A Concise and General Entry into (*R*)-4-Hydroxy-2-Substituted Cyclopent-2-enones from D-Glucose: Chiral Intermediates for the Synthesis of PGE_2, (−)-Pentenomycin I, and Allethrin

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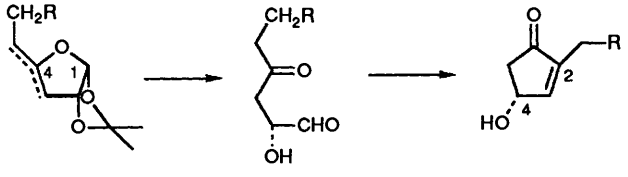
A general strategy for the transformation of D-glucose into different 2-substituted (*R*)-4- hydroxycyclopent-2-enones is described. This has been illustrated by the synthesis of (*R*)-2-[(1,3-dithian-2-yl)methyl]-4-hydroxycyclopent-2-enone, (*R*)-2-benzyloxymethyl-4-hydroxycyclopent-2-enone, and (*R*)-2-allyl-4-hydroxycyclopent-2-enone, which are potential chiral synthons for prostaglandin E_2, the antibiotic (−)-pentenomycin I, and the synthetic insecticide allethrin, respectively. The second chiral synthon was obtained by two different routes, one of them involving a novel palladium(0)-catalysed rearrangement of a vinyloxirane intermediate.

The cyclopentanoid class of natural products has attracted considerable attention due to the wide range of structural and stereochemical features along with remarkably diverse types of biological activity. Various members of this family have been the targets of synthetic endeavours in the past two decades, leading to the development of many original and versatile methods for the construction of single or polycyclic five-membered rings.[1] Perhaps the most significant accomplishments in this regard are those syntheses, in the prostanoid area, that rely on conjugate addition of organometallic derivatives to substituted cyclopentenones.[2] This strategy, which associates both convergency and efficacy, has been elegantly illustrated in the works of Noyori and Johnson that have recently culminated in the 'triply convergent' total synthesis of prostaglandin E_2 from (*R*)-4-hydroxycyclopentenone.[3]

Despite the existence of numerous approaches to substituted (*R*)-4-hydroxycyclopentenones[4] there is still room for improvement in both generality and flexibility. In an effort to address the chiral synthesis of 2-substituted (*R*)-4-hydroxycyclopentenones, we devised a strategy based upon the use of a D-glucose derivative which would allow for both stereochemical control and flexibility in introduction of substituents at C-2.

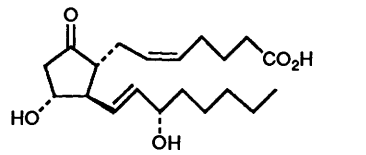
Although the pioneering work of Ferrier[5a] has provided a general and efficient method for the conversion of C-5–C-6 unsaturated pyranosides into functionalised cyclohexane derivatives,[5] it is only very recently that the chemical literature has witnessed the successful transformation of carbohydrates into five-membered carbocycles.[6,7]



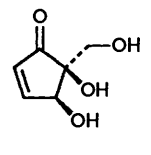
Scheme 1.

Our strategy, as outlined in Scheme 1, originates from the recognition that C-4 unsaturated furanosides (**A**) are masked forms of acyclic 2-hydroxy-4-keto aldehydes (**B**) that can possibly be unveiled upon acidic treatment. These intermediates would then be amenable to an intramolecular aldolisation–dehydration sequence to provide the desired 2-substituted (*R*)-4-hydroxycyclopentenones of general structure (**C**). While this work was in progress, we became aware of a similar approach utilised by Moffat [illegible] workers[7] in their total synthesis of the antibiotic (−)-pentenomycin I.

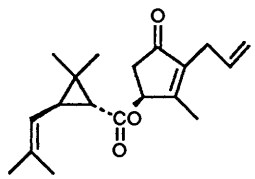
Herein we disclose full experimental details of the implementation of our strategy that led to the synthesis of three different 2-substituted (*R*)-4-hydroxycyclopentenones, two of which have been the subject of preliminary communications.[8]



PGE_2



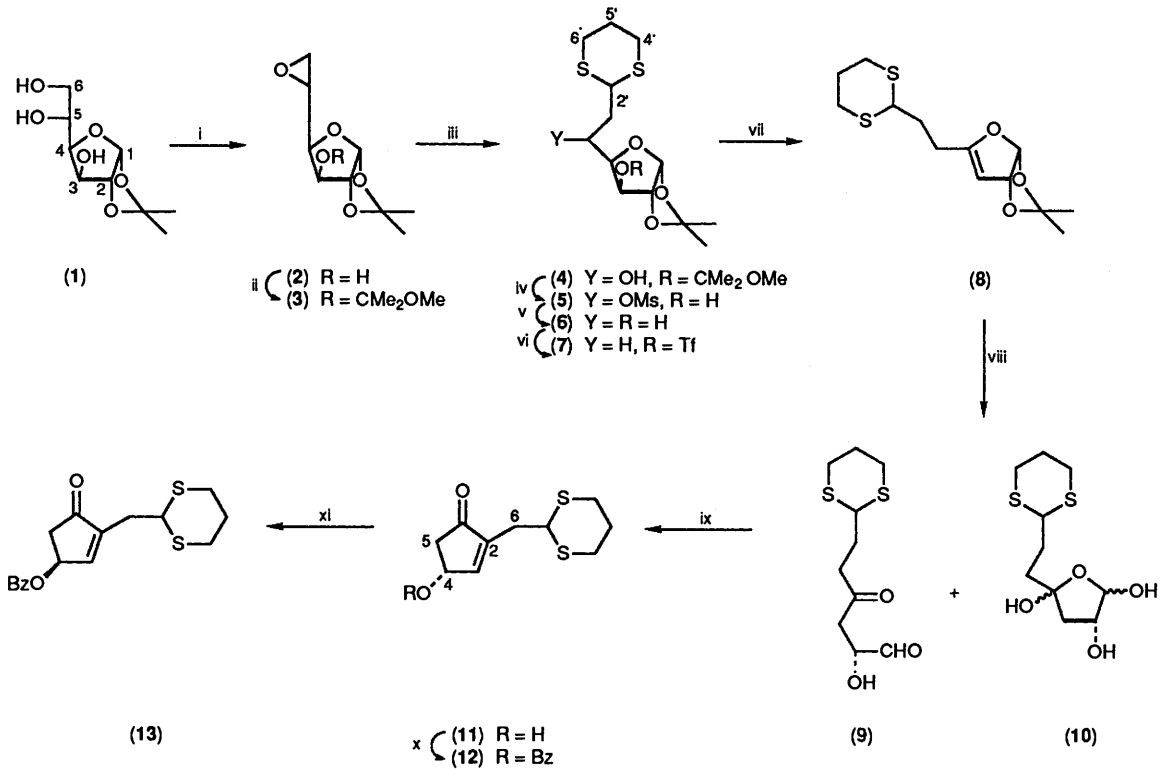
(−)-pentenomycin I



Allethrin

Our first objective was the synthesis of the 2-dithianylmethyl-4-hydroxycyclopent-2-enone (**11**) (Scheme 2), a potential chiral synthon for the preparation of PGE_2. The strategy outlined in Scheme 2 indicates that the preparation of compound (**11**) from 1,2-isopropylidene-α-D-glucofuranose (**1**) will require prior homologation of the starting sugar by an aldehyde equivalent which should allow an elaboration of the α side-chain of PGE_2 through the well precedented Wittig procedure.[2] To achieve this homologation, the epoxide (**2**)[9] (Scheme 2) presented itself as an ideally suited candidate for deoxyalkylation at C-6 by the 2-lithio-1,3-dithiane carbanion.[10] Subsequent functional-group manipulations involving deoxygenation at C-5 and elimination of the C-3 hydroxy group will then furnish the unsaturated furanoside (**8**).

