respectively, with CrO_3–pyridine. The cyanomesylate **21** was obtained from **19** under conditions of thermodynamic control. Thus, treatment of **19** with sodium cyanide in tetrahydrofuran–water (2:1) for 5 h at room temperature in the presence of sodium hydrogencarbonate, followed by mesylation of the intermediate cyanohydrin **20**, afforded **21**. The cyanomesylates **27** and **32** were prepared from the uloses **25** and **30**, respectively, by treatment with sodium cyanide in ether–water (2:1) for 24 h at room temperature, followed by mesylation of the respective cyanohydrins **26** and **31**. The cyanohydrins **20**, **26**, and **31** were not isolated, but their absolute configurations were assumed to be the same as those of the corresponding cyanomesylates, as in previous mesylations of cyanohydrins, no epimerisation was observed[8,10,14,15].

Only one of the two possible epimeric cyanomesylates was obtained in each reaction. Since the only difference between **19** and **25** is the 2-substituent, the different stereochemistry of the two cyanomesylates obtained from them, **21** (*gluco*) and **27** (*allo*), respectively, could be due to the steric (silyl group) and/or neighboring (benzoyl) group participating effects, which may oppose and favour, respectively, the formation of the thermodynamic (*gluco*) product.

According to related additions of hydrogen cyanide to methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-uloses, the compound with the equatorial (**27**) and axial CN (**21**) should be[16,17] the products of kinetic and thermodynamic control, respectively. However, under similar conditions of thermodynamic control, methyl 2,6-dideoxy-4-*O*-methyl-α-D-*threo*-hexopyranosid-3-ulose afforded the corresponding D-*xylo*-cyanohydrin (cyanomesylate) in which the CN group is equatorial[18].



Treatment of the cyanomesylates **27** and **32** with DBU in acetonitrile afforded spiro derivatives **28** (77%) and **33** (73%), respectively. Similar treatment of the benzoate **21** gave a mixture of the spiro derivative **22** (12%) and its *N*-benzoyl derivative **3** (20%). Partial deprotection of the base-sensitive benzoyl group and O → N migration may explain the formation of **23** and the low yield of this reaction.

Assignment of the absolute configurations at the C-3 position of cyanomesylates and spiropyranosyl derivatives was based on the n.m.r. data. The coupled ^{13}C-n.m.r. spectra of the cyanomesylates **21** and **27** contained signals at 111 and 114 p.p.m., respectively, for CN. The coupling constant $J_{CN,H-2}$ and $J_{CN,H-4}$ values of 7 Hz for **21** indicate[19,20] CN to be *trans*-diaxial to H-2 and H-4. On the other hand, the low values (~0 Hz) of $J_{CN,H-2}$ and $J_{CN,H-4}$ for **27** suggested CN to be *gauche* to H-2 and H-4, and, thus, equatorial. The coupled ^{13}C-n.m.r. spectrum of **32** contained a signal (dd) centered at 114 p.p.m. for CN. The $J_{CN,H-1}$ and $J_{CN,H-3}$ values (1 and 7 Hz, respectively) indicate CN to be axial. These assignments were confirmed by n.O.e. experiments carried out on the corresponding spiro derivatives **22**, **23**, **28**, and **33**. Irradiation of the NH_2 group of **22** caused n.O.e. of the signal for H-3′ and of the multiplet that included signals for H-4 and H-5. It was assumed that the n.O.e. involved only the signal for H-5, since there was no effect on the signal for H-2 which is located on the same face of the molecule as H-4.

Irradiation of the NH_2 group of **28** induced n.O.e. of the signals for H-3′, H-2, and H-4. These results indicated that the NH protons of **22** and **23** are below the plane of the pyranose ring, whereas the NH_2 group of **28** is above the plane. Finally, irradiation of the NH_2 group of the spiro derivative **33** showed n.O.e. of the signals for H-3′, H-1, and H-6*ax*, and of a multiplet that included signals for H-4, H-3, and H-6*eq*. This last effect probably involved H-4 because n.O.e. was also observed for the signal for H-1, which is an indication that H-1, H-4, and NH_2 are on the same side of the molecule.

In an extension of this work, we decided to study whether formation of spiro derivatives would be applicable to other ester derivatives of the cyanohydrins having acidic protons α to the carbonyl group, for example, α-acetoxynitriles such as **4**. Thus, acetylation of cyanohydrin **2** with acetic anhydride–pyridine gave acetate **4** (84%), treatment of which with DBU–acetonitrile did not afford the spirolactone **16**, but gave cyanohydrin **10**, the epimer of **2**. This result can be explained by deacetylation of **4** to give **2**, followed by epimerisation under the basic reaction conditions to the thermodynamically more stable cyanohydrin **10**. The lack of an aldol-type reaction of **4** may be due to the lower basicity of the acetate methyl protons (pK_a 25) compared to that of the mesylate methyl protons (pK_a 23).

