Unsaturated Carbohydrates. Part 31.[1] Trichothecene-related and Other Branched *C*-Pyranoside Compounds

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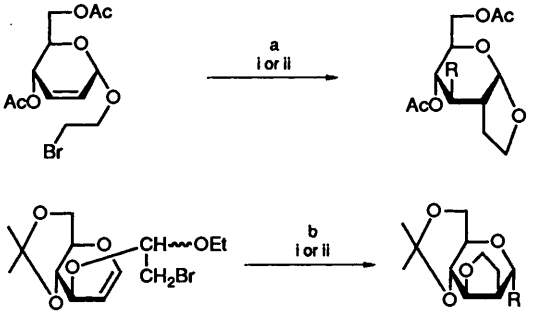
The *C*-glycosidic alkene **21**, on treatment with tributyltin hydride and a radical initiator, underwent intramolecular radical cyclisation to give the 2-oxabicyclo[3.2.1]octane derivative **23** which is structurally related to the sesquiterpenoid trichothecenes. The unsaturated acetals **27** and **29**, formed using methods encountered in the first part of the work, permitted branch-point substituents to be introduced regio- and stereo-specifically at C-3 and at C-4 (carbohydrate numbering) of compounds of this type. Methods are thus available for the synthesis of pyranoid derivatives bearing several *C*-substituents.

Our interest in the synthetic merits of highly selective and efficient free radical reactions of some carbohydrate derivatives was attracted by bromine-radical-substitution processes which were first observed in this laboratory and which have since been studied at some length.[2] Concurrently, our experience with sugar derivatives containing unsaturated functionality[3] drew our attention to the opportunities offered by the application of free radical, carbon–carbon bond-forming addition reactions to such compounds for the elaboration of complex structures of the type found in many natural products and related biologically active compounds. The highly sophisticated work of Fraser-Reid's group illustrates well the power of the methods applied in the carbohydrate field.[4]

Free radical reactions throughout organic chemistry now provide very important methods for carbon–carbon bond formation.[5] In particular, intramolecular reactions have been of value and, in carbohydrate chemistry, cyclisation of radicals on *O*-substituent groups onto double bonds within sugar structures ($S^{\bullet}$–$C^{C=C}$ processes)[6] allow, in effect, stereospecific introduction of branch-points.[6,7] Alternatively, radicals derived at sugar carbon centres may be trapped by alkene or alkyne bonds within *O*-substituents ($C^{\bullet}$–$S^{C=C}$) to give additional cyclic systems,[8] carbohydrate carbon radicals may react intramolecularly with alkene groups within the same carbon chain or extended carbon chain to give carbocycles ($C^{\bullet}$–$C^{C=C}$),[9] and *O*-substituent radicals, on reaction with multiple bonds on other *O*-substituents, afford 'extra-carbohydrate' ring systems ($S^{\bullet}$–$S^{C=C}$).[4]

In addition to simple radical cyclisation processes of the above type, dramatic synthetic progress has been made by causing the radicals formed by initial cyclisations onto multiple bonds to react consecutively either intermolecularly or intramolecularly with further multiple bonds thereby, respectively, increasing the size of the carbon framework (serial cyclisations),[10] or increasing, by one, the number of rings formed in the process (tandem cyclisations).[5] We have reported examples of the serial type of reaction[6,11] (*e.g.*, Scheme 1a), and Lopez and Fraser-Reid have carried out related studies involving cyclisation of glycal derivatives[12] (Scheme 1b). Fraser-Reid and colleagues have also described very sophisticated tandem reactions of branched carbohydrate derivatives.[4]

In the present work we set out to investigate synthetic routes to the 2-oxabicyclo[3.2.1]octane system of the trichothecene group of fungal, sesquiterpenoid mycotoxins[13] (*e.g.* **1**) using radical-cyclisation procedures, and we here report initial findings and the development of a stereospecific route to 3,4-dibranched hexopyranoid *C*-glycosides which emerged in an extension of the work. Previously, starting from the *C*-glycosidic derivative **2**, Tsang and Fraser-Reid[14] have elaborated compounds with the trichothecene framework from carbohydrate precursors by stepwise heterolytic processes, while Fetizon *et al.*[15] carried out a photochemical cycloaddition of ethyne to a carbohydrate-derived 1-en-3-one to obtain the cyclobutene **3**, which they converted into the bicyclo[3.2.1]octane derivative **4** by deacetoxylation, followed in turn by tertiary alcohol formation at the carbonyl centre and formic acid-catalysed rearrangement.

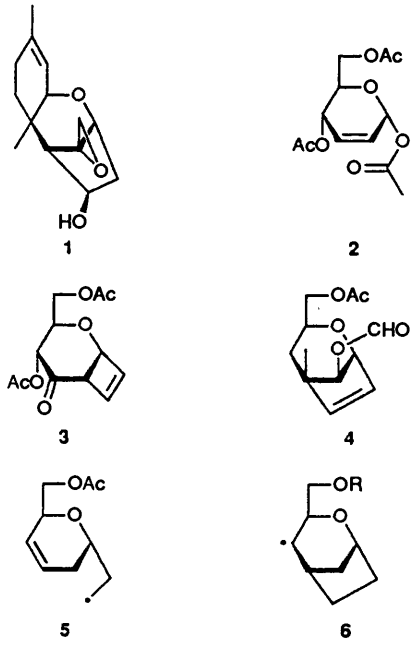


R = CH_2CH_2CN or $CH_2CH=CH_2$ (reagents i or ii, respectively

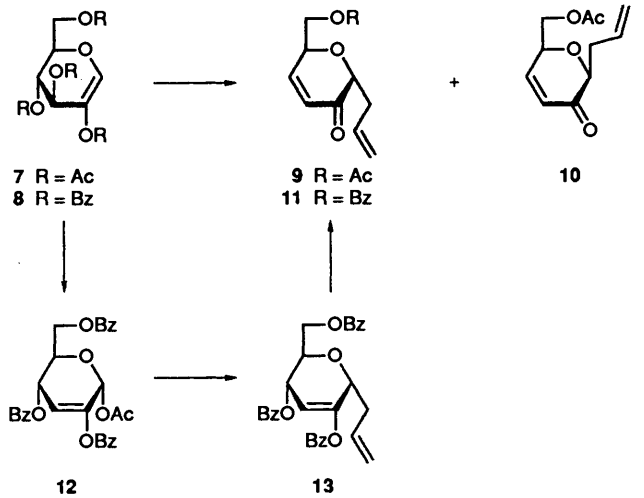
Scheme 1 *Reagents:* i, Bu_3SnH, AIBN, CH_2=CHCN; ii, CH_2=$CHCH_2SnBu_3$, AIBN