To facilitate deoxygenation at C-5, it was deemed necessary to protect the C-3 hydroxy group prior to epoxide opening. Treatment of the epoxide (**2**) with 2-methoxypropene[11] in the presence of a catalytic amount of trifluoroacetic acid (TFA) furnished the acetal (**3**) in almost quantitative yield. Subsequent reaction of compound (**3**) with 2-lithio-1,3-dithiane



Scheme 2. *Reagents:* i, PPh_3–DEAD; ii, 2-methoxypropene, TFA; iii, 2-lithio-1,3-dithiane on (**3**); iv, (*a*) MsCl, Et_3N, 4-DMAP, (*b*) TFA; v, $NaBH_4$; vi, Tf_2O, pyridine; vii, DBU on (**7**); viii, 80% HCOOH; ix, 0.1M-NaOH; x, BzCl, pyridine; xi, PPh_3–DEAD, $PhCO_2H$ on (**11**). Ms = $MeSO_2$, Tf = CF_3SO_2.

in tetrahydrofuran and hexamethylphosphoric triamide (THF–HMPT) produced alcohol (**4**) in 93% yield which, after treatment with mesyl chloride and triethylamine according to Crossland and Servis' method,[12] followed by acidic hydrolysis, gave the mesyl ester (**5**) in 90% isolated yield. Hydroxy group-assisted reduction of the mesyl ester with sodium borohydride in HMPT[13] cleanly provided the deoxy sugar (**6**) in 80% isolated yield. The installation of the C-3–C-4 double bond was then initiated by triflate* formation at C-3 [ester (**7**), 97% isolated yield] with triflic anhydride and pyridine.[14] Subsequent elimination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in Et_2O at ambient temperature furnished the relatively stable enol ether (**8**) in nearly quantitative yield.

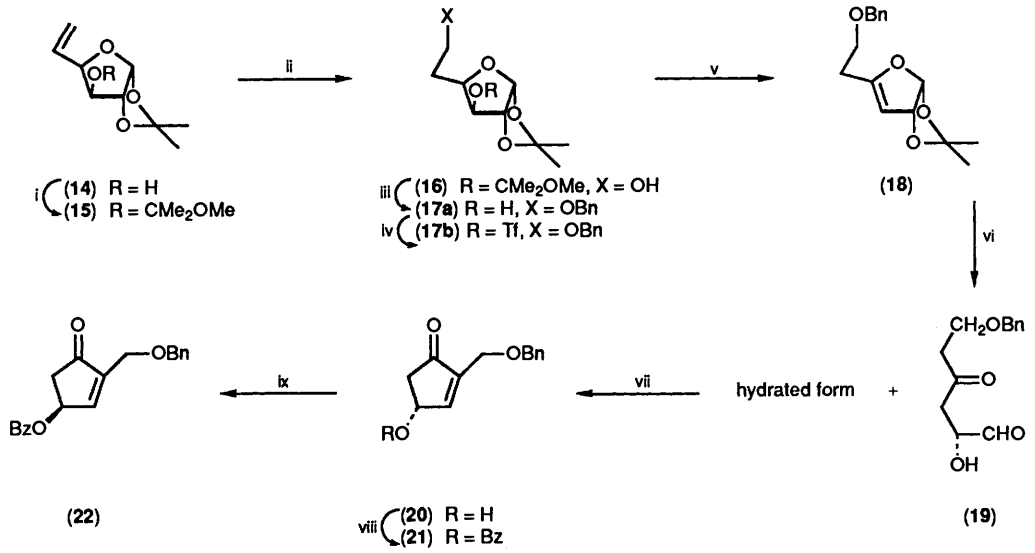
Treatment of compound (**8**) with 80% formic acid in THF (1:1) afforded an inseparable mixture of (*R*)-2-hydroxy-4-keto aldehyde (**9**) and its hydrated equivalent (**10**)[7,15] in 66% isolated yield. The hydrated form of compound (**9**) most probably adopts the more stable cyclic structure (**10**) as has been suggested for a similar case by Moffat.[7] Assignment of structure (**9**) resulted from the analysis of its spectral data; of diagnostic significance were the IR absorptions at 3 400 cm^{-1} (ν_{OH}) and 1 650–1 700 cm^{-1} (ν_{CO}, ν_{CHO}); and the signal δ 9.7 (CHO) in the ^1H NMR spectrum which integrated for less than one proton. The complexity of the ^1H NMR spectrum, together with the mass spectrum, pointed to the presence of the hydrated form(**10**).

The mixture of keto aldehyde (**9**) and its hydrated form (**10**) was then subjected to cyclisation under a variety of conditions [lithium di-isopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), piperidinium acetate, piperidinium toluene-*p*-sulphonate, Al_2O_3, KOH, DBU, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)]. All these bases proved unsatisfactory, leading to complicated product mixtures. Finally, treatment of the mixture of compounds (**9**) and (**10**) under Crombie's conditions[16] (0.1M-NaOH in ethanol) furnished the desired hydroxycyclopentenone (**11**) in a modest 35% isolated yield. The difficulties encountered might be a result of the sensitive nature[17] of compound (**9**) which is prone to polymerisation and whose hydrated form seems to be particularly stable under basic conditions.[7] In addition, the existence of a competitive retro-aldol process cannot be ruled out. It should, however, be noted that comparable yields have been reported in aldol condensations of similar 2-hydroxy keto aldehyde derivatives.[18] Clearly, room for improvement remains for this cyclisation step.

Structural assignment for the hydroxycyclopentenone (**11**) was supported by its high-field (400 MHz) ^1H NMR spectrum which showed characteristic resonances: a singlet at δ 7.35 for 3-H, an ABX system for the 5-H protons at δ 2.28 and 2.80 (*J* 2.6 and 18 Hz), and a multiplet at δ 4.89 for 4-H; all these values matched well with the literature data.[19]

Having secured the preparation of compound (**11**), we turned our attention to the determination of its optical purity. To this end, we used the method developed by Hinckley which makes use of ^1H NMR analysis in the presence of a chiral shift reagent.[20,21] In order to carry out this study, both the (*R*)- and (*S*)- enantiomer of the hydroxycyclopentenone (**11**) or a derivative thereof were needed. Consequently, (*R*)-benzoate (**12**), $[\alpha]_D^{20}$ +52°, was prepared by standard procedure in 82% yield; epimerisation at the hydroxy position was effected by treatment of compound (**11**) with diethyl azodicarboxylate (DEAD) and triphenylphosphine in the presence of benzoic acid[22] to afford the (*S*)-benzoate (**13**). That complete epimerisation at C-4 did indeed take place was evidenced by the optical rotation of compound (**13**), $[\alpha]_D^{20}$ −53°. When

* Trifluoromethanesulphonate.

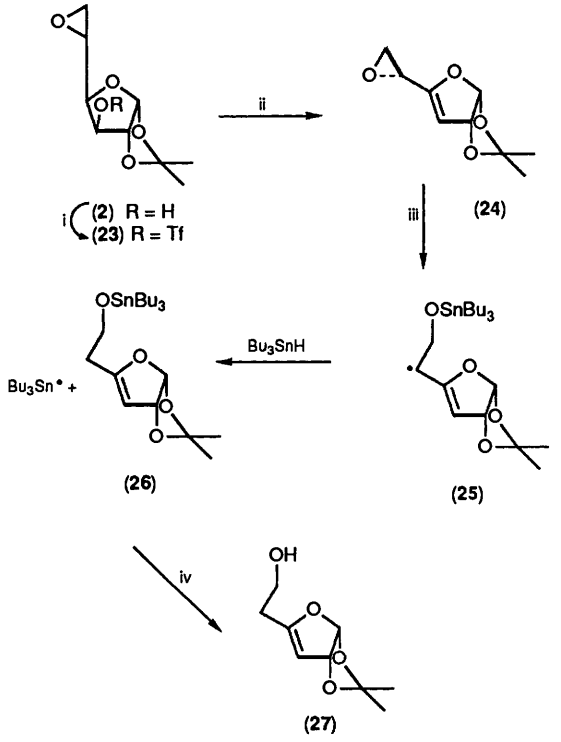


Scheme 3. *Reagents:* i, 2-Methoxypropene, TFA; ii, 9-BBN, H_2O_2–NaOH on (**15**); iii, (*a*) BnBr, NaH, DMF, (*b*) TFA; iv, Tf_2O, pyridine; v, DBU on (**17b**); vi, 80% HCO_2H; vii, 0.1M-NaOH; viii, BzCl, pyridine; ix, PPh_3–DEAD, $PhCO_2H$ on (**20**). Bn = $PhCH_2$.

compound (**12**) was analysed by high-field (400 MHz) ^1H NMR spectroscopy in the presence of $Eu(tfc)_3$,* the protons 3-H, 4-H, and 5-H were found to be significantly deshielded, while no extra signal could be detected in the spectrum. Under the same conditions, the ^1H NMR spectrum of the mixture of benzoates (**12**) and (**13**) showed that protons 3-H [(*R*)] and 3-H [(*S*)] as well as 4-H [(*R*)] and 4-H [(*S*)] gave rise to well resolved signals, thereby demonstrating that the two enantioners (**12**) and (**13**) were clearly distinguishable by the ^1H NMR spectrum in the presence of $Eu(tfc)_3$. Consequently, the hydroxycyclopentenone (**11**) was optically pure and it could be concluded that no racemisation had occurred during the aldol condensation step.