EXPERIMENTAL

General. — Solvents were dried and purified by standard methods. T.l.c. was performed on Silica Gel 60 F_{254} (Merck). Silica Gel 60 (230–400 mesh) (Merck) was used for flash-column chromatography. Melting points were obtained with a Reichert–Jung Kofler micro hot-stage apparatus and are uncorrected. Microanalyses were obtained with a Heareus CHN-O-RAPID instrument. Optical rotations were determined with a Perkin–Elmer 141 polarimeter. I.r. spectra were obtained using a Shimadzu IR-435 spectrometer. The ^1H- and ^{13}C-n.m.r. spectra (internal Me_4Si) were obtained variously with Varian EM-390 and XL-300, and Bruker AM-200 and WP-80-SY spectrometers. Proximities were established conventionally on the basis of n.O.e. effects.

Synthesis of the cyanomesylates **3**, **11**, **21**, **27**, *and* **32**. — A mixture of the ulose (**1**, **19**, **25**, or **30**; 1 mmol), water (10 mL), ether (20 mL), sodium hydrogencarbonate (2 mmol), and sodium cyanide (1 mmol) was stirred vigorously at room temperature for 3–15 h. The organic phase was separated, the aqueous phase was washed with ether (2 × 50 mL), the combined ethereal phases were dried (Na_2SO_4) and filtered, and the solvent was evaporated. To a solution of the residue (cyanohydrin **2**, **10**, **20**, **26**, or **31**) in dry pyridine (4 mL) was added mesyl chloride (3 mmol). The mixture was stirred at 8–10° for 1–2 days, poured into ice and water, and extracted with chloroform (2 × 50 mL). The combined extracts were washed with M HCl (50 mL), aqueous sodium hydrogencarbonate (50 mL), and brine (50 mL), dried (Na_2SO_4), and filtered, and the solvent was evaporated. The residue was purified by flash-column chromatography or by crystallisation.

Synthesis of 2(3)-spiro-(4′-amino-1′,2′-oxathiole-2′,2′-dioxide) derivatives **5**, **12**, **18**, **22**, **23**, **28**, *and* **33**. — To a solution of the cyanomesylate (**3**, **11**, **21**, **27**, or **32**, 1 mmol)

in dry acetonitrile (10 mL) was added DBU (1 mmol). The mixture was stirred at room temperature for 3–48 h, then filtered, and the solvent was evaporated. The residue was purified by flash-column chromatography or by crystallisation.

5-O-(tert-butyldimethylsilyl)-3-C-cyano-1,2-O-isopropylidene-3-O-mesyl-α-D-ribofuranose (**3**). — Prepared from **1**[9], **3** (60%) had m.p. 94–95° (from hexane, $[\alpha]_D$ +39° (*c* 0.5, chloroform); ν_{max}^{Nujol} 1370, 1170 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^1H, δ 0.80 (s, 9 H, ^tBu), 1.30, 1.47 (2 s, 6 H, CMe_2), 3.10 (s, 3 H, Ms), 3.88 (m, 2 H, H-5,5), 4.15 (m, 1 H, H-4), 4.97 (d, 1 H, $J_{1,2}$ 4 Hz, H-2), 5.83 (d, 1 H, H-1); ^{13}C, δ 18.24 (CSi), 25.76 [$(CH_3)_3CSi$], 40.44 (CH_3SO_2), 61.72 (C-5), 79.73 (C-3,4), 82.07 (C-2), 104.07 (C-1), 114.11 (CN).

Anal. Calc. for $C_{16}H_{29}NO_7SSi$: C, 47.15; H, 7.17; N, 3.43. Found: C, 46.97; H, 7.20; N, 3.60.

3-O-Acetyl-5-O-(tert-butyldimethylsilyl)-3-C-cyano-1,2-O-isopropylidene-α-D-ribofuranose (**4**). — To a solution of **2** (0.32 g, 1 mmol) in dry pyridine (8 mL) was added slowly acetic anhydride (0.3 mL, 3 mmol). The mixture was stirred at room temperature for 2 h, then poured into ice and water (50 mL). The solid was collected and crystallised from hexane to give **4** (0.31 g, 84%), m.p. 95–96°, $[\alpha]_D$ +68° (*c* 0.5, chloroform); ν_{max}^{Nujol} 1755 cm^{-1} (OAc). ^1H-N.m.r. data ($CDCl_3$): δ 0.90 (s, 9 H, ^tBu), 1.33, 1.50 (2 s, 6 H, Me_2C), 2.11 (s, 3 H, OAc), 4.03 (m, 2 H, H-5,5), 4.26 (m, 1 H, H-4), 5.26 (d, 1 H, H-2), 5.95 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1).

Anal. Calc. for $C_{17}H_{29}NO_6Si$: C, 54.96; H, 7.87; N, 3.77. Found: C, 54.82; H, 8.00; N, 3.97.

[5-O-(tert-Butyldimethylsilyl)-1,2-O-isopropylidene-α-D-ribofuranose]-3-spiro-5'-(4'-amino-1',2'-oxathiole-2',2'-dioxide) (**5**). — Obtained from **3** (reaction for 5 h), with crystallisation from $CHCl_3$–hexane (1:1), **5** (76%) had m.p. 197–198°, $[\alpha]_D$ +10° (*c* 0.5, chloroform); ν_{max}^{KBr} 3435, 3200 (NH_2), 1650 (C=C–N), 1340, 1160 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^1H, δ 0.87 (s, 9 H, ^tBu), 1.36, 1.61 (2 s, 6 H, Me_2C), 3.95 (m, 2 H, H-5,5), 4.34 (m, 1 H, H-4), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.74 (bs, 2 H, NH_2), 5.57 (s, 1 H, H-3'), 5.89 (d, 1 H, H-1); ^{13}C, δ 18.29 (CSi), 25.77 [$(CH_3)_3CSi$], 59.69 (C-5), 79.16, 81.60 (C-4,3'), 88.14 (C-3), 91.19 (C-2), 103.72 (C-1), 153.53 (C-4').