The approach to the trichothecene skeleton assessed in the work now reported was based on the generation of hexose-derived radicals with the structural feature **5** and their cyclisation to 2-oxabicyclo[3.2.1]octane radicals **6** which, in principle, could lead to the formation of further fused cyclohexane rings involving C-4–C-6 of the initial hexose either by serial addition, at C-4, of a three-carbon-atom substituent which can be bonded to C-6 or, conceivably, by a tandem cyclisation involving radical addition to unsaturated groups in chain-extensions from C-6. The target **1** made it desirable that the initial species **5** should also have a carbonyl (or masked-carbonyl) group at C-2 (carbohydrate numbering). Formation of bicyclo[3.2.1]octane ring systems by radical cyclisation procedures is uncommon,[5] but not unknown.[16]

To gain access to compounds from which radicals containing feature **5** could be obtained use was made of the following data: (i) allylsilanes, used with Lewis acid catalysts, react with protected glycosyl halides and glycosides to give C-1-allylated products,[17] (ii) with acylated glycals these reagents lead to 2,3-unsaturated allyl *C*-glycosides,[18] and (iii), 2-hydroxyglycal esters with oxygen[19]—and, particularly, carbon[20]—nucleophiles, in the presence of Lewis acids, are converted into

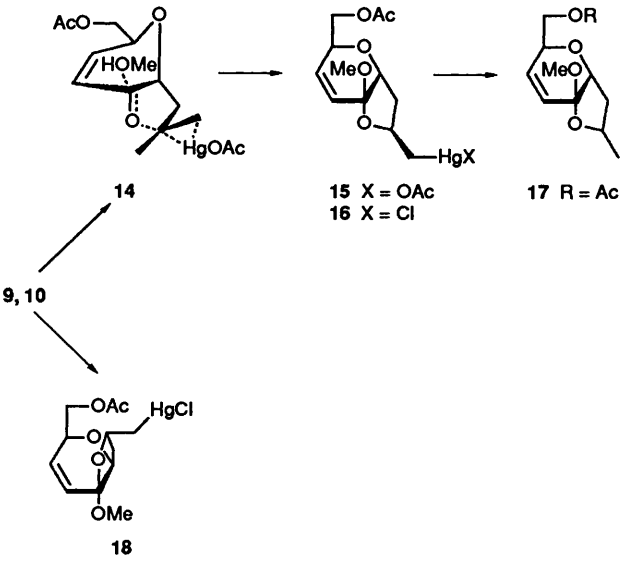


glycosidic enones directly related to radical **5** and having a desirable carbonyl group at C-2. Tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol **7** (tetra-*O*-acetyl-2-hydroxy-D-glucal) was therefore treated in benzene with allyltrimethylsilane and boron trifluoride–diethyl ether as catalyst to give the enone **9** in a 3:1 mixture with its β-anomer **10** (Scheme 2). Best yields (75%) were obtained when the products were isolated prior to completion of the reaction and when unchanged starting material was reprocessed.



Scheme 2

Reaction of compounds **9** and **10** with mercury(II) acetate in methanol occurred selectively at the more electron-rich double bond of the allyl group, but rather than giving the products of direct methoxymercuriation, they afforded mixed compounds (**15** and the precursor of **18**), formed by methanol attack at the carbonyl carbon atoms of enones **9** and **10** and ring closure by bonding of the carbonyl oxygen atoms to the non-terminal carbon atom of mercurinium intermediates. The reactions, consequently, were entirely regiospecific, and are analogous to the well known formation of tetrahydrofuran derivatives from γ-keto epoxides under nucleophilic conditions.[21] Chloride exchange gave a mixture from which the crystalline product **16** (from **9**) was obtained in 47% yield (Scheme 3). It is assigned the illustrated D-*arabino* configuration* on the grounds that strong precedents lead to the expectation that the major enone **9** will have the α-configuration.[17,18,20] In concurrence, compound **16** had $[\alpha]_D$ −129,† whereas the L-*ribo*-isomer **18** (formed from compound **10**) had $[\alpha]_D$ +43, which is consistent with their containing methyl β-D-(or α-L-) and methyl α-D- (or β-L-) furanoside components, respectively.[22] The configurations at C-8 of the 2,6-anhydrononitols (**15** *et seq.*) were assigned on the basis of the expectation that the mercuriomethyl groups would be *exo*-oriented following ring closure by attack of the carbonyl group oxygen atoms at C-8 and by way of transition states (**14** for the α-compound **9**) having C-9 in the *exo*-orientation.

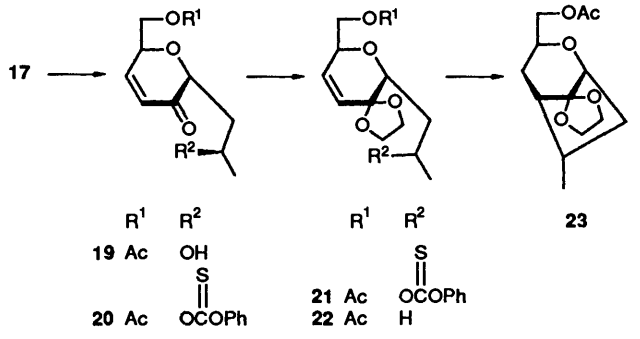


Scheme 3

Reduction of the mercurial **16** with tributyltin hydride gave the acetal **17**, which was converted by mild acid-catalysed hydrolysis into the alcohol **19**, from which the phenoxy(thiocarbonyl)derivative[23] **20** was produced (Scheme 4). Generation of a free radical at C-8 by treatment of this ester with tributyltin hydride and azoisobutanonitrile (AIBN) as radical initiator led largely to deoxygenation[24] at this centre partly, it was assumed, because radicals of the type produced are nucleophilic in character and the polarisation of the C-3 double bond disfavours radical cyclisation to C-4. To overcome this factor the spiro-ketal **21** was made, and on treatment with tributyltin hydride and AIBN it gave, as main product (35% isolated, unoptimised), a compound assigned the 2-oxabicyclo-[3.2.1] structure **23** largely on the basis of its NMR spectra. It contained no double bond or aromatic group, and its ^{13}C DEPT spectrum[25] showed the presence of two methine, two methylene and one methyl carbon atoms without bonded oxygen neighbours. The alternative structure obtainable by bonding of the C-8 radical to C-3 is excluded on steric grounds and because of the normal favouring of 5-*exo*-ring closures relative to 6-*endo*-processes; the configuration at the *C*-methyl-substituted C-6 (bicyclo-octane numbering) was not assigned although the substituent group would be expected to be *exo*-oriented.[5] A by-product of the cyclisation reaction was, as expected, the deoxyderivative **22** formed by hydrogen abstraction by the C-8 radical. It was recognisable by the presence, in its mass spectrum, of a molecular ion with *m/z* 256 (as for the product of cyclisation) but, in addition, [M − $CH_3CH_2CH_2$-

* Compounds **9** *et seq*, are named as 2,6-anhydrononitol derivatives.
† Values for $[\alpha]_D$ are now given in units of 10^{-1} deg cm^2 g^{-1}.