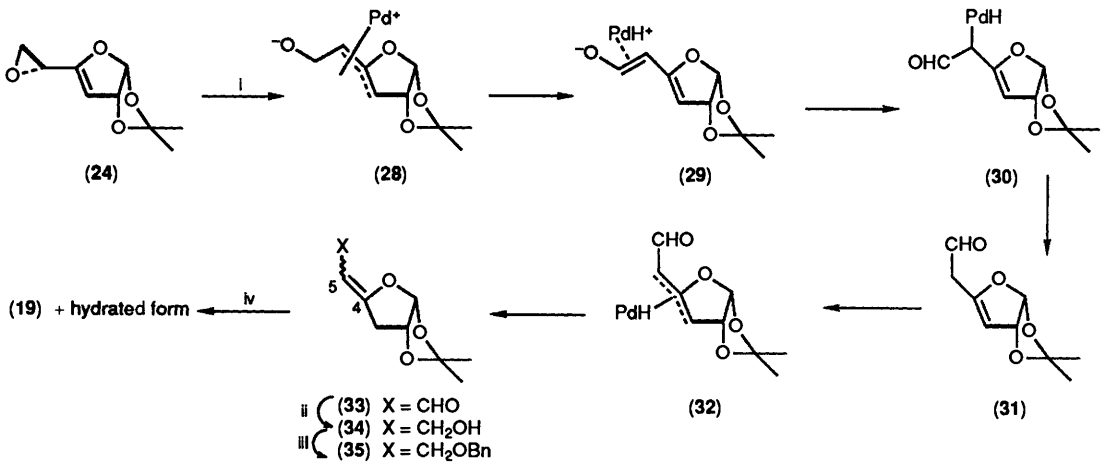
In order to illustrate the versatility of this strategy, we sought to carry out the synthesis of (*R*)-2-benzyloxymethyl-4-hydroxycyclopent-2-enone (**20**) (Scheme 3) en route to the antibiotic (−)-pentenomycin I.[7,23] We envisioned access to compound (**20**) by two different approaches. The first one, depicted in Scheme 3, began with the 5,6-unsaturated sugar (**14**) readily available from the epoxide (**2**) by Paulsen's procedure.[24] Protection of the C-3 hydroxy group as described previously[14] furnished the acetal (**15**) in essentially quantitative yield. Hydroboration of the olefin (**15**) with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF followed by oxidation (H_2O_2–NaOH) provided the primary alcohol (**16**).[11] The latter was transformed into its benzyl ether which, upon acidic treatment, yielded the 5-deoxy sugar (**17a**). Formation of the C-3–C-4 unsaturated sugar (**18**) resulted from trifluoromethylsulphonylation of the 3-hydroxy group to give compound (**17b**) (98% yield) followed by triflate elimination.

Hydrolysis of compound (**18**) with 80% formic acid afforded the (*R*)-2-hydroxy-4-oxo aldehyde (**19**) and its hydrated form in 65% combined yield after chromatographic purification. The structure of the keto aldehyde (**19**) was deduced from its spectral data. Treatment of this mixture under the previously used conditions produced the (*R*)-2-benzyloxymethyl-4-hydroxycyclopentenone (**20**) in 30% isolated yield. The optical purity of the hydroxycyclopentenone (**20**) was convincingly established through high-field ^1H NMR analysis of the (*R*)-benzoate (**21**) and the (*S*)-benzoate (**22**) in the presence of $Eu(tfc)_3$. In order to develop a concise route to the alcohol (**20**), it appeared to us that ready access to the unsaturated sugar (**18**) would be most desirable and would avoid extensive manipulation of the carbohydrate nucleus. We envisaged that the vinylic oxirane (**24**), available in two steps from the epoxide (**2**), would be a suitable precursor to compound (**18**), provided that regioselective reduction of compound (**24**) to the corresponding primary alcohol (**27**) could be achieved. Although examples of regioselective reductions of allylic terminal epoxides to primary alcohols have been reported in the literature, they are very often highly dependent upon the structure of the epoxide.[25] As yet no general method is available to achieve such a transformation.



Scheme 4. *Reagents:* i, Tf_2O, pyridine; ii, DBU on (**23**); iii, Bu_3SnH, AIBN; iv, hydrolysis upon work-up or chromatography.

* Tris[3-trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) derivative.



Scheme 5. *Reagents and conditions:* i, $Pd(PPh_3)_4$, CH_2Cl_2; ii, DIBAH, −30 °C, THF; iii, BnBr, NaH, DMF; iv, 80% HCO_2H on (**35**).

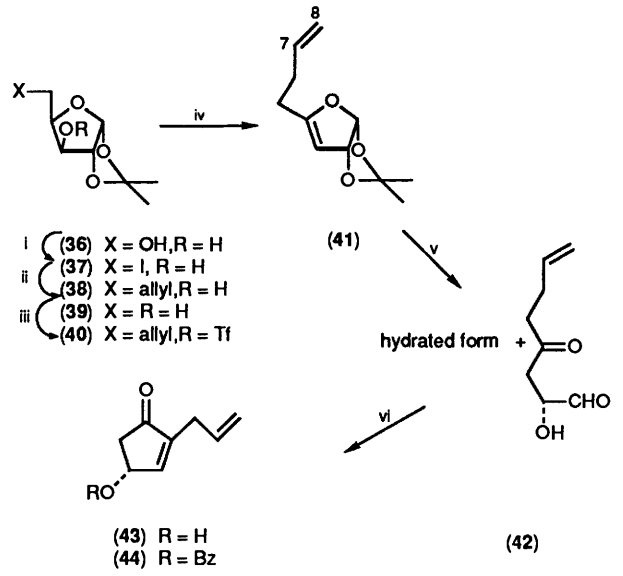
Treatment of the epoxide (**2**) with triflic anhydride and pyridine afforded the triflate (**23**) in 87% isolated yield, and which, upon DBU-catalysed elimination, gave the allylic epoxide (**24**) in 94% yield (Scheme 4). When the allylic epoxide (**24**) was treated with tributyltin hydride and catalytic azoisobutyronitrile (AIBN) in refluxing benzene, the homoallylic alcohol (**27**) was obtained in 32% yield (Scheme 4). While this yield was unacceptably low for our purpose, this reaction represents, to the best of our knowledge, the first example of radical reduction of an allylic epoxide. A plausible mechanism for this reaction is depicted in Scheme 4. Given the oxophilicity of tin, one can assume attack on the epoxide (**24**) by the tributyltin radical which generates alkoxystannane (**25**) possessing a stabilised allylic radical centred at C-5. Subsequent radical trapping by tributyltin hydride in the propagation step gives compound (**26**), which undergoes hydrolysis of the labile tin–oxygen bond in the work-up to provide the homoallylic alcohol (**27**). A related example is to be found in the work of Barton *et al.*[26] specifically concerned with the reduction of α-epoxyxanthates by tributyltin hydride. In this study, the resulting α-epoxy radical was shown to undergo readily a Wharton-type fragmentation leading to an allylic alcohol. Finally, it has been recently demonstrated that a derivative of the epoxide (**2**) underwent free-radical reductive opening[27] by reaction with NaI and Bu_3SnH to give mainly the corresponding secondary alcohol, presumably through halogenohydrin formation followed by deiodination. Despite the obvious synthetic potentialities of free-radical reduction of allylic epoxides the disappointingly low yield obtained in our case dissuaded us from pursuing this path further.