Anal. Calc. for $C_{16}H_{29}NO_7SSi$: C, 47.15; H, 7.17; N, 3.43. Found: C, 46.98; H, 7.04; N, 3.64.

(1,2-O-Isopropylidene-α-D-ribofuranose)-3-spiro-5'-(4'-amino-1',2'-oxathiole-2',2'-dioxide) (**6**). — Compound **5** (0.4 g, 1 mmol) was stirred with methanolic 0.1M HCl (15 mL) at room temperature for 40 min. The solution was neutralised with 0.1M NaOH–MeOH and the solvent was evaporated. Flash-column chromatography (ethyl acetate) of the residue gave amorphous **6** (0.25 g, 86%), $[\alpha]_D$ +47° (*c* 0.5, methyl sulfoxide), ν_{max}^{Nujol} 3430 (OH), 3400, 3200 (NH_2), 1650 cm^{-1} (C=C–N). N.m.r. data ($CDCl_3$): ^1H, δ 0.87 (s, 9 H, ^tBu), 1.36, 1.61 (2 s, 6 H, Me_2C), 3.95 (m, 2 H, H-5,5), 4.34 (m, 1 H, H-4), 4.62 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.74 (bs, 2 H, NH_2), 5.57 (s, 1 H, H-3'), 5.89 (d, 1 H, H-1); ^{13}C, δ 18.29 (CSi), 25.77 [$(CH_3)_3CSi$], 59.69 (C-5), 79.19, 81.60 (C-4,3'), 88.14 (C-3), 91.19 (C-2), 103.72 (C-1), 153.53 (C-4').

Anal. Calc. for $C_{10}H_{15}NO_7S$: C, 40.95; H, 5.15; N, 4.77. Found: C, 41.12; H, 5.31; N, 5.00.

*3-C-[(E)-1-Amino-2-(methoxysulfonyl)vinyl]-5-O-*tert*-butyldimethylsilyl-1,2-O-isopropylidene-α-D-ribofuranose* (**7**). — Sodium (0.05 g, 2 mmol) was reacted with dry methanol (10 mL), then **5** (0.8 g, 2 mmol) was added. The solution was stirred at room temperature for 30 min, then neutralised with M HCl–MeOH, and the solvent was evaporated. Flash-column chromatography (hexane–ethyl acetate, 3:1) of the residue gave **7** (0.61 g, 70%), m.p. 67–68°, $[\alpha]_D$ −5° (*c* 0.5, chloroform); ν_{max}^{KBr} 3460, 3345 (NH_2), 1615 (C=C–N), 1340, 1150 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^{1}H, δ 0.86 (s, 9 H, ^{t}Bu), 1.36, 1.60 (2 s, 6 H, Me_2C), 3.70–4.10 (m, 3 H, H-4,5,5), 3.75 (s, 3 H, Ms), 4.45 (d, 1 H, $J_{1,2}$ 4 Hz, H-2), 4.72 (s, 1 H, H-2'), 5.97 (d, 1 H, H-1), 6.28 (bs, 2 H, NH_2); ^{13}C, δ 18.23 (CSi), 25.84 [(CH_3)$_3$CSi], 54.75 (SO_2CH_3), 61.22 (C-5), 79.24 (C-3), 80.82, 83.07, 84.14 (C-2,4,2'), 104.78 (C-1), 158.41 (C-3').

Anal. Calc. for $C_{15}H_{33}NO_8SSi$: C, 46.45; H, 7.56; N, 3.18. Found: C, 46.48; H, 7.63; N, 3.21.

(1,2,5-Tri-O-acetyl-α- and -β-D-ribofuranose)-3-spiro-5'-(4'-acetamido-1',2'-oxathiole-2',2'-dioxide) (**8** *and* **9**). — To a solution of **6** (0.44 g, 1.5 mmol) in pyridine (12 mL) was added slowly acetic anhydride (0.3 mL, 3 mmol). The mixture was stirred at room temperature for 2 h, the solvent was evaporated, and the residue was stirred with 10 mL of trifluoroacetic acid–water (9:1) at room temperature for 3 h. The solvent was evaporated, and the residue was stirred with acetic anhydride (5 mL) and pyridine (15 mL) for 12 h at room temperature. The solvents were evaporated and flash-column chromatography (ethyl acetate–hexane, 1:2) of the residue gave, first, **8** (0.2 g, 32%), isolated as a syrup, $[\alpha]_D$ +25° (*c* 0.5, chloroform); ν_{max}^{film} 3200 (NH_2), 1755 (C=O ester), 1700 (C=O amide), 1640 cm^{-1} (C=C–N). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.10, 2.15, 2.20, 2.23 (4 s, 12 H, 3 OAc and NHAc), 4.35 (m, 2 H, H-5,5), 4.76 (m, 1 H, H-4), 5.55 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-2), 6.53 (d, 1 H, H-1), 7.45 (s, 1 H, H-3'), 8.30 (bs, 1 H, NH).