CHO]$^{\cdot+}$ and [M − $CH_3CH_2CH_2CHO$ − $CH_3COO^{\cdot}$]$^+$ ions, formed by retro-Diels–Alder processes, were present. Attempts to use compound **21** in serial and tandem cyclisations aimed at the development of a route to products with complete trichothecene structures will be reported elsewhere.



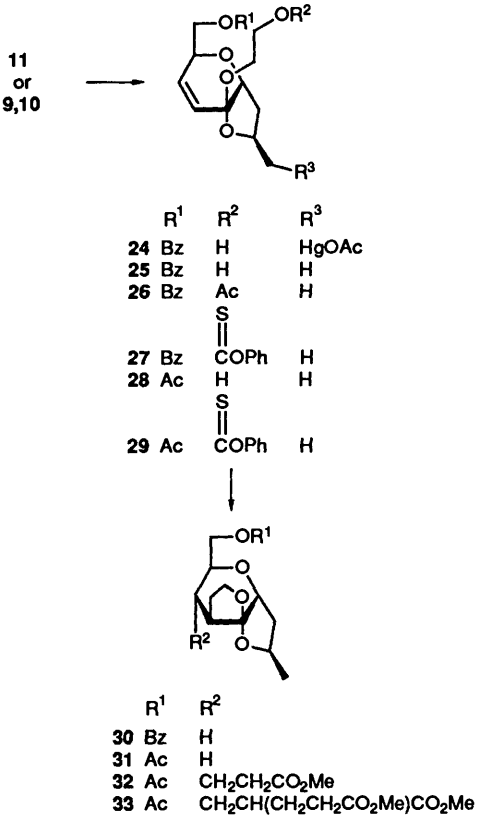
Scheme 4

With a method available to permit the introduction of alkoxy groups at C-5 using enones like compound **9**, opportunity was taken to use a 2-hydroxyethoxy derivative to develop methods for the introduction of branch-points at the double-bond carbon centres of compounds of this series. Initial experiments were conducted with the benzoyl analogue **11** of enone **9**. When the benzoylated alkene **8** was treated with allyltrimethylsilane and boron trifluoride, a complex series of products was formed. However, 1-*O*-acetyl-2,4,6-tri-*O*-benzoyl-3-deoxy-α-D-*erythro*-hex-2-enoside **12**, obtained readily from the glycal **8** by heating it in acetic acid,[26] reacted to give the tribenzoyl *C*-glycoside **13** and its β-anomer in the ratio 3:1. From these mixed products the α-anomer **13** crystallised in 16% yield thereby allowing us the opportunity to work thenceforth with pure substances. The enone **11** was produced by heating of compound **13** in benzene in the presence of boron trifluoride (Scheme 2).

Treatment of the benzoylated enone **11** with mercury(II) acetate in acetonitrile containing ethane-1,2-diol, followed by reduction of the product **24** with tributyltin hydride, afforded the ketal **25** in 63% yield. That this compound had the assigned structure (and was not the possible 2-hydroxypropyl *C*-glycosidic spirodioxolane product of rearrangement) was shown by acetylation of the hydroxy group and by observing that in the NMR spectrum of the acetate **26** the carbon and proton resonances of a *methylene* group were deshielded (δ 62.4 ⟶ 63.8 and δ 3.7 ⟶ 4.2), respectively. The alcohol **25** was converted into the phenoxy(thiocarbonyl) derivative **27** and hence (Scheme 5), in 43% isolated yield, into the tricyclic ketal **30**, the NMR spectra of which indicated that it had undergone addition at the double bond and contained one methyl, three methylene, and one methine carbon atoms which were not bonded to oxygen.

The above ring-closure reaction was repeated with the more accessible epimerically mixed acetates **9** and **10** *via* the alcohols **28** (67% obtained) and the *arabino*-phenyl thiocarbonate **29**, which was chromatographically separated from the *ribo*-isomer and obtained in 50% yield. Radical cyclisation gave the C-3-branched derivative **31** (90%) which was shown by its DEPT ^{13}C NMR spectrum to be a structural analogue of compound **30**. Alternatively, compounds **9** and **10** were converted into the tricycle **31** by way of the bromoethyl analogues of the thiocarbonate **29**.

When the radical cyclisation of compound **29** was carried out in the presence of methyl acrylate, three products (gas chromatographic retention times 19.7, 24.6 and 28.1 min) were formed in the proportions 17:56:27, each being devoid of double bonds and, therefore, having undergone cyclisation. The most mobile was identical with compound **31**, the main product was compound **32**, formed by serial cyclisation and trapping of the C-3 radical by the acrylate, and the least mobile was the diacrylate adduct **33** (mass spectrometric determinations). The new substituents at C-3 of the di-branched products **32** and **33** were assigned the *trans*-orientation with respect to the new ring formed at C-4 on the basis of the stereochemical features of many analogous cyclisation/trapping reactions that have been reported.[10,12,27]



Scheme 5

Experimental

NMR spectra were measured in deuteriochloroform with tetramethylsilane as internal reference by use of a Varian FT80A (^{13}C spectra) or Brucker AC300E (^1H spectra) instrument. *J*-Values are given in Hz. Gas chromatography/mass spectrometry was carried out using a Hewlett Packard HP5995 system fitted with a split injector (20:1), a 12 m Hewlett Packard HP-1 fused silica column (0.2 mm i.d.; 0.33 μ film of cross-linked methyl silicone gum) and an open split interface to the mass spectrometer. Mass spectra were scanned repetitively for 25–650 amu with applied ionising voltage of 70 eV. Accurate masses were determined by use of ammonia chemical ionisation on a VG 70-250S instrument.

Optical rotations were determined for chloroform solutions (0.5–2.0 g/100 cm^3) with a Perkin-Elmer 241 automatic polarimeter.

M.p.s were measured by use of a Reichert Jung Thermovar hot-stage apparatus and are uncorrected. Light petroleum refers to the fraction boiling in the range 60–80 °C.