To overcome these difficulties, we sought an alternative approach based upon a rearrangement of the allylic epoxide (**24**). Recently, Noyori's group has demonstrated that vinylic oxiranes can be transformed into dienols and/or β,γ-unsaturated ketones upon reaction with palladium(0) derivatives.[28]

Accordingly, the epoxide (**24**) was treated with a catalytic amount of palladium tetrakistriphenylphosphine in dichloromethane at ambient temperature to provide a mixture of two isomeric α,β-unsaturated aldehydes (**33**) in 85% isolated yield (Scheme 5). The mass spectrum of the mixture showed the molecular ion peak at *m/z* 184 which corresponded with the molecular weight of the substrate thereby indicating that isomerisation of the latter did take place. The ^1H NMR spectrum, on the other hand, revealed the presence of two aldehydes in a 3:1 ratio as evidenced by the two resonances at δ 9.8 [d, *J* 9 Hz, 6-H (*Z*)] and 9.5 [d, *J* 8 Hz, 6-H (*E*)]. The presence of these aldehydes, which can only be located at C-6, was further substantiated by the IR absorption at 1 640–1 660 cm^{-1}. Two vinyl signals at δ 5.65 [m, $J_{5,6}$ 8 Hz, 5-H (*E*)] and 5.12 [m, $J_{5,6}$ 9 Hz, 5-H (*Z*)], the irradiation of which clearly showed coupling to the aldehyde protons, were assigned to 5-H. These data are consistent with two isomeric enal systems as a result of the (*E*)- and (*Z*)-configuration for the C-4–C-5 double bond. Assignment of each resonance to the (*E*)- or (*Z*)-isomer was based upon the literature precedents which indicate that the proton of an α,β-unsaturated aldehyde is more deshielded in the (*Z*)-isomer.[29] The olefinic protons of trisubstituted vinyl ethers,[30] or C-5–C-6 pyranosides[31] and C-4–C-5 furanosides,[32] have different chemical shifts depending on whether they are in a *cis* or *trans* relationship with the oxygen atom. In addition, protons 3-H_2 gave rise to a more complex set of signals as a consequence of their non-equivalence in the (*E*)-isomer. Indeed, the aldehyde which is closer to 3-H^β in the (*E*)-isomer is expected to have a more pronounced effect on its chemical shift, thus allowing assignment of each proton to be made.

Examination of the literature revealed that only one example of a similar rearrangement was known at the time this work was being conducted.[33] In an effort to gain some insight into the mechanism of this rather unusual rearrangement, we devised experiments based upon the use of regioselectively labelled allylic epoxides. Thus, when the epoxide (**24**) possessing two deuteriums at C-6 was treated with $Pd(PPh_3)_4$ the resulting aldehydes were shown by ^1H NMR and mass spectroscopy to have incorporated some deuterium at C-5. In addition, the use of epoxide (**24**) with a deuterium at C-5 led to the formation of aldehydes with some deuterium incorporation at C-3. Clearly, a 1,2-hydride shift (C-6 to C-5) had occurred, presumably through the sequence (**28**) ⟶ (**32**) depicted in Scheme 5, followed by a 1,3-hydride shift (C-5 to C-3). Competitive direct hydride transfer from C-6 to C-3 cannot, however, be ruled out at this point. Although this study did not provide unambiguous evidence for the proposed mechanism, due to deuterium scrambling, the migration of deuterium from C-6 to C-5 can only be accounted for if one assumes attack of the Pd(0) complex at C-5, a possibility consistent with the well known nucleophilic character of $Pd(PPh_3)_4$. Furthermore, such nucleophilic opening of epoxide by a palladium complex has been considered in a recent mechanistic study of the Pd(0)-catalysed rearrangement of α-epoxy ketones.[34]

Treatment of aldehydes (**33**) with di-isobutylaluminium hydride (DIBAH) in THF at −30 °C provided the allylic alcohols (**34**) in 94% isolated yield (Scheme 5). At this stage we were able to separate the (*E*)- and (*Z*)-isomer by silica gel chromatography. Subsequently, the mixture of alcohols (**34**) was transformed into the benzyl ethers (**35**). Hydrolysis of compounds (**35**) with formic acid led to the previously obtained



Scheme 6. *Reagents:* i, CI_4, PPh_3, pyridine; ii, allylstannane, Bu_3SnH, AIBN; iii, Tf_2O, pyridine; iv, DBU; v, 80% HCO_2H; vi, (*a*) 0.1 M-NaOH, (*b*), BzCl, pyridine.

mixture of keto aldehyde (**19**) and its hydrated form in 76% isolated yield.

Since (*R*)-4-benzyloxy-2-benzyloxymethylcyclopent-2-enone was previously transformed[23c] into the antibiotic (−)-pentenomycin I, the preparation of the hydroxycyclopentenone (**20**) by two different approaches constitutes a formal synthesis of this antibiotic.

In order to extend the scope of our strategy further, we embarked on the synthesis of yet another hydroxycyclopentenone, which would provide an access to allethrin, one of the pyrethrin[35] group of insecticides. This compound, which is one of the most powerful insecticides of this family, had been previously prepared by nucleophilic displacement of the mesyl group of (*R*)-2-allyl-4-mesyloxy-3-methylcyclopent-2-enone with the sodium salt of chrysanthemic acid.[36] Since our work has demonstrated that the esterification of (*R*)-4-hydroxycyclopentenones by a carboxylic acid does take place with inversion of configuration under Mitsunobu's conditions, we thought that (*R*)-2-allyl-4-hydroxycyclopent-2-enone (**43**) would be a useful intermediate to allethrin.

Access to compound (**43**) according to our general strategy rested upon the preparation of the extended-chain sugar (**41**) (Scheme 6). This compound was envisaged as arising from deoxyallylation at C-5 of 1,2-isopropylidene-α-D-xylofuranose (**36**). Recently, Keck *et al.*[37] have developed a method of allylation at C-6 of pyranosides based upon the use of a free-radical reaction. In order to obtain compound (**41**) by using this method, compound (**36**) was selectively transformed to the iodo sugar (**37**) by treatment with tetraiodomethane and pyridine.[38] Heating of the iodide (**37**) in refluxing toluene in the presence of allyltributylstannane[39] and a catalytic amount of AIBN afforded the extended-chain sugar (**38**) in 45% isolated yield along with the deoxy sugar (**39**) (24%) and 18% recovered starting material.

Compound (**38**) was then transformed into diene (**41**) in 84% overall yield using the trifluoromethane sulphonylation–elimination procedure previously described. Hydrolysis of the vinyl ether (**41**) as before gave the corresponding 2-hydroxy-4-keto aldehyde (**42**) and its hydrated form in 72% combined isolated yield. Intramolecular cyclisation of compound (**42**) gave the expected (*R*)-2-allyl-4-hydroxycyclopentenone (**43**) which was characterized as its *O*-benzoate (**44**) (20% overall yield).

In conclusion, in the course of this work we have been able to achieve the chiral synthesis of three different 2-substituted (*R*)-4-hydroxycyclopentenones which are valuable intermediates toward the preparation of such natural products as prostaglandin E_2 and the antibiotic (−)-pentenomycin I, as well as the synthetic insecticide allethrin. Also noteworthy here is the original Pd(0)-catalysed rearrangement of the vinylic oxirane (**24**) to α,β-unsaturated aldehydes (**33**) whose subsequent transformation provided a short route to the antibiotic (−)-pentenomycin I.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Jouan and Roussel Quick polarimeter. IR spectra (neat) were recorded on a Perkin-Elmer 297 spectrophotometer. ^1H NMR spectra were obtained with a Bruker W80 (80 MHz) (unless otherwise stated), in deuteriochloroform solution containing tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on Bruker WP60 or Bruker WM400 spectrometers. Chemical shifts (^1H and ^{13}C) are quoted in δ-values (ppm) relative to the reference [doubly primed numbers in the NMR attribution of compounds (**12**), (**21**), and (**44**) refer to the benzoate group]. Electron impact mass spectra (EIMS) including high-resolution (HR) were recorded on a KRATOS/AEI MS50, and a modified AEI MS9 instrument was used for recording the chemical ionisation mass spectra (CIMS) for which the indicated reactant gases were employed. TLC was conducted on 'F 1500 LS 2S4' (Schleicher & Schüll) precoated silica gel plates. Preparative TLC (PLC) was run on 20 × 20 cm plates with 1 mm thick layers. Silica gel columns for chromatography utilized E. Merck 'silicagel 60,' 70–230 mesh A.S.T.M. Solvents were distilled shortly before use from an appropriate drying agent. All reactions were run under an inert atmosphere (nitrogen) in oven-dried glassware which was cooled before use under a stream of dry nitrogen.