Anal. Calc. for $C_{15}H_{19}NO_{11}S$: C, 42.75; H, 4.54; N, 3.32. Found: C, 42.61; H, 4.57; N, 3.23.

Eluted second was **9** (0.13 g, 21%), isolated as a syrup, $[\alpha]_D$ +41° (*c* 0.5, chloroform); ν_{max}^{film} 3200 (NH), 1750 (C=O ester), 1700 (C=O amide), 1640 cm^{-1} (C=C–N). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.00, 2.10, 2.20, 2.26 (4 s, 12 H, 3 OAc and NHAc), 4.26 (m, 2 H, H-5,5), 4.56 (m, 1 H, H-4), 5.55 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 6.20 (d, 1 H, H-1), 7.40 (s, 1 H, H-3'), 8.40 (bs, 1 H, NH).

Anal. Calc. for $C_{15}H_{19}NO_{11}S$: C, 42.75; H, 4.54; N, 3.32. Found: C, 42.72; H, 4.39; N, 3.10.

*5-O-(*tert*-butyldimethylsilyl)-3-C-cyano-1,2-O-isopropylidene-3-O-mesyl-α-D-xylofuranose* (**11**). — Epimerisation of the cyanohydrin **2** (0.49 g, 1.5 mmol) on treatment with DBU (0.2 mL, 1.5 mmol) in acetonitrile (15 mL) afforded the cyanohydrin **10**, which was converted into **11**. Chromatography (hexane–ethyl acetate, 5:1) gave **11** as a syryp (71%), $[\alpha]_D$ +7° (*c* 0.5, chloroform); ν_{max}^{film} 1370, 1185 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^{1}H, δ 0.79 (s, 9 H, ^{t}Bu), 1.21, 1.46 (2 s, 6 H, Me_2C), 3.11 (s, 3 H, Ms), 3.80 (m, 2 H, H-5,5), 4.39 (m, 1 H, H-4), 5.02 (d, 1 H, $J_{1,2}$ 4 Hz, H-2), 5.86 (d, 1 H, H-1); ^{13}C, δ 18.09

(CSi), 25.62 [$(CH_3)_3CSi$], 40.01 (CH_3SO_2), 58.78 (C-5), 81.14 (C-3), 82.28 (C-4), 83.71 (C-2), 104.73 (C-1), 112.40 (CN).

Anal. Calc. for $C_{16}H_{29}NO_7SSi$: C, 47.15; H, 7.17; N, 3.43. Found: C, 47.36; H, 7.27; N, 3.45.

[5-O-(tert-Butyldimethylsilyl)-1,2-O-isopropylidene-α-D-xylofuranose]-3-spiro-5'-(4'-amino-1',2'-oxathiole-2',2'-dioxide) (**12**). — Obtained from **11** (reaction for 4 h), with crystallisation from $CHCl_3$–hexane, **12** (71%) had m.p. 199–200°, $[\alpha]_D$ +2° (*c* 0.5, chloroform); ν_{max}^{KBr} 3475, 3380 (NH_2), 1640 (C=C–N), 1375, 1155 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^1H, δ 0.77 (s, 9 H, ^{t}Bu), 1.24, 1.49 (2 s, 6 H, Me_2C), 3.80 (d, 2 H, $J_{4,5}$ 7 Hz, H-5,5), 4.34 (t, 1 H, H-4), 4.59 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.67 (bs, 2 H, NH_2), 5.41 (s, 1 H, H-3'), 5.87 (d, 1 H, H-1); ^{13}C, δ 18.02 (CSi), 25.66 [$(CH_3)_3CSi$], 59.85 (C-5), 77.03, 81.39, 85.24 (C-2,4,3'), 85.24 (C-3), 104.87 (C-1), 151.90 (C-4').

Anal. Calc. for $C_{16}H_{29}NO_7SSi$: C, 47.15; H, 7.17; N, 3.43. Found: C, 47.30; H, 6.98; N, 3.50.

3-C-[(E)-1-Amino-2-(methoxysulfonyl)vinyl]-5-O-(tert-butyldimethylsilyl)-1,2-O-isopropylidene-α-D-xylofuranose (**13**). — Sodium (0.05 g, 2 mmol) was reacted with dry methanol (10 mL), then **12** (0.8 g, 2 mmol) was added. The solution was stirred at room temperature for 30 min, then neutralised with M HCl–MeOH, and the solvent was evaporated. Chromatography (hexane–ethyl acetate, 4:1) of the residue gave **13** (0.56 g, 64%), isolated as a syrup, $[\alpha]_D$ +77° (*c* 0.5, chloroform); ν_{max}^{film} 3480, 3360 (NH_2), 1615 (C=C–N), 1335, 1145 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^1H, δ 0.89 (s, 9 H, ^{t}Bu), 1.33, 1.54 (2 s, 6 H, Me_2C), 4.10 (m, 3 H, H-4,5,5), 4.34 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.97 (s, 1 H, H-2'), 6.00 (d, 1 H, H-1), 6.13 (s, 1 H, HO-3), 6.33 (bs, 2 H, NH_2); ^{13}C, δ 17.88 (CSi), 25.44 [$(CH_3)_3CSi$], 54.80 (SO_2CH_3), 65.45 (C-5), 78.36, 82.68, 85.86 (C-2,4,2'), 82.01 (C-3), 105.33 (C-1), 157.22 (C-3').