1-O-*Acetyl*-2,6-*anhydro*-3,4,7,8,9-*pentadeoxy*-D-threo-/-L-erythro-*nona*-3,8-*dien*-5-*ulose* **9**/**10**.—Tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol **7** (2 g) and allyltrimethylsilane (1.4 g, 2 mol equiv.) were stirred at 20 °C in benzene (35 cm^3) under nitrogen with slow addition of boron trifluoride–diethyl

ether (0.8 cm^3) during 3 h. The solution was washed successively with aq. $NaHCO_3$ (×2) and water, and dried ($MgSO_4$). Evaporation of the solvent, followed by radial chromatography, gave the *title compounds* (0.51 g) as a 3 : 1 mixture, and the starting alkene (1.0 g). The latter was treated as above to give a second fraction of the former (total 0.95 g, 75%), $[\alpha]_D$ −70 (Found: *m/z* MNH_4^+, 228.1234. $C_{11}H_{18}NO_4$ requires *m/z*, 228.1236); *m/z* 210 (M^+), 169 ($M - CH_2CH{=}CH_2)^+$, 168 ($M - CH_2{=}CO)^{\bullet+}$, 150 ($M - AcOH)^{\bullet+}$ and 137 ($M - CH_2OAc)^+$; δ_H D-*threo*-epimer **9**: 2.10 (3 H, s, Ac), 2.54 (2 H, m, 7-H_2), 4.21 (1 H, dd, $J_{1,2}$ 4.0, $J_{1,1'}$ 11.8, 1-H), 4.3–4.4 (1 H, m, 6-H), 4.44 (1 H, dd, $J_{1',2}$ 6.5, 1-H′), 4.7 (1 H, m, 2-H), 5.1–5.2 (2 H, m, 9-H_2), 5.8–5.9 (1 H, m, 8-H), 6.17 (1 H, dd, $J_{3,4}$ 10.5, $J_{2,4}$ 2.2, 4-H) and 6.95 (1 H, dd, $J_{2,3}$ 2.7, 3-H); L-*erythro*-epimer **10** (resolvable differences only): δ 6.19 (1 H, dd, $J_{3,4}$ 10.3, $J_{2,4}$ 2.6, 4-H) and 6.95 (1 H, dd, $J_{2,3}$ 1.6, 3-H); δ_C D-*threo*-epimer **9** (L-*erythro*-epimer **10**): 20.8 (20.8) (CO*Me*), 34.0 (33.9) (C-7), 63.7 (64.9) (C-1), 68.7, 77.5 (72.4, 80.2) (C-2,-6), 117.9 (117.5) (C-9), 127.4 (128.3) (C-4), 133.3 (133.7) (C-8), 146.2 (147.0) (C-3), 170.7 (170.7) (*C*OMe) and 195.3 (195.3) (C-5).

Methyl 1-O-*Acetyl*-2,6-*anhydro*-9-*chloromercurio*-3,4,7,9-*tetradeoxy*-D-arabino-*non*-3-*en*-5-*ulo*-5,8-*furanoside* **16**.—The enones **9**/**10** (1.65 g) and mercury(II) acetate (2.6 g, 1 mol equiv.) were stirred in methanol (30 cm^3) for 10 min under nitrogen. The solvent was removed, and the residue was dissolved in dichloromethane (50 cm^3) and shaken successively with saturated aq. sodium chloride followed by water, and the organic solution was dried ($MgSO_4$). Evaporation of the solvent gave a syrup (3.34 g, 89%), from which the title compound crystallised on addition of ethyl acetate and light petroleum. Further material was collected by radial chromatography to give a total crop of 1.75 g (47%). Recrystallisation from the same solvents gave *the* D-arabino-*compound* as needles, m.p. 114–115 °C, $[\alpha]_D$ −129 (Found: C, 30.2; H, 3.6; Cl, 7.1. $C_{12}H_{17}ClHgO_5$ requires C, 30.2; H, 3.6; Cl, 7.4%); δ_H 1.64 (1 H, dd, $J_{7,7'}$ 14.2, $J_{7,8}$ 2.8, $J_{6,7}$ 0, 7-H), 2.10 (3 H, s, OAc), 2.18 (1 H, dd, $J_{8,9}$ 1.9, $J_{9,9'}$ 12.5, $J_{H,Hg}$ 105, 9-H), 2.42 (1 H, dd, $J_{8,9'}$ 4.8, 9-H′), 2.65 (1 H, ddd, $J_{6,7'}$ 5.7, $J_{7',8}$ 8.7, 7-H′), 3.31 (3 H, s, OMe), 4.01 (1 H, dd, $J_{1,2}$ 3.3, $J_{1,1'}$ 12.2, 1-H), 4.18 (1 H, d, 6-H), 4.40 (1 H, dd, $J_{1',2}$ 7.7, 1-H′), 4.7–4.8 (2 H, m, 2- and 8-H), 5.90 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.6, 3-H) and 6.25 (1 H, dd, $J_{2,4}$ 1.9, 4-H); δ_C 21.0 (COMe), 39.6, 41.0 (C-7, -9), 48.6 (OMe), 62.5 (C-1), 71.1, 75.9, 78.4 (C-2, -6, -8), 101.4 (C-5), 123.6, 128.1 (C-3, -4) and 170.8 (*C*OMe).

The L-*ribo*-isomer **18** was isolated by radial chromatography as an oil (0.64 g, 17%), $[\alpha]_D$ +43; δ_H 1.64 (1 H, dd, $J_{7,7'}$ 14.4, $J_{7,8}$ 3.9, $J_{6,7}$ 0, 7-H), 2.11 (3 H, s, OAc), 2.26 (1 H, dd, $J_{8,9}$ 3.2, $J_{9,9'}$ 12.4, 9-H), 2.43 (1 H, dd, $J_{8,9'}$ 4.7, 9-H′) 2.70 (1 H, ddd, $J_{6,7'}$ 6.2, $J_{7',8}$ 8.7, 7-H′), 3.30 (3 H, s, OMe), 3.96 (1 H, d, 6-H), 4.2–4.4, 4.7 (4 H, m, 1-H_2, 2- and 8-H), 5.91 (1 H, dd, $J_{3,4}$ 10.5, $J_{2,3}$ 0.9, 3-H) and 6.22 (1 H, dd, $J_{2,4}$ 1.7, 4-H); δ_C 21.0 (CO*Me*), 40.3, 40.8 (C-7, -9), 48.6 (OMe), 65.5 (C-1), 73.6, 77.1, 81.4 (C-2, -6, -8), 101.9 (C-5), 123.6, 129.8 (C-3, -4) and 170.8 (*C*OMe).