5,6-*Anhydro*-1,2-O-*isopropylidene*-3-O-(1-*methoxy*-1-*methyl ethyl*)-α-D-*glucofuranose* (**3**).—To a solution of the epoxide (**2**) (500 mg, 2.47 mmol) in dry dichloromethane (20 ml) was added 2-methoxypropene (720 mg, 10 mmol) with a catalytic amount of TFA. After 4 h at room temperature, the reaction mixture was diluted with dichloromethane (20 ml) and washed successively with saturated aqueous sodium hydrogen carbonate and brine. The organic phase was decanted and dried over sodium sulphate. Evaporation of the solvent afforded compound (**3**) (673 mg, quant.) as an oil, which was used in the next step without further purification; $[\alpha]_D^{20}$ − 46° (*c* 0.9 in $CHCl_3$); R_F 0.6 [hexane–ethyl acetate (3:2)]; δ 5.90 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.57 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.37 (1 H, d, $J_{3,4}$ 4 Hz, 3-H), 3.67 (1 H, dd, $J_{4,5}$ 7, $J_{4,3}$ 4 Hz, 4-H), 3.32 (4 H, s and m, OMe and 5-H), 2.82 (2 H, m, 6-H_2), and 1.5, 1.4, and 1.3 (12 H, together 4 s, 4 × Me) (HR, EIMS) *m/z* 259.1191 (6, M^+ − Me, $C_{12}H_{19}O_6$ requires *m/z* 259.1182) (CIMS, NH_3) *m/z* 292 (100, MNH_4^+) and 260 (40, MNH_4^+ − MeOH).

6-*Deoxy*-6-C-(1′,3′-*dithian*-2′-*yl*)-1,2-O-*isopropylidene*-3-O-(1-*methoxy*-1-*methyl ethyl*)-α-D-*glucofuranose* (**4**).—To a solution of purified 1,3-dithiane (1.8 g, 15 mmol) in dry THF (20 ml) cooled at −78 °C under nitrogen was added dropwise BuLi (11 ml of a 1.6M solution in hexane; 18 mmol). The reaction mixture was allowed to warm to −30 °C and the mixture was stirred for 2 h; the solution was then cooled to −78 °C and a solution of epoxide (**3**) (3.58 g, 13 mmol) in THF–HMPT [15 ml (1:2)] was added dropwise. The reaction mixture was gradually warmed to 0 °C, stirred at this temperature for further 2 h, and then poured into ice-cold brine and extracted with diethyl ether

(5 × 50 ml). Drying of the organic phase followed by evaporation under reduced pressure furnished compound (**4**) (5.765 g) as a slightly coloured thick syrup. An analytical sample of *compound* (**4**) was obtained by PLC [hexane–ethyl acetate (3:2)]; $[\alpha]_D^{20}$ − 8° (*c* 0.93 in $CHCl_3$); R_f 0.46 [hexane–ethyl acetate (3:2)]; δ 5.92 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.52 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.4–4.2 (3 H, m, 2'-, 5-, and 3-H), 4.0 (1 H, br d, 4-H), 3.75 (1 H, br d, OH), 3.3 (3 H, s, OMe), 2.9 (4 H, m, 4- and 6'-H_2), 2.1 (4 H, m, 5'- and 6-H_2), and 1.52, 1.42, and 1.32 (12 H, together 4 s, 4 × Me) (HR, EIMS) *m/z* 394.1489 (75, M^+, $C_{17}H_{30}O_6S_2$ requires *M*, 394.1484) 379 (60, M^+ − Me), 363 (32, M^+ − OMe), 322 (55, M^+ − C_4H_9O), 132 (100, $C_5H_8S_2^+$), and 119 (100, $C_4H_7S_2^+$).

6-*Deoxy*-6-C-(1',3'-*dithian*-2'-*yl*)-1,2-O-*isopropylidene*-5-O-*methylsulphonyl*-α-D-*glucofuranose* (**5**).—The residue (5.765 g) previously obtained was dissolved in dry chloroform (70 ml) and maintained under nitrogen. To this solution were added successively dry triethylamine (2.8 ml, 20 mmol), 4-(dimethylamino)pyridine (4-DMAP) (10 mg), and redistilled methanesulphonyl chloride (1.95 g, 17 mmol), dropwise. The reaction mixture was stirred for 2 h at 0 °C and then diluted with chloroform (50 ml); usual work-up afforded a crude mixture (6.3 g), which was dissolved in 100 ml chloroform–methanol (4:1, 100 ml). To this solution was added TFA (0.5 ml) and the mixture was stirred at room temperature for 1 h. The reaction mixture was treated with excess of solid sodium hydrogencarbonate for 0.15 h, then filtered and the filtrate was evaporated to dryness. Purification by column chromatography [chloroform–methanol (98:2)] furnished compound (**5**) [4.620 g, 90% from (**2**)] as a powder. An analytical sample of *compound* (**5**) was obtained by crystallisation from methanol; m.p. 135–138 °C (decomp.) (Found: C, 41.5; H, 6.0; S, 23.8. $C_{14}H_{24}O_7S_3$ requires C, 41.98; H, 6.04; S, 24.01%); $[\alpha]_D^{20}$ + 3° (*c* 1.0 in $CHCl_3$); R_F 0.6 [dichloromethane–methanol (98:2)]; δ 5.90 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.17 (1 H, dt, $J_{5,6}$ 4, $J_{5,4}$ 9 Hz, 5-H), 4.55 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.45–4.0 (4 H, m, OH, 3-H, 4-, and 2'-H), 3.2 (3 H, s, OMs), 2.87 (4 H, m, 4'- and 6'-H_2), 2.45–2.0 (4 H, m, 6- and 5'-H_2), and 1.5 and 1.32 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 400.0683 (30, M^+. $C_{14}H_{24}O_7S_3$ requires *M*, 400.0684).

5,6-*Dideoxy*-6-C-(1',3'-*dithian*-2'-*yl*)-1,2-O-*isopropylidene*-α-D-xylo-*hexofuranose* (**6**).—To a solution of the mesyl ester (**5**) (1.6 g, 4 mmol) in dry HMPT (12 ml) was added portionwise sodium borohydride (0.6 g, 17 mmol) under nitrogen. After being stirred overnight at 80 °C, the solution was cooled to 0 °C and neutralised by careful addition of 2M-aqueous hydrochloric acid. The reaction mixture was extracted with ethyl acetate (5 × 50 ml); the organic phase was dried and the ethyl acetate was evaporated off under reduced pressure. Purification of the remaining HMPT solution by chromatography [hexane–acetone (3:1)] afforded the *deoxy sugar* (**6**) (0.982 g, 80%) as a powder; m.p. 88 °C (Found: C, 50.95; H, 7.4; S, 20.9. $C_{13}H_{22}O_4S_2$ requires C, 50.97; H, 7.42; S, 20.93%); $[\alpha]_D^{20}$ − 7° (*c* 1.0 in $CHCl_3$); R_f 0.31 [hexane–acetone (3:1)]; δ 5.85 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.5 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.0 (3 H, m, 2'-, 3-, and 4-H), 3.82 (4 H, m, 4'- and 6'-H_2), 2.3 (1 H, m, OH), 2.25–1.82 (6 H, m, 5'-, 5-, and 6-H_2), and 1.44 and 1.25 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 306.0950 (35, M^+. $C_{13}H_{22}O_4S_2$ requires *M*, 306.0959).

5,6-*Dideoxy*-6-C-(1',3'-*dithian*-2'-*yl*)-1,2-O-*isopropylidene*-3-O-*trifluoromethylsulphonyl*-α-D-xylo-*hexofuranose* (**7**).—To a stirred solution of the alcohol (**6**) (0.940 g, 3.07 mmol) in dry chloroform (25 ml), cooled to −10 °C under nitrogen, was added dry pyridine (1 ml, 12.4 mmol) followed by trifluoromethanesulphonic anhydride (1.07 g, 3.8 mmol), dropwise. After 1 h the reaction mixture was washed successively with ice-cold 0.5M-aqueous HCl, saturated aq. $NaHCO_3$, and brine. The organic phase was dried and the solvent was evaporated off to yield a residue (1.570 g), which was purified by filtration over a short silica gel column (diethyl ether) to furnish triflate (**7**) (1.3 g, 97%) as an oil. An analytical sample of *triflate* (**7**) was obtained by crystallisation from pentane at 5 °C; m.p. 75 °C (Found: C, 38.3; H, 4.8; S, 21.7. $C_{14}H_{21}F_3O_6S_3$ requires C, 38.43; H, 4.82; S, 21.93%); $[\alpha]_D^{20}$ − 9° (*c* 9.5 in $CHCl_3$); R_f 0.5 [hexane–ethyl acetate (3:1)]; δ 6.0 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.12 (1 H, d, $J_{3,4}$ 3 Hz, 3-H), 4.75 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.35 (1 H, m, 4-H), 4.07 (1 H, m, 2'-H), 2.9 (4 H, m, 4'- and 6'-H_2), 2.0 (6 H, m, 5'-, 5-, and 6-H_2), and 1.55 and 1.35 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 438.0462 (90, M^+. $C_{14}H_{21}F_3O_6S_3$ requires *M*, 438.0452), 423 (85, M^+ − Me), and 273 (37, 423 − CF_3SO_2H).