Anal. Calc. for $C_{17}H_{33}NO_8SSi$: C, 46.45; H, 7.56; N, 3.18. Found: C, 46.47; H, 7.65, N, 3.26.

3-C-Cyano-1,2:3,5-di-O-isopropylidene-α-D-xylofuranose (**14**). — A solution of the cyanohydrin **10** (2.0 g, 6 mmol) in 0.1M HCl–MeOH (40 mL) was stirred at room temperature for 20 min, then neutralised with M NaOH–MeOH. The solvent was evaporated, the residue was suspended in dry acetone (40 mL), and 4 Å molecular sieves (3 g), *p*-toluenesulfonic acid (0.3 g, 6 mmol), and triethyl orthoformate (3 mL, 18 mmol) were added. The mixture was stirred at room temperature for 18 h, then neutralised with saturated aqueous $NaHCO_3$, and filtered, and the solvent was evaporated. Chromatography (hexane–ethyl acetate, 4:1) of the residue gave **14** (0.68 g, 45%), m.p. 94–95° (from hexane), $[\alpha]_D$ +53° (*c* 0.5, chloroform); ν_{max}^{KBr} 2210 cm^{-1} (CN). ^1H-N.m.r. data ($CDCl_3$), δ 1.37, 1.42, 1.54, 1.66 (4 s, 12 H, Me_2C), 4.19 (m, 3 H, H-4,5,5), 4.54 (d, 1 H, $J_{1,2}$ 4 Hz, H-2), 6.02 (d, 1 H, H-1).

Anal. Calc. for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.60; H, 6.53; N, 5.50.

5-O-(tert-butyldimethylsilyl)-1,2-O-isopropylidene-3-O-mesyl-3-C-methoxyiminomethyl-α-D-ribofuranose (**15**). — Sodium (0.02 g, 1 mmol) was reacted with dry methanol (6 mL), then **3** (0.4 g, 1 mmol) was added. The resulting solution was stirred at

room temperature for 1 h, then neutralised with M HCl–MeOH, and the solvent was evaporated. Chromatography (hexane–ethyl acetate, 4:1) of the residue gave **15** (0.23 g, 54%), isolated as a syrup, $[\alpha]_D$ +50° (*c* 0.5, chloroform); ν_{max}^{film} 3320 (NH), 1665 (C=N), 1365, 1170 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^{1}H, δ 0.80 (s, 9 H, ^{t}Bu), 1.30, 1.50 (2 s, 6 H, Me_2C), 3.15 (s, 3 H, Ms), 3.57 (m, 2 H, H-5,5), 3.71 (s, 3 H, OMe), 4.19 (t, 1 H, $J_{4,5}$ 6 Hz, H-4), 5.09 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 5.82 (d, 1 H, H-1), 8.12 (bs, 1 H, NH); ^{13}C, δ 18.17 (CSi), 25.80 [$(CH_3)_3CSi$], 40.64 (CH_3SO_2), 53.82 (OCH_3), 61.81 (C-5), 80.91, 80.92 (C-2,4), 90.04 (C-3), 105.68 (C-1), 165.05 (C=NH).

Anal. Calc. for $C_{17}H_{33}NO_8SSi$: C, 46.44; H, 7.56; N, 3.18. Found: C, 46.21; H, 7.59; N, 3.15.

(1,2:5,6-Di-O-isopropylidene-α-D-allofuranose)-3-spiro-5'-(4'-amino-1',2'-oxathiole-2',2'-dioxide) (**18**). — Prepared from **17**[22] (reaction for 7 h), with chromatography (hexane–ethyl acetate, 1:2), **18** (66%) had m.p. 197° (dec.) (from chloroform), $[\alpha]_D$ +18 (*c* 0.5, methyl sulfoxide); ν_{max}^{KBr} 3420, 3330 (NH_2), 1650 (C=C–N), 1375, 1160 cm^{-1} (SO_2). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.23, 1.33, 1.36, 1.53 (4 s, 12 H, Me_2C), 3.90 (m, 2 H, H-6,6), 4.23 (m, 2 H, H-4,5), 4.66 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 5.63 (s, 1 H, H-3'), 6.06 (d, 1 H, H-1), 6.43 (bs, 2 H, NH_2).

Anal. Calc. for $C_{14}H_{21}NO_8S$: C, 46.27; H, 5.82; N, 3.85. Found: C, 45.98; H, 5.71; N, 3.95.

Methyl 2-O-benzoyl-4,6-O-benzylidene-α-D-ribo-hexopyranosid-3-ulose (**19**). — Dichloromethane (15 mL) and dry pyridine (1.5 mL, 18.6 mmol) were added over CrO_3 (1.86 g, 18.6 mmol), the resulting mixture was stirred at room temperature for 10 min, and then acetic anhydride (1.76 mL, 18.6 mmol) and a solution of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[21] (1.2 g, 3.1 mmol) in dichloromethane (7 mL) were added. The mixture was stirred at room temperature for 15 min, poured into ethyl acetate (100 mL), and filtered through a wet (ethyl acetate) short column of silica gel (30 g), using ethyl acetate as the eluent to give **19** (1.18 g, 89%) as a white solid, m.p. 209–211° (lit.[21] m.p. 210–212°); ν_{max}^{KBr} 1770 (C=O), 1737 cm^{-1} (C=O benzoyl).