Methyl 1-O-*Acetyl*-2,6-*anhydro*-3,4,7,9-*tetradeoxy*-D-arabino-*non*-3-*en*-5-*ulo*-5,8-*furanoside* **17**.—The chloromercurio compound **16** (2 g) and tributyltin hydride (1.83 g, 1.5 mol equiv.) were stirred in dichloromethane (20 cm^3) under nitrogen at 20 °C for 5 h. Filtration through silica and removal of the solvent gave a syrup, which was dissolved in acetonitrile (100 cm^3) and extracted (×5) with light petroleum. Evaporation of the acetonitrile and purification by radial chromatography gave the *title compound* (0.96 g, 95%), $[\alpha]_D$ −71 (Found: C, 59.6; H, 7.5. $C_{12}H_{18}O_5$ requires C, 59.5; H, 7.5%); δ_H 1.34 (3 H, d, $J_{8,9}$ 6.2, 9-H_3), 1.57 (1 H, ddd, $J_{7,7'}$ 13.6, $J_{7,8}$ 6.0, $J_{6,7}$ 2.1, 7-H), 2.10 (3 H, s, OAc), 2.52 (1 H, ddd, $J_{6,7'}$ 7.6, $J_{7',8}$ 6.5, 7-H′), 3.30 (3 H, s, OMe), 4.04 (1 H, dd, $J_{1,2}$ 2.9, $J_{1,1'}$ 11.6, 1-H), 4.2–4.45 (4 H, m, 1-H′, 2-, 6- and 8-H), 5.91 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.4, 3-H) and 6.24 (1 H, dd, $J_{2,4}$ 1.8, 4-H); δ_C 20.9 (CO*Me*), 22.0 (C-9) 38.4 (C-7), 48.3 (OMe), 62.7 (C-1), 71.2, 74.4, 76.1 (C-2, -6, -8), 100.3 (C-5), 123.9, 128.3 (C-3, -4) and 170.8 (*C*OMe).

1-O-*Acetyl*-2,6-*anhydro*-3,4,7,9-*tetradeoxy*-8-O-*phenoxy*-(*thiocarbonyl*)-D-arabino-*non*-3-*en*-5-*ulose* **20**.—The methyl furanoside **17** (0.275 g) and toluene-*p*-sulfonic acid (PTSA) (0.43 g, 2 mol equiv.) were stirred in a mixture of dichloromethane (5 cm^3) and water (0.5 cm^3) at 20 °C for 3 h. Further dichloromethane (50 cm^3) was added and the solution was washed successively with saturated aq. $NaHCO_3$ and water, and dried ($MgSO_4$). Evaporation of the solvent and separation by radial chromatography gave the alcohol **19** (0.20 g, 78%), $[\alpha]_D$ −90; δ_H 1.25 (3 H, d, $J_{8,9}$ 6.3, 9-H), 1.8–2.0 (2 H, m, 7-H_2), 2.13 (3 H, s, OAc), 2.76 (1 H, d, OH), 3.95 (1 H, m, 8-H), 4.11 (1 H, dd, $J_{1,2}$ 2.8, $J_{1,1'}$ 11.2, 1-H), 4.6–4.75 (3 H, m, 1-H′, 2- and 6-H) 6.20 (1 H, dd, $J_{3,4}$ 10.5, $J_{2,4}$ 1.8, 4-H) and 6.94 (1 H, dd, $J_{2,3}$ 2.9, 3-H); δ_C 20.9 (CO*Me*), 23.5 (C-9), 38.4 (C-7), 62.4 (C-1), 64.1, 70.0, 74.6 (C-2, -6, -8), 127.8 (C-4), 145.5 (C-3), 171.1 (*C*OMe) and 195.9 (C-5).

The alcohol **19** (50 mg), phenyl chlorothiocarbonate (42 mg, 1.1 mol equiv.) and pyridine (70 mg, 3 mol equiv.) were stirred in dichloromethane (3 cm^3) for 16 h. Further dichloromethane (50 cm^3) was added and the solution was washed successively with saturated aq. $NaHCO_3$, dil. hydrochloric acid, and water, and dried ($MgSO_4$). Evaporation of the solvent and chromatographic separation gave the *title ester* (58 mg, 73%), $[\alpha]_D$ −69 (Found: *m/z*, MNH_4^+, 382.1307. $C_{18}H_{24}NO_6S$ requires *m/z*, 382.1324); δ_H 1.49 (3 H, d, $J_{8,9}$ 6.2, 9-H), 1.8–2.6 (2 H, m, 7-H_2), 2.06 (3 H, s, OAc), 4.0–4.6 (4 H, m, 1-H_2, 2- and 6-H), 5.3–5.7 (1 H, m, 8-H), 6.17 (1 H, dd, $J_{3,4}$ 10.5, $J_{2,4}$ 1.9, 4-H), 6.93 (1 H, dd, $J_{2,3}$ 2.9, 3-H) and 7.0–7.4 (5 H, m, OPh); δ_C 19.5 (C-9), 20.7 (CO*Me*), 35.7 (C-7), 63.2 (C-1), 69.9, 73.7 (C-2, -6), 78.1 (C-8, 122.1, 127.6, 129.5, 153.6 (Ph), 126.5 (C-4), 145.8 (C-3), 170.5 (*C*OMe) and 194.6 (C-5, C=S).

(1R,3S,5S)-3-*Acetoxymethyl*-6-*methyl*-2-*oxaspiro*{*bicyclo*-[3.2.1]*octane*-8,2′-[1,3]*dioxolane*} **23**.—The thiocarbonyl ester **20** (0.155 g), ethane-1,2-diol (2 cm^3) and PTSA (0.08 g) were heated under reflux in benzene (30 cm^3) with azeotropic removal of water for 4 h. Ethyl acetate (50 cm^3) was added and the solution was washed successively with saturated aq. $NaHCO_3$ and water, and dried ($MgSO_4$). Removal of the solvent and purification by radial chromatography gave 1-*O*-acetyl-2,6-anhydro-3,4,7,9-tetradeoxy-8-*O*-phenoxy(thiocarbonyl)-D-*arabino*-non-3-en-5-ulose ethylene ketal **21** (0.12 g, 69%), $[\alpha]_D$ −57; δ_H 1.50 (3 H, d, $J_{8,9}$ 6.2, 9-H_3), 1.85–2.15 (2 H, m, 7-H_2), 2.05 (3 H, s, OAc), 3.9–4.55 (8 H, m, 1-H_2, 2- and 6-H and OCH_2CH_2O), 5.60 (1 H, m, 8-H) 5.86, 5.90 (2 H, 2 d, $J_{3,4}$ 11, 3- and 4-H) and 7.1–7.45 (5 H, m, OPh); δ_C 19.8 (C-9), 21.0 (CO*Me*), 33.9 (C-7), 63.4, 64.7, 65.8 (C-1, OCH_2CH_2O), 70.3, 70.5 (C-2, -6), 78.7 (C-8), 101.5 (C-5), 122.1, 128.3, 129.5, 153.3 (Ph), 126.4, 128.6 (C-3, -4), 171.0 (*C*OMe) and 194.5 (C=S).