3,5,6-*Trideoxy*-6-C-(1',3'-*dithian*-2'-*yl*)-1,2-O-*isopropylidene*-α-D-glycero-*hex*-3-*enofuranose* (**8**).—To a stirred solution of the triflate (**7**) (240 mg, 0.54 mmol) in dry diethyl ether (15 ml) maintained under dry nitrogen was added dropwise DBU (130 mg, 0.8 mmol). The reaction mixture was stirred overnight at room temperature, then diluted with diethyl ether (40 ml) and washed successively with ice-cold solutions of 0.05M-HCl, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure to afford the *enol ether* (**8**) (153 mg, 98%) as an oil. An analytical sample was obtained by crystallisation from pentane; m.p. 55 °C (Found: C, 54.2; H, 7.0; S, 22.0. $C_{13}H_{20}O_3S_2$ requires C, 54.13; H, 6.99; S, 22.23%); $[\alpha]_D^{20}$ − 4° (*c* 16.40 in $CHCl_3$); R_f 0.55 [hexane–ethyl acetate (4:1)]; δ 6.05 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 5.25 (1 H, br d, $J_{2,1}$ 5, $J_{2,3}$ 2 Hz, 2-H), 5.0 (1 H, d, $J_{3,2}$ 2 Hz, 3-H), 4.07 (1 H, t, $J_{2',6}$ 6 Hz, 2'-H), 2.87 (4 H, dd, J_{gem} 4, $J_{4',5'} = J_{6',5'}$ = 7 Hz, 4'- and 6'-H_2), 2.32 (2 H, m, 5-H_2), 2.05 (4 H, m, 5'- and 6-H_2), and 1.47 (6 H, s, 2 Me) (HR, EIMS) *m/z* 288.0859 (67, M^+. $C_{13}H_{20}O_3S_2$ requires *M*, 288.0854), 273 (8, M^+ − Me), 259 (16, M^+ − CHO), 230 (35, M^+ − Me_2CO), 145 (75, $C_6H_9S_2^+$), 132 (100, $C_5H_8S_2^+$), and 119 (77, $C_4H_7S_2^+$).

(R)-6-(1',3'-*Dithian*-2'-*yl*)-2-*hydroxy*-4-*oxo hexanal* (**9**).—Enol ether (**8**) (100 mg, 0.35 mmol) was dissolved in dry THF (3 ml) under a slow stream of nitrogen in the presence of a catalytic amount of hydroquinone. The solution was stirred and 80% aqueous formic acid (3 ml) was added dropwise. After 20 min at room temperature, the reaction mixture was cooled to 0 °C and neutralised by cautious addition of 4M-aqueous sodium hydroxide. Extraction with diethyl ether (3 × 20 ml) followed by usual work-up afforded a residue (90 mg), which was purified by silica gel chromatography. Elution with hexane–ethyl acetate (3:5) furnished the *aldehyde* (**9**) and its hydrated form (**10**) (57 mg, 66%) as an oil; R_f 0.38 and 0.28 [hexane–ethyl acetate (3:5)]; ν_{max}(neat) 3 400 (OH) and 1 650–1 700 cm^{-1} (CO, CHO); δ 9.7 (s, CHO), 4.0 (t, $J_{2',6}$ 7 Hz, 2'-H), 3.42 (m, 2-H), 2.82 (m, 3-, 5-, 4'-, and 6'-H_2), and 2.06 (m, 5'- and 6-H_2) (CIMS, NH_3) *m/z* 266 (100, MNH_4^+) and 249 (55, MH^+) (HR, EIMS) *m/z* 248.0536 (30, M^+. $C_{10}H_{16}O_3S_2$ requires *M*, 248.0540), 219 (5, M^+ − CHO), 175 (10, $C_7H_{11}OS_2^+$), 132 (100, $C_5H_8S_2^+$), and 119 (45, $C_4H_7S_2^+$).

(R)-2-[(1',3'-*Dithian*-2'-*yl*)*methyl*]-4-*hydroxycyclopent*-2-*enone* (**11**).—Hydroxy keto aldehyde (**9**)/(**10**) (100 mg) was dissolved in absolute ethanol (25 ml) in the presence of a catalytic amount of hydroquinone. The stirred solution was maintained under a slow stream of dry nitrogen and 0.1M-aqueous sodium hydroxide (8 ml) was added dropwise. After 4 h at ambient temperature the reaction mixture was acidified

(pH 3) at 0 °C by cautious addition of 2M-aq. HCl. Extraction with diethyl ether (3 × 25 ml) followed by usual work-up furnished a residue (95 mg), which was purified by silica gel column chromatography. Elution with hexane–ethyl acetate (1:1) gave the 4-*hydroxycyclopentenone* (**11**) (24 mg, 35%) as an oil; $[\alpha]_D^{20}$ + 7° (*c* 0.3 in $CHCl_3$); R_f 0.36 [diethyl ether–ethyl acetate (9:1)]; ν_{max} 3 400–3 500 (OH) and 1 670 cm^{-1} (CO); δ (400 MHz) 7.35 (1 H, br s, 3-H), 4.89 (1 H, m, 4-H), 4.19 (1 H, t, $J_{2',6}$ 7 Hz, 2'-H), 2.8 (5 H, m, 4'- and 6'-H_2, and 5-H^{β}), 2.64 (2 H, d, $J_{6,2'}$ 7 Hz, 6-H_2), 2.28 (1 H, dd, $J_{5\alpha,5\beta}$ 18, $J_{5\alpha,4}$ 2 Hz, 5-H^{α}), 2.05 (1 H, td, $J_{5'eq,5'ax}$ 14, $J_{5'eq,6'eq} = J_{5'eq,6'ax}$ = 4 Hz, 5'-H^{eq}), 1.98 (1 H, br s, OH), and 1.81 (1 H, dt, $J_{5'ax,5'eq} = J_{5'ax,6'ax}$ = 14, $J_{5'ax,6'eq}$ 6 Hz, 5'-H^{ax}) (HR, EIMS) *m/z* 230.0441 (80, M^+. $C_{10}H_{14}O_2S_2$ requires *M*, 230.0435) and 119 (100, $C_4H_7S_2^+$).

(R)-4-*Benzoyloxy*-2-[(1',3'-*dithian*-2'-*yl*)*methyl*]*cyclopent*-2-*enone* (**12**).—A solution of compound (**11**) (10 mg, 0.04 mmol) and benzoyl chloride (15 mg, 0.1 mmol) in dry pyridine (2 ml) was stirred overnight at room temperature under nitrogen. The reaction mixture was then diluted with diethyl ether (20 ml) and poured into ice–water; the organic phase was decanted and washed successively with aqueous 0.5M-HCl, saturated aq. $NaHCO_3$, and brine, then dried over sodium sulphate. Evaporation under reduced pressure gave a residue (40 mg), which was purified by silica gel column chromatography [hexane–ethyl acetate (3:1)] to provide the *benzoate* (**12**) (11 mg, 82%) as an oil; $[\alpha]_D^{20}$ + 52° (*c* 1.3 in $CHCl_3$); R_f 0.43 [hexane–ethyl acetate (3:1)]; δ (400 MHz) 8.0 (2 H, dd, $J_{2'',3''} = J_{6'',5''}$ = 8, $J_{2'',6''}$ 3 Hz, 2''- and 6''-H), 7.57 (1 H, t, $J_{4'',3''} = J_{4'',5''}$ = 8 Hz, 4''-H), 7.47 (1 H, d, $J_{3,4}$ 2.5 Hz, 3-H), 7.42 (2 H, t, $J_{3'',4''} = J_{3'',2''} = J_{5'',4''} = J_{5'',6''}$ = 8 Hz, 3''- and 5''-H), 6.02 (1 H, m, $J_{4,3}$ 2.5, $J_{4,5\beta}$ 6, $J_{4,5\alpha}$ 2 Hz, 4-H), 4.26 (1 H, t, $J_{2',6}$ 7 Hz, 2'-H), 2.98 (1 H, dd, $J_{5\beta,5\alpha}$ 18, $J_{5\beta,4}$ 6 Hz, 5-H^{β}), 2.8 (4 H, m, 4'- and 6'-H_2), 2.78 (1 H, dd, $J_{6a,6b}$ 14, $J_{6a,2'}$ 7 Hz, 6-H^a), 2.71 (1 H, dd, $J_{6b,6a}$ 14, $J_{6b,2'}$ 7 Hz, 6-H^b), 2.52 (1 H, dd, $J_{5\alpha,5\beta}$ 18, $J_{5\alpha,4}$ 2 Hz, 5-H^{α}), 2.09 (1 H, td, $J_{5'eq,5'ax}$ 14, $J_{5'eq,6'eq} = J_{5'eq,4'eq}$ = 4 Hz, 5'-H^{eq}), and 1.85 (1 H, dt, $J_{5'ax,5'eq} = J_{5'ax,6'ax}$ = 14, $J_{5'ax,6'eq}$ 6 Hz, 5'-H^{ax}) (HR, EIMS) *m/z* 334.0691 (78, M^+. $C_{17}H_{18}O_3S_2$ requires *M*, 334.0697), 212 (85, M^+ − $PhCO_2H$), 119 (100, $C_4H_7S_2^+$), and 105 (95, $PhCO^+$).