Methyl 2-O-benzoyl-4,6-O-benzylidene-3-C-cyano-3-O-mesyl-α-D-glucopyranoside (**21**). — Prepared from the ulose **19**, with chromatography (ethyl acetate–hexane, 1:4), **21** (38%) had m.p. 165–167° (from ethyl acetate–hexane), $[\alpha]_D$ +82.5° (*c* 1, chloroform); ν_{max}^{KBr} 1735 (C=O), 1375, 1185 cm^{-1} (SO_2). N.m.r. data: ^{1}H [$(CD_3)_2CO$], δ 3.23 (s, 3 H, Ms), 3.46 (s, 3 H, OMe), 4.00 (t, 1 H, $J_{6ax,6eq} \approx J_{6ax} \approx$ 10 Hz, H-6*ax*), 4.14–4.26 (m, 1 H, H-5), 4.47 (dd, 1 H, $J_{5,6eq}$ 4.81 Hz, H-6*eq*), 4.52 (d, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.27 (d, 1 H, $J_{1,2}$ 3.95 Hz, H-2), 5.56 (d, 1 H, H-1), 5.88 (s, 1 H, *H*CPh), 7.37–8.20 (m, 10 H, 2 Ph); ^{13}C ($CDCl_3$), δ 40.07 (CH_3SO_2), 56.17 (OCH_3), 61.07 (C-5), 68.42 (C-6), 72.65 (C-2), 79.01 (C-3), 79.32 (C-4), 97.38 (C-1), 102.17 (HCPh), 111.57 (CN, $J_{CN,H-2} = J_{CN,H-4} \approx$ 7 Hz), 126.29, 128.39, 128.61, 129.53, 130.39, 133.96, 136.09 (C_6H_5), 165.02 (PhCO).

Anal. Calc. for $C_{23}H_{23}NO_9S$: C, 56.43; H, 4.73; N, 2.86; S, 6.55. Found: C, 56.47; H, 4.57; N, 2.58; S, 6.78.

(Methyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside)-3-spiro-5'-(4'-amino-1',2'-oxathiole-2',2'-dioxide) (**22**) *and (methyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside)-3-spiro-5'-(4'-benzamido-1',2'-oxathiole-2',2'-dioxide)* (**23**). — Pre-

pared from **21** (reaction for 48 h), with chromatography (hexane–ethyl acetate, 3:1), amorphous **23** (20%) had $[\alpha]_D$ +28° (*c* 1, acetone); ν_{max}^{KBr} 3250 (NH), 1735 (C=O ester), 1700 (C=O amide), 1640 cm^{-1} (C=C–N). N.m.r. data [$(CD_3)_2CO$]: ^1H, δ 3.57 (s, 3 H, OMe), 3.83 (t, 1 H, $J_{6ax,6eq} \simeq J_{5,6ax} \simeq 9.3$ Hz, H-6*ax*), 4.21–4.09 (m, 1 H, H-5), 4.33 (d, 1 H, $J_{4,5}$ 10.3 Hz, H-4), 4.33 (dd, 1 H, $J_{5,6eq}$ 4.9 Hz, H-6*eq*), 5.40 (d, 1 H, H-2), 5.64 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 5.70 (s, 1 H, *H*CPh), 7.15–7.86 (m, 15 H, 3 Ph), 7.72 (s, 1 H, H-3′), 10.47 (bs, 1 H, NH); ^{13}C, δ 57.75 (OCH_3), 62.22 (C-5), 69.44 (C-6), 72.09 (C-2), 80.40 (C-4), 91.45 (C-3), 98.10 (C-1), 102.09 (*C*HPh), 109.40 (C-3′), 141.39 (C=*C*NHBz), 165.36, 167.19 (2 C=O).

Anal. Calc. for $C_{30}H_{27}NO_{10}S$: C, 60.70; H, 4.58; N, 2.36; S, 5.40. Found: C, 60.68; H, 4.50; N, 2.43; S, 5.24.

Eluted second was amorphous **22** (12%), $[\alpha]_D$ +42° (*c* 1, acetone); ν_{max}^{KBr} 3400, 3320 (NH_2), 1730 (C=O ester), 1650 cm^{-1} (C=C–N). N.m.r. data [$(CD_3)_2CO$]: ^1H, δ 3.57 (s, 3 H, OMe), 3.90 (m, 1 H, H-6*ax*), 4.25 (m, 2 H, H-4,5), 4.44 (m, 1 H, H-6*eq*), 5.35 (d, 1 H, $J_{1,2}$ 4.6 Hz, H-2), 5.52 (d, 1 H, H-1), 5.75 (s, 1 H, H-3′), 5.78 (s, 1 H, C*H*Ph), 6.43 (bs, 2 H, NH_2), 7.32–8.06 (m, 10 H, 2 Ph); ^{13}C, δ 56.37 (OCH_3), 61.59 (C-5), 69.42 (C-6), 72.68 (C-2), 80.70 (C-4), 90.40 (C-3), 93.84 (C-3′), 97.88 (C-1), 101.83 (H*C*Ph), 152.74 (C-4′), 165.74 (C=O).