The phenoxy(thiocarbonyl) ketal **21** (55 mg) was heated in refluxing benzene (5 cm^3) under nitrogen for 16 h during which tributyltin hydride (80 mg, 2 mol equiv.) and AIBN (5 mg) in benzene (3 cm^3) were added slowly. The solvent was removed and the residue was dissolved in acetonitrile (50 cm^3) and extracted with light petroleum. Evaporation of the acetonitrile and purification by radial chromatography gave the *title compound* (13 mg, 35%), $[\alpha]_D$ +15 (Found: *m/z*, MH^+, 257.1379. $C_{13}H_{21}O_5$ requires *m/z*, 257.1389); δ_H 1.10 (3 H, d, *J* 7.2, CH*Me*), 2.10 (3 H, s, OAc), 1.25–2.45 (6 H, ms, 4- and 7-H_2, 5- and 6-H) and 3.8–4.2 (8 H, m, 1- and 3-H, CH_2OAc, OCH_2CH_2O); δ_C 1.49 (6-Me), 21.0 (CO*Me*), 27.2, 33.3 (C-4, -7), 29.7 (C-6), 42.2 (C-5), 64.5, 65.2, 67.1 (CH_2OAc, OCH_2CH_2O), 66.0 (C-3), 76.8 (C-1), 113.5 (C-8) and 171.1 (*C*OMe).

2,6-*Anhydro*-1,3,5-*tri*-O-*benzoyl*-4,7,8,9-*tetradeoxy*-D-lyxo-*nona*-4,8-*dienitol* **13**.—1-*O*-Acetyl-2,4,6-tri-*O*-benzoyl-3-deoxy-α-D-*erythro*-hex-2-enopyranose **12**[26] (3 g) and allyltrimethylsilane (2.7 g, 4.0 mol equiv.) were stirred for 3 h in benzene (50 cm^3) under nitrogen with slow addition of boron trifluoride–diethyl ether (1 cm^3). The mixed esters were processed as for compound **9** above, and the *title compound* with its C-6 epimer (0.84 g) and the starting material (1.5 g) were isolated. The last was treated a second time as above, and a second fraction of the allyl compounds (total 1.7 g, 59%) was obtained as a 3:1 mixture of D-*lyxo*- and L-*ribo*-isomers.

Crystallisation from methanol gave the lyxo-*compound* (0.46 g, 16%), m.p. 67–69 °C; $[\alpha]_D$ +56 (Found: C, 72.2; H, 5.5. $C_{30}H_{26}O_7$ requires C, 72.3; H, 5.3%); δ_H 2.5–2.7 (2 H, m, 7-H_2), 4.4–4.7 (4 H, m, 1-H_2, 2- and 6-H), 5.05–5.2 (2 H, m, 9-H_2), 5.73 (1 H, m, 3-H), 5.85–6.05 (2 H, m, 4- and 8-H and 7.4–8.1 (15 H, m, 3 × OBz); δ_C D-*lyxo*-epimer (L-*ribo*-epimer): 35.5 (36.3) (C-7), 63.2 (64.2) (C-1), 66.7, 70.5, 70.7 (67.3, 74.2, 74.5) (C-2, -3, -6), 111.8 (113.9) (C-4), 117.8 (117.8) (C-9), 128.3, 128.4, 128.7, 129.6, 129.7, 129.8, 133.1, 133.3, 133.5 (3 × Ph), 133.9 (133.7) (C-8), 151.8 (150.9) (C-5) and 163.9, 165.9, 166.3 (3 × *C*OPh).

2,6-*Anhydro*-1-O-*benzoyl*-3,4,7,8,9-*pentadeoxy*-D-threo-*nona*-3,8-*dien*-5-*ulose* **11**.—The diene **13** (0.47 g) was stirred in benzene (10 cm^3) containing boron trifluoride–diethyl ether (0.1 cm^3) under nitrogen at 50 °C for 5 min. Benzene (50 cm^3) was added and the solution was washed successively with aq. $NaHCO_3$, then water and dried ($MgSO_4$). Chromatography on silica gel gave the *title compound* (0.24 g, 93%), $[\alpha]_D$ −82 (Found: *m/z*, MNH_4^+, 290.1404. $C_{16}H_{20}NO_4$ requires *m/z*, 290.1392); δ_H 2.56 (2 H, t, *J* 6.8, 7-H_2), 4.4–4.6 (2 H, m, 1-H′ and 6.H), 4.67 (1 H, dd, $J_{1,2}$ 6.3, $J_{1,1'}$ 11.7, 1-H), 4.83 (1 H, ddd, $J_{1',2}$ 10.6, 2-H), 5.05–5.2 (2 H, m, 9-H_2), 5.87 (1 H, m, 8-H), 6.20 (1 H, dd, $J_{3,4}$ 10.5, $J_{2,4}$ 2.2, 4-H), 7.03 (1 H, dd, $J_{2,3}$ 2.7, 3-H) and 7.4–8.1 (5 H, m, OBz); δ_C 34.0 (C-7), 64.3 (C-1), 68.9, 77.5 (C-2, -6), 117.9 (C-9), 127.4 (C-4), 128.5, 129.6, 133.7 (Ph), 133.4 (C-8), 146.3 (C-3), 166.1 (*C*OPh) and 195.3 (C-5).

2,6:5,2′-*Dianhydro*-1-O-*benzoyl*-3,4,7,9-*tetradeoxy*-4-C-(2′-*hydroxyethyl*)-D-altro-*non*-5-*ulo*-5,8-*furanose* **30**.—The enone **11** (0.38 g), mercury(II) acetate (0.45 g, 1.0 mol equiv.) and ethane-1,2-diol (1 cm^3) in dry acetonitrile (10 cm^3) were stirred under nitrogen at room temperature for 2 h. The solvent was removed and the residual adduct **33** was dissolved in dichloromethane (50 cm^3) and the solution was washed with water (× 2) and dried ($MgSO_4$). After the dichloromethane had been reduced to 10 cm^3, tributyltin hydride (0.81 g, 2 mol equiv.) was added and the mixture was stirred under nitrogen at 20 °C for 1 h. Filtration through silica gel and removal of the solvent gave a syrup, which was dissolved in acetonitrile (50 cm^3) and extracted (× 5) with light petroleum. Removal of the acetonitrile and chromatography on silica gel gave 2-hydroxyethyl 2,6-anhydro-1-*O*-benzoyl-3,4,7,9-tetradeoxy-D-*arabino*-non-3-en-5-ulo-5,8-furanoside **25** (0.30 g, 63%) as an oil, $[\alpha]_D$ −62; δ_H 1.35 (3 H, d, $J_{8,9}$ 6.1, 9-H_3), 1.61 (1 H, ddd, $J_{7,7'}$ 15.7, $J_{7,8}$ 6.0, $J_{6,7}$ 2.1, 7-H), 2.55 (1 H, ddd, $J_{6,7'} = J_{7',8}$ = 6.8, 7-H′), 3.6–3.75 (4 H, m, OCH_2CH_2O), 4.30 (1 H, m, 8-H), 4.32 (1 H, dd, $J_{1,2}$ 3.0, $J_{1,1'}$ 11.5, 1-H), 4.40 (1 H, dd, 6-H), 4.55 (1 H, m, 2-H), 4.66 (1 H, dd, $J_{1,2}$ 6.9, 1-H′), 5.99 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.5, 3-H), 6.26 (1 H, dd, $J_{2,4}$ 1.7, 4-H) and 7.4–8.1 (5 H, m, OBz); δ_C 22.0 (C-9), 38.3 (C-7), 62.2, 62.4, 64.0 (C-1, OCH_2CH_2O), 71.1, 74.7, 76.8 (C-2, (6, -8), 100.5 (C-5), 124.2, 128.5 (C-3, -4), 128.4, 129.7, 133.2 (Ph) and 166.3 (*C*OPh).