(S)-4-*Benzoyloxy*-2-[(1',3'-*dithian*-2'-*yl*)*methyl*]*cyclopent*-2-*enone* (**13**).—Hydroxycyclopentenone (**11**) (9 mg, 0.04 mmol), triphenylphosphine (20.5 mg, 0.08 mmol), and benzoic acid (9.5 mg, 0.08 mmol) were dissolved in dry THF (2 ml) under nitrogen. A solution of DEAD (13.6 mg, 0.08 mmol) in dry THF (2 × 0.2 ml) was added dropwise to the stirred mixture. After 2 h at room temperature the reaction mixture was taken up in diethyl ether (20 ml) and washed successively with saturated aq. $NaHCO_3$ and brine. Evaporation to dryness gave a residue, which was purified by PLC [hexane–ethyl acetate (3:1)]. The (S)-*benzoate* (**13**) (9 mg, 71%) was thus obtained as an oil; $[\alpha]_D^{20}$ − 53° (*c* 0.9 in $CHCl_3$). Spectral data (MS, NMR) of the title compound were identical with those of its enantiomer (**12**).

5,6-*Dideoxy*-1,2-O-*isopropylidene*-3-O-(1-*methoxy*-1-*methyl*-*ethyl*)-α-D-xylo-*hex*-5-*enofuranose* (**15**).—The unsaturated sugar (**14**) was treated with 2-methoxypropene as described previously to afford *compound* (**15**) as an oil in quantitative yield; $[\alpha]_D^{20}$ − 15° (*c* 1.4 in $CHCl_3$); R_f 0.46 [hexane–ethyl acetate (4:1)]; δ (60 MHz) 5.82 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.8 (1 H, dd, $J_{5,6}$ 18, $J_{5,6'}$ 9.5 Hz, 5-H), 5.15 (2 H, m, $J_{6,5}$ 18, $J_{6',5}$ 9.5 Hz, 6-H_2), 4.43 (2 H, m, 2- and 4-H), 4.12 (1 H, d, $J_{3,4}$ 3 Hz, 3-H), 3.10 (3 H, s, OMe), and 1.5, 1.33, and 1.29 (12 H, together 4 s, 4 Me) (CIMS, isobutane) *m/z* 259 (5, MH^+), 227 (52, MH^+ − MeOH), 201 (10, MH^+ − Me_2CO), and 169 (85, 227 − Me_2CO) (HR, EIMS) *m/z* 243.1238 (60, M^+ − Me. $C_{12}H_{19}O_5$ requires *m/z*, 243.1232), 227 (9, M^+ − OMe), 211 (52, 243 − MeOH), 185 (90, 243 − Me_2CO), 169 (100, 227 − Me_2CO), and 73 (100, $C_4H_9O^+$).

5-*Deoxy*-1,2-O-*isopropylidene*-3-(1-*methoxy*-1-*methyl ethyl*)-α-D-xylo-*hexofuranose* (**16**).—To a solution of the olefin (**15**) (2.170 g, 8.4 mmol) in dry THF (30 ml) at 0 °C was added dropwise 9-BBN (20 ml of a 0.5M solution in hexane; 10 mmol). The mixture was stirred overnight at room temperature under an inert atmosphere. The reaction mixture was cooled to 0 °C and excess of hydride was destroyed by addition of water (0.5 ml); oxidation was carried out by successive addition of aqueous 4M-sodium hydroxide (5 ml) and 30% hydrogen peroxide (7 ml); the mixture was stirred for 2 h at 50 °C, then cooled to ambient temperature and saturated with anhydrous potassium carbonate; the organic phase was decanted and dried. Evaporation of solvent furnished an oily residue (4.8 g), which was used in the next step without further purification. An analytical sample was obtained by PLC [diethyl ether–hexane (4:1)]; $[\alpha]_D^{20}$ − 9° (*c* 1.7 in $CHCl_3$); R_f 0.44 [diethyl ether–hexane (4:1)]; δ 5.9 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.5 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.26 (2 H, m, 3-, and 4-H), 3.87 (2 H, m, 6-H_2), 3.47 (3 H, s, OMe), 2.42 (1 H, br s, OH), 2.0 (2 H, m, 5-H_2), and 1.5, 1.37, and 1.32 (12 H, together 4 s, 4 × Me) (HR, EIMS) *m/z* 261.1331 (5, M^+ − Me. $C_{12}H_{21}O_6$ requires *m/z*, 261.1338), 245 (10, M^+ − OMe), 229 (32, 261 − MeOH), 187 (55, 245 − Me_2CO), 171 (60, 229 − Me_2CO), 129 (95, $C_6H_9O_3^+$), 100 (90, 129 − CHO), and 73 (100, $C_4H_9O_3^+$).

6-O-*Benzyl*-5-*deoxy*-1,2-O-*isopropylidene*-α-D-xylo-*hexofuranose* (**17a**).—The foregoing residue (4.8 g) was dissolved in dry dimethylformamide (DMF) (15 ml) under an inert atmosphere and to this stirred solution at 0 °C was added sodium hydride (0.59 g of a 55% dispersion in oil; 13.5 mmol) followed by benzyl bromide (2.15 g, 12.6 mmol). After being stirred overnight at room temperature, the mixture was poured into ice–water and extracted with diethyl ether (3 × 50 ml). Usual work-up furnished a residue (5.350 g), which was dissolved in chloroform–methanol (5:1). To this solution was added TFA (0.5 ml); after 1 h at ambient temperature, the reaction mixture was neutralised by addition of solid sodium hydrogen carbonate. Filtration and evaporation of the filtrate afforded a solid residue, which was purified by silica gel column chromatography [hexane–ethyl acetate (3:1)] to give *compound* (**17a**) [1.720 g, 74% from olefin (**14**)] as a powder; $[\alpha]_D^{20}$ + 21° (*c* 8.9 in $CHCl_3$); R_f 0.34 [hexane–ethyl acetate (3:1)]; m.p. 85 °C (Found: C, 65.3; H, 7.6. $C_{16}H_{22}O_5$ requires C, 65.29; H, 7.53%); δ 7.25 (5 H, s, Ph), 5.85 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.5 (3 H, d, $J_{2,1}$ 4 Hz, 2-H and CH_2Ph), 4.25 (1 H, dd, $J_{4,3}$ 3, $J_{4,5}$ 7 Hz, 4-H), 4.07 (1 H, t, $J_{3,4} = J_{3,OH}$ = 3 Hz, 3-H), 3.6 (2 H, m, 6-H_2), 3.17 (1 H, d, $J_{OH,3}$ 3 Hz, OH), 2.0 (2 H, m, 5-H_2), and 1.5 and 1.3 (6 H, together 2 s, 2 × Me) (EIMS) *m/z* 294 (55, M^+), 279 (90, M^+ − Me), 236 (20, M^+ − Me_2CO), 159 (20, oxonium), 107 (100, $PhCHOH^+$), and 91 (100, $C_7H_7^+$).

6-O-*Benzyl*-5-*deoxy*-1,2-O-*isopropylidene*-3-O-*trifluoro*-*methylsulphonyl*-α-D-xylo-*hexofuranose* (**17b**).—Alcohol (**17a**) was treated as previously described to afford the *triflate* (**17b**) (98%) as an oil; $[\alpha]_D^{20}$ + 3° (*c* 1.0 in $CHCl_3$); R_f 0.7 [hexane–ethyl acetate (7:1 v/v)]; δ 7.22 (5 H, s, Ph), 5.9 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.05 (1 H, d, $J_{3,4}$ 2 Hz, 3-H), 4.7 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.5 (3 H, m, 4-H, CH_2Ph), 3.57 (2 H, t, $J_{6,5}$ 6 Hz, 6-H_2), 2.0 (2 H, q, $J_{5,6} = J_{5,4}$ = 6 Hz, 5-H_2), and 1.5 and 1.3 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 426.0971 (7, M^+ $C_{17}H_{21}F_3O_7S$ requires *M*, 426.096).