Anal. Calc. for $C_{23}H_{23}NO_9S$: C, 56.43; H, 4.73; N, 2.86; S, 6.55. Found: C, 56.60; H, 4.80; N, 2.90; S, 6.65.

Methyl 4,6-O-benzylidene-2- and -3-O-(tert-*butyldimethylsilyl*)*-α-*D*-glucopyranoside* (**24** *and* **29**). — A mixture of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (Aldrich, 3 g, 10.6 mmol), pyridine (20 mL), and *tert*-butyldimethylsilyl chloride (2.26 g, 15 mmol) was stirred at room temperature for 3 days, then concentrated. A solution of the residue in chloroform was washed with cold M HCl (50 mL), water (2 x 50 mL), and finally with brine (50 mL), dried (Na_2SO_4), filtered, and concentrated. Flash-column chromatography (hexane–ethyl acetate, 8:1) of the residue afforded, first, **24** (2.30 g, 58%), m.p. 82–83° (from ethyl acetate–hexane), $[\alpha]_D$ +50° (*c* 1, methanol). ^1H-N.m.r. data ($CDCl_3$), δ 0.94 (s, 9 H, ^{t}Bu), 3.44 (s, 3 H, OMe), 3.44–4.36 (m, 6 H, H-2,3,4,5,6,6), 4.65 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.54 (s, 1 H, *H*CPh), 7.29–7.62 (m, 5 H, Ph).

Anal. Calc. for $C_{20}H_{32}O_6Si$: C, 60.58; H, 8.13. Found: C, 60.39; H, 8.33.

Eluted second was **29**, isolated as a syrup (1.02 g, 26%), $[\alpha]_D$ +65° (*c* 1, methanol). ^1H-N.m.r. data ($CDCl_3$), δ 0.90 (s, 9 H, ^{t}Bu), 3.45 (s, 3 H, OMe), 4.80 (s, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.53 (s, 1 H, C*H*Ph), 7.30–7.65 (m, 5 H, Ph).

Anal. Calc. for $C_{20}H_{32}O_6Si$: C, 60.58; H, 8.13. Found: C, 60.43; H, 8.40.

*Methyl 4,6-O-benzylidene-2-*O-(tert-*butyldimethylsilyl*)*-α-*D*-ribo-*hexopyranosid-3-ulose* (**25**). — Compound **24** (0.8 g, 2.02 mmol) was oxidised as described for the synthesis of ulose **19**, to give, after work-up, syrupy **25** (0.61 g, 77%); ν_{max}^{film} 1750 cm^{-1} (C–O); which was used in the next step without purification.

*Methyl 4,6-O-benzylidene-2-*O-(tert-*butyldimethylsilyl*)*-3-*C*-cyano-3-*O*-mesyl-α-*D*-allopyranoside* (**27**). — Prepared from **25**, with chromatography (ethyl acetate–hexane, 1:6), **27** (42%) was isolated as a syrup, $[\alpha]_D$ +25° (*c* 1, chloroform); ν_{max}^{KBr} 1375, 1185 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^1H, δ 0.90 (s, 9 H, ^{t}Bu), 3.11 (s, 3 H, Ms), 3.36 (s, 3

H, Me), 3.66 (t, 1 H, $J_{6ax,6eq} \approx J_{5,6ax} \approx 10.2$ Hz, H-6*ax*), 3.77 (d, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 3.99 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-2), 4.10 (m, 1 H, H-5), 4.29 (dd, 1 H, $J_{5,6eq}$ 5.1 Hz, H-6*eq*), 4.62 (d, 1 H, H-1), 5.55 (s, 1 H, *H*CPh), 7.26–7.47 (m, 5 H, Ph); ^{13}C, δ 18.10 (CSi), 25.23 [$(CH_3)_3C$], 40.12 (CH_3SO_2), 56.28 (OCH_3), 58.02 (C-5), 68.54, 72.99 (C-2,6), 79.37 (C-4), 99.71 (C-1), 102.06 (HCPh), 114.80 (CN), 126.22, 128.25, 129.29, 136.17 (C_6H_5).

Anal. Calc. for $C_{22}H_{33}NO_8SSi$: C, 52.88; H, 6.66; N, 2.80; S, 6.42. Found: C, 53.20; H, 6.91; N, 3.10; S, 6.65.

[Methyl 4,6-O-benzylidene-2-O-(tert-*butyldimethylsilyl*)*-*α*-*D*-allopyranoside]-3-spiro-5′-(4′-amino-1′,2′-oxathiole-2′,2′-dioxide)* (**28**). — Prepared from **27** (reaction for 48 h) and chromatography (hexane–acetone, 2:1), **28** (77%) had m.p. 240° (dec.), $[\alpha]_D$ +57° (*c* 1, methyl sulfoxide); ν_{max}^{KBr} 3400, 3360 (NH_2), 1660 (C=C–N), 1305, 1165 cm^{-1} (SO_2). N.m.r. data [$(CD_3)_2SO$]: ^{1}H, δ 0.85 (s, 9 H, ^{t}Bu), 3.34 (s, 3 H, OMe), 3.69 (t, 1 H, $J_{6ax,6eq} \approx J_{5,6ax} \approx 9.8$ Hz, H-6*ax*), 3.91 (m, 1 H, H-5), 3.98 (d, 1 H, $J_{3,4}$ 9.3 Hz, H-4), 4.22 (d, 1 H, H-2), 4.29 (dd, 1 H, $J_{5,6eq}$ 4.5 Hz, H-6*eq*), 4.75 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 5.46 (s, 1 H, H-3′), 5.57 (s, 1 H, *H*CPh), 6.72 (bs, 2 H, NH_2), 7.32–7.47 (m, 5 H, Ph); ^{13}C, δ 17.56 (CSi), 25.20 [$(CH_3)_3CSi$], 55.13 (OCH_3), 58.60 (C-5), 68.06 (C-2,6), 74.90 (C-4), 88.55 (C-3,3′), 99.32 (C-1), 100.39 (HCPh), 126.21, 127.64, 128.60, 137.12 (C_6H_5), 158.34 (C-4′).