The derived acetate **26** gave δ_H 1.35 (3 H, d, $J_{8,9}$ 6.2, 9-H_3), 1.58 (1 H, ddd, $J_{7,7'}$ 13.5, $J_{7,8}$ 5.9, $J_{6,7}$ 1.9, 7-H), 2.05 (3 H, s, OAc), 2.55 (1 H, m, 7-H′), 3.65–3.9 (2 H, m, OCH_2CH_2OAc), 4.15 (2 H, m, OCH_2CH_2OAc), 4.25–4.7 (5 H, m, 1-H_2, 2-, 6- and 8-H), 6.00 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.5, 3-H), 6.22 (1 H, dd, $J_{2,4}$ 1.7, 4-H) and 7.4–8.1 (5 H, m, OBz); δ_C 21.0 (CO*Me*), 22.0 (C-9), 38.4 (C-7), 58.9 (CH_2CH_2OAc), 63.8, 63.9 (C-1, CH_2CH_2OAc), 71.2, 74.7, 76.6 (C-2, -6, -8), 100.6 (C-5), 124.1, 128.5 (C-3, -4), 128.4, 129.8, 133.2 (Ph), 166.3 (*C*OPh) and 171.0 (*C*OMe).

The hydroxyethyl compound **25** (0.17 g), phenyl chlorothiocarbonate (0.10 g, 1.1 mol equiv.) and pyridine (0.12 g, 3 mol equiv.) were stirred in dichloromethane (5 cm^3) for 1 h, when further solvent (50 cm^3) was added and the solution was washed successively with saturated aq. $NaHCO_3$, dil. hydrochloric acid, and water, and dried ($MgSO_4$). Removal of the solvent and column chromatographic separation gave the thiocarbonate **27** (0.08 g, 34%); δ_H 1.34 (3 H, d, $J_{8,9}$ 6.2, 9-H) 1.4–1.7 (1 H, m, 7-H), 2.3–2.7 (1 H, m, 7-H′), 3.75–4.0 (2 H, m, 1-H_2), 4.1–4.9 (7 H, m, OCH_2CH_2O, 2-, 6- and 8-H), 5.95 (1 H, dd, $J_{3,4}$ 10, $J_{2,3}$ 2.9, 3-H), 6.25 (1 H, dd, $J_{2,4}$ 0.5, 4-H) and 7.0–8.1 (10 H, m, OPh and OBz).

The ester (0.08 g) was heated under nitrogen in refluxing benzene (5 cm^3), and tributyltin hydride (0.075 g, 1.5 mol equiv) and AIBN (5 mg) in benzene were added during 16 h. Removal of the solvent gave a syrup, which was dissolved in acetonitrile (50 cm^3) and the solution was extracted with light petroleum. Evaporation of the acetonitrile and separation by radial chromatography gave the *tricyclic product* **30** (25 mg, 43%), $[\alpha]_D$ +1 (Found: *m/z*, MH^+, 319.1531. $C_{18}H_{23}O_5$ requires *m/z*, 319.1545); δ_H 1.31 (3 H, d, $J_{8,9}$ 6.2, 9-H_3), 1.4–2.5 (7 H, ms, 1′-, 3- and 7-H_2 and 4-H), 3.95 (2 H, m, 2-H_2), 4.15–4.25 (3 H, m, 2-, 6- and 8-H), 4.29 (1 H, dd, $J_{1,2}$ 4.0, $J_{1,1'}$ 11.5, 1-H), 4.42 (1 H, dd, $J_{1',2}$ 5.9, 1-H′) and 7.4–8.1 (5 H, m, OBz); δ_C 21.6 (C-9), 30.0, 30.1, 38.2 (C-3, -7, -1′), 40.0 (C-4), 66.4. 66.5 (C-1, -2′), 71.0, 73.1, 77.1 (C-2, -6, -8), 114.6 (C-5), 128.4, 129.7, 130.0, 133.1 (Ph) and 166.5 (*C*OPh).

2′-*Hydroxyethyl* 1-O-*Acetyl*-2,6-*anhydro*-3,4,7,9-*tetradeoxy*-D-arabino-/-L-ribo-*non*-3-*en*-5-*ulo*-5,8-*furanoside* **28**.—The C-6 epimers **9**/**10** (0.83 g), mercury(II) acetate (1.26 g, 1 mol equiv.) and ethane-1,2-diol (0.5 g, 2.0 mol equiv.) in acetonitrile (10 cm^3) were stirred for 2 h at 20 °C under nitrogen. Isolation and reduction of the adducts as for compound **25** gave the D-*arabino*-**28**, L-*ribo*-2-hydroxyethyl ulosides (0.71 g, 67%; 3:1), $[\alpha]_D$ −52 (Found: *m/z*, MNH_4^+, 290.1613. $C_{13}H_{24}NO_6$ requires *m/z*, 290.1604); *m/z* 272 $(M)^{\bullet+}$, 212 $(M - AcOH)^{\bullet+}$, 211 $(M - OCH_2CH_2OH)^+$, 199 $(M - CH_2OAc)^+$ and 151 $(M - OCH_2CH_2OH - AcOH)^+$; δ_H(D-*arabino*-epimer **28**) 1.34 (3 H, d, $J_{8,9}$ 6.2, 9-H), 1.60 (1 H, m, 7-H), 2.11 (3 H, s, OAc), 2.52 (1 H, m, 7-H′), 3.6–3.75 (4 H, m, 1′- and 2′-H_2), 4.0–4.5 (5 H, m, 1-H_2, 2-, 6- and 8-H), 5.92 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.4, 3-H) and 6.23 (1 H, dd, $J_{2,4}$ 1.5, 4-H); (L-*ribo*-epimer, resolvable differences only) δ_H 1.35 (3 H, d, $J_{8,9}$ 6.2, 9-H) and 2.10 (3 H, s, OAc); δ_C D-*arabino*-epimer (L-*ribo*-epimer) 21.0 (21.0) (CO*Me*), 22.0 (22.1) (C-9), 38.1 (38.3) (C-7), 62.2, 62.5, 62.6 (62.2, 62.3, 65.8) (C-1, -1′, -2′), 71.0, 74.7, 76.3 (72.2, 75.2, 81.1) (C-2, -6, -8), 100.5 (101.4) (C-5), 124.3, 128.4 (124.1, 129.8) (C-3, -4) and 170.9 (170.9) (*C*OMe).