Anal. Calc. for $C_{22}H_{33}NO_8SSi$: C, 52.88; H, 6.66; N, 2.80; S, 6.42. Found: C, 52.54; H, 6.17; N, 2.45; S, 6.29.

Methyl 4,6-O-benzylidene-3-O-(tert-*butyldimethylsilyl*)*-*α*-*D*-*arabino*-hexopyranosid-2-ulose* (**30**). — Compound **29** (1.3 g, 3.28 mmol) was oxidised, as described for the synthesis of ulose **19**, to give syrupy **30** (1.06 g, 82%); ν_{max}^{film} 1750 cm^{-1} (C=O); which was used immediately in the next step without purification.

Methyl 4,6-O-benzylidene-3-O-(tert-*butyldimethylsilyl*)*-2-C-cyano-2-O-mesyl-*α*-*D*-glucopyranoside* (**32**). — Prepared from **30**, with chromatography (hexane–acetone, 8:1), **32** (86%) had m.p. 134–136° (from ether), $[\alpha]_D$ +13° (*c* 1, chloroform); ν_{max}^{KBr} 1375, 1180 cm^{-1} (SO_2). N.m.r. data ($CDCl_3$): ^{1}H, δ 0.87 (s, 9 H, ^{t}Bu), 3.23 (s, 3 H, Ms), 3.52 (s, 3 H, OMe), 3.72–3.85 (m, 2 H, H-4,6*ax*), 3.90 (m, 1 H, $J_{4,5} \approx J_{5,6ax} \approx 9.0$, $J_{5,6eq}$ 4 Hz, H-5), 4.24 (d, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 4.29 (dd, 1 H, $J_{6ax,6eq}$ 9.5 Hz, H-6*eq*), 5.46, 5.55 (2 s, 2 H, H-1, *H*CPh), 7.34–7.47 (m, 5 H, Ph); ^{13}C, δ 18.06 (CSi), 25.54 [$(CH_3)_3C$], 40.13 (CH_3SO_2), 56.41 (OCH_3), 62.43 (C-5), 68.36 (C-6), 71.67 (C-3), 80.27 (C-4), 81.41 (C-2), 98.97, 102.24 (C-1 and HCPh), 114.15 (CN, $J_{C,H}$ 1, $J_{C,H}$ 7 Hz), 126.02, 126.19, 128.15, 129.21, 136.64 (C_6H_5).

Anal. Calc. for $C_{22}H_{33}NO_8SSi$: C, 52.88; H, 6.66; N, 2.80; S, 6.42. Found: C, 52.70; H, 6.52; N, 3.10; S, 6.62.

[Methyl 4,6-O-benzylidene-3-O-(tert-*butyldimethylsilyl*)*-*α*-*D*-glucopyranoside]-2-spiro-5′-(4′-amino-1′,2′-oxathiole-2′,2′-dioxide)* (**33**). — Prepared from **32** (reaction for 3 h), with chromatography (hexane–ethyl acetate, 1:1), **33** (73%) had m.p. 182–184° (dec.), $[\alpha]_D$ +46° (*c* 1, acetone); ν_{max}^{KBr} 3450, 3360 (NH_2), 1645 (C=C–N), 1315, 1150 cm^{-1} (SO_2). N.m.r. data [$(CD_3)_2CO$]: ^{1}H, δ 0.81 (s, 9 H, ^{t}Bu), 3.50 (s, 3 H, OMe), 3.97–4.10 (m, 2 H, H-5,6*ax*), 4.20–4.33 (m, 3 H, H-3,4,6*eq*), 4.89 (s, 1 H, H-1), 5.61 (s, 1 H, H-3′), 5.85 (s, 1 H, *H*CPh), 5.65 (bs, 2 H, NH_2), 7.34–7.60 (m, 5 H, Ph); ^{13}C, δ 18.87 (CSi), 26.34 [$(CH_3)_3C$], 56.43 (OCH_3), 63.15 (C-5), 68.67 (C-6), 72.94 (C-3), 80.66 (C-4), 89.64 (C-2), 91.87 (C-3′), 101.93, 102.98 (C-1 and HCPh), 155.38 (C-4′).

Anal. Calc. for $C_{22}H_{33}NO_8SSi$: C, 52.88; H, 6.66; N, 2.80; S, 6.42. Found: C, 52.62; H, 6.33; N, 2.83; S, 6.50.

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