1-O-*Acetyl*-2,6:5,2′-*dianhydro*-3,4,7,9-*tetradeoxy*-4-C-(2′-*hydroxyethyl*)-D-altro-*non*-5-*ulo*-5,8-*furanose* **31**.—The mixed hydroxyethyl compounds (**28** + isomer) (0.20 g), phenyl chlorothiocarbonate (0.19 g, 1.5 mol equiv.) and pyridine (0.29 g, 5 mol equiv.) were stirred in dichloromethane (5 cm^3) for 3 h. Further dichloromethane (20 cm^3) was added and the solution was washed successively with saturated aq. $NaHCO_3$, dil. hydrochloric acid, and water, and was then dried ($MgSO_4$). Evaporation of the solvent and purification on a column of silica gel gave 2-[phenoxy(thiocarbonyloxy)]ethyl 1-*O*-acetyl-2,6-anhydro-3,4,7,9-tetradeoxy-D-*arabino*-non-3-en-5-ulo-5,8-furanoside **29** (0.145 g, 50%), $[\alpha]_D$ −44; δ_H 1.35 (3 H, d, $J_{8,9}$ 6.2, 9-H_3), 1.59 (1 H, ddd, $J_{7,7'}$ 13.9, $J_{7,8}$ 5.8, $J_{6,7}$ 1.9, 7-H), 2.11 (3 H, s, OAc), 2.56 (1 H, ddd, $J_{6,7'} = J_{7',8}$ = 6.4, 7-H′), 3.85–4.7 (9 H,

m, 1-, 1′- and 2′-H_2, 2-, 6- and 8-H), 5.93 (1 H, dd, $J_{3,4}$ 10.6, $J_{2,3}$ 3.3, 3-H), 6.20 (1 H, dd, $J_{2,4}$ 1.5, 4-H) and 7.1–7.45 (5 H, m, OPh); δ_C 21.0 (CO*Me*), 22.0 (C-9), 38.3 (C-7), 58.3, 62.7 (C-1, -1′), 71.3, 74.9, 76.2 (C-2, -6, -8), 73.2 (C-2′), 100.7 (C-5), 124.0, 128.6 (C-3, -4), 121.9, 126.6, 129.6, 153.4 (Ph), 170.9 (*C*OMe) and 195.2 (C=S).

The phenoxy(thiocarbonyl) ester **29** (0.135 g) was then heated in refluxing benzene (5 cm^3) under nitrogen for 6 h during which time tributyltin hydride (0.145 g, 1.5 mol equiv.) and AIBN (5 mg) in benzene (3 cm^3) were added slowly. Removal of the solvent gave a syrup, which was dissolved in acetonitrile (50 cm^3) and extracted (× 5) with light petroleum. Evaporation of the acetonitrile and purification by radial chromatography gave the *title compound* (75 mg, 90%), $[\alpha]_D$ −2.5 (Found: *m/z*, MH^+, 257.1394. $C_{13}H_{21}O_5$ requires *m/z*, 257.1389); *m/z* 256 (M^+), 213 $(M - Ac)^+$, 196 $(M - AcOH)^+$ and 183 $(M - CH_2OAc)^+$; δ_H 1.29 (3 H, d, $J_{8,9}$ 6.2, 9-H), 1.4–2.55 (7 H, m, 3-, 4′- and 7-H_2 and 4-H), 2.08 (3 H, s, OAc) and 3.85–4.4 (7 H, m, 1-, 4″-H_2 and 2-, 6- and 8-H); δ_C 20.8 (CO*Me*), 21.6 (C-9), 30.0, 30.2, 38.3 (C-3, -7, - 4′), 40.2 (C-4), 65.9, 66.4 (C-1, -4″), 70.9, 73.1, 77.1 (C-2, -6, -8), 114.5 (C-5) and 170.8 (*C*OMe).

1-O-*Acetyl*-2,6:5,2′-*dianhydro*-3,4,7,9-*tetradeoxy*-4-C (2′-*hydroxyethyl*)-3-C-[2-(*methoxycarbonyl*)*ethyl*]-D-glycero-D-manno-*non*-5-*ulo*-5,8-*furanose* **32**.—The phenoxy(thiocarbonyl) ester **29** (85 mg) and methyl acrylate (0.25 g, 15 mol equiv.) were heated in refluxing benzene (5 cm^3) under nitrogen for 16 h during which tributyltin hydride (90 mg, 1.5 mol equiv.) and AIBN (5 mg) in benzene (3 cm^3) were added slowly. The solvent was removed and the residue was dissolved in acetonitrile (50 cm^3), which was extracted (× 5) with light petroleum. Evaporation of the acetonitrile and separation by radial chromatography gave a crude oil (55 mg) shown by gas chromatography/mass spectrometry to consist of three compounds in the proportions 17:56:27: (i) compound **31** (inseparable from authentic material by gas chromatography); (ii) the *title compound* **32** [Found: *m/z*, MH^+, 343.1765. $C_{17}H_{27}O_7$ requires *m/z*, 343.1757; $M^{\bullet+}$, 342; $(M - OMe)^+$, 311; $(M - CH_3CO)^+$, 299; $(M - AcOH)^{\bullet+}$, 282; $(M - CH_2OH_2)^+$, 269; $(M - OMe - AcOH)^+$, 251] (iii) the *product* **33** formed by trapping of two methyl acrylate groups [Found: *m/z* MH^+, 429.2144. $C_{21}H_{33}O_9$ requires *m/z*, 429.2125; $M^{\bullet+}$, 428; $(M - OMe)^+$, 397; $(M - AcOH)^{\bullet+}$, 368; $(M - OMe - MeOH)^+$, 365; $(M - CH_2OAc)^+$, 355; $(M - OMe - AcOH)^+$, 337; $(M - CH_2OAc - MeOH)^+$, 323].

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