6-O-*Benzyl*-3,5-*dideoxy*-1,2-O-*isopropylidene*-α-D-glycero-*hex*-3-*enofuranose* (**18**).—This *compound* was obtained in 98% yield after column chromatography [hexane–ethyl acetate (4:1)], using the triflate (**17b**) and the procedure employed for the preparation of compound (**8**); $[\alpha]_D^{20}$ + 4° (*c* 1.24 in $CHCl_3$); R_f 0.64 [hexane–acetone (4:1)]; δ 7.3 (5 H, s, Ph), 6.0 (1 H, d, $J_{1.2}$ 4 Hz, 1-H), 5.25 (1 H, dd, $J_{2.1}$ 4, $J_{2.3}$ 2 Hz, 2-H), 5.0 (1 H, d, $J_{3.2}$ 2 Hz, 3-H), 4.5 (2 H, s, CH_2Ph), 3.62 (2 H, d, $J_{6.5}$ 6 Hz, 6-H_2), 2.45 (2 H, t, $J_{5.6}$ 6 Hz, 5-H_2), and 1.42 (6 H, s, 2 × Me); δ_C(15.08 MHz) 160.07 (C-4), 138.46 (C-1′), 128.42 (C-3′ and -5′), 127.87 (C-2′, -4′, and -6′), 112.05 (CMe_2), 106.02 (C-1), 98.84 (C-3), 84.17 (C-2), 73.16 (CH_2Ph), 66.58 (C-6), 29.27 (C-5), 28.11 (Me), and 28.0 (Me) (HR, EIMS) *m/z* 276.1345 (1, M^+. $C_{16}H_{20}O_4$ requires *M*, 276.1361).

(R)-6-*Benzyloxy*-2-*hydroxy*-4-*oxohexanal* (**19**).—Enol ether (**18**) (630 mg, 2.28 mmol) was treated with 80% formic acid as described for compound (**9**); silica gel chromatography [hexane–ethyl acetate (3:7)] afforded the *title compound* along with its hydrated equivalent (352 mg, 65%); R_f 0.32 and 0.38 [hexane–ethyl acetate (3:5)]; ν_{max} 3 400 (OH) and 1 700–1 660 cm^{-1} (CO, CHO); δ 9.7 (s, CHO), 7.25 (s, Ph), 4.5 (s, CH_2Ph), 3.67 (t, $J_{6.5}$ 6 Hz, 6-H), 3.37 (d, 2-H), 2.92 (d, 3-H), and 2.7 (t, $J_{5.6}$ 6 Hz, 5-H); (CIMS, NH_3) *m/z* 254 (100, MNH_4^+) and 236 (35, MNH_4^+ − H_2O) (HR, EIMS) *m/z* 236.1054 (2, M^+. $C_{13}H_{16}O_4$ requires *M*, 236.1049), 218 (10, M^+ − H_2O), 207 (15, M^+ − CHO), 130 (80, M^+ − PhCHO), 107 (100, $PhCHOH^+$), 91 (100, $C_7H_7^+$), and 73 ($C_3H_5O_2^+$).

(R)-2-*Benzyloxymethyl*-4-*hydroxycyclopent*-2-*enone* (**20**).—The keto aldehyde (**19**) and its hydrated form (100 mg) were dissolved in absolute ethanol (20 ml) under a slow stream of nitrogen. To this stirred solution at 0 °C, was added during 10 min, aq. 0.1M-sodium hydroxide solution (15 ml). After 5 h at room temperature, the reaction mixture was acidified to pH 3 (2M-HCl) and then extracted with diethyl ether (3 × 30 ml). The extracts were combined and worked up as usual to leave a residue (112 mg), purification of which by silica gel chromatography [hexane–ethyl acetate (7:13)] furnished the *cyclopentenone* (**20**) (28 mg, 30%) as an oil; $[\alpha]_D^{20}$ + 12° (*c* 1.2 in $CHCl_3$); R_f 0.49 [hexane–ethyl acetate (3:7)]; δ (400 MHz) 7.43 (1 H, d, $J_{3.4}$ 2 Hz, 3-H), 7.33 (5 H, m, Ph), 4.95 (1 H, m, 4-H), 4.58 (2 H, s, CH_2Ph), 4.2 (2 H, d, $J_{6.3}$ 1.5 Hz, 6-H_2), 2.82 (1 H, dd, $J_{5\beta.5\alpha}$ 18, $J_{5\beta.4}$ 6.5 Hz, 5-H^β), 2.33 (1 H, dd, $J_{5\alpha.5\beta}$ 18, $J_{5\alpha.4}$ 2 Hz, 5-H^α), and 2.21 (1 H, br s, OH) (HR, CIMS, isobutane) *m/z* 219.1015 (100, MH^+. $C_{13}H_{15}O_3$ requires *m/z*, 219.1021), 201 (5, MH^+ − H_2O), 129 (80, $C_6H_9O_3^+$), and 91 (90, $C_7H_7^+$).

(R)-4-*Benzoyloxy*-2-*benzyloxymethyl* *cyclopent*-2-*enone* (**21**).—Benzoylation of compound (**20**) was carried out under standard conditions with benzoyl chloride and pyridine. Purification by PLC [hexane–ethyl acetate (4:1)] afforded the title compound (85%) as an oil; $[\alpha]_D^{20}$ + 58° (*c* 1.1 in $CHCl_3$); R_f 0.3 [hexane–ethyl acetate (4:1)]; ν_{max}(neat) 1 710 (CO, ketone and ester) and 1 260 cm^{-1} (CO ester); δ (400 MHz) 8.0 (2 H, dd, $J_{2'',3''} = J_{6'',5''} = 8$, $J_{2'',6''}$ 3 Hz, 2″- and 6″-H), 7.59 (2 H, m, $J_{3.4}$ 2, $J_{4'',3''} = J_{4'',5''} = 8$ Hz, 3″- and 4″-H), 7.45 (2 H, t, $J_{3'',4''} = J_{5'',4''} = J_{3'',2''} = J_{5'',6''} = 8$ Hz, 3- and 4″-H), 7.33 (5 H, m, CH_2Ph), 6.05 (1 H, m, $J_{4.3}$ 2, $J_{4.5\alpha}$ 2.5, $J_{4.5\beta}$ 6 Hz, 4-H), 4.6 (2 H, s, CH_2Ph), 4.27 (2 H, s, 6-H_2), 3.0 (1 H, dd, $J_{5\beta.5\alpha}$ 18, $J_{5\beta.4}$ 6 Hz, 5-H^β), and 2.55 (1 H, dd, $J_{5\alpha.5\beta}$ 18, $J_{5\alpha.4}$ 2.5 Hz, 5-H^α); δ_C (100.62 MHz) 203.4 (C-1), 166.2 (CO ester), 153.2 (C-3), 147.2 (C-2), 137.72 (C-1′), 133.52 (C-4″), 129.85 (C-6″, -2″), 129.62 (C-1″), 128.61 (C-4′, -3″, -5″), 128.05 and 127.92 (C-2′, -6′, -3′, -5′), 73.6 (C-4), 71.05 (CH_2Ph), 64.05 (C-6), and 42.2 (C-5) (EIMS) *m/z* 216 (85, M^+ − PhCHO), 94 (100, $C_6H_6O^+$), and 91 (90, $C_7H_7^+$) (CIMS, isobutane) *m/z* 323 (100, MH^+) and 95 (100, $C_6H_7O^+$).

(S)-4-*Benzoyloxy*-2-*benzyloxymethylcyclopent*-2-*enone* (**22**).—The (*S*)-benzoate (**22**) was prepared from compound (**20**) according to the procedure described for compound (**13**). Purification by PLC [hexane–ethyl acetate (4:1)] gave the *title compound* (74%) as an oil; $[\alpha]_D^{20}$ − 62° (*c* 1.2 in CH_2Cl_2). Spectral data (MS, NMR) of compound (**22**) were identical with those of its enantiomer (**21**).

5,6-*Anhydro*-1,2-O-*isopropylidene*-3-O-*trifluoromethylsulphonyl*-α-D-*glucofuranose* (**23**).—The epoxide (**2**) (500 mg, 2.47 mmol) was treated with trifluoromethanesulphonic anhydride as previously described [see compound (**7**)]. Filtration over a short column of silica gel [hexane–ethyl acetate (3:1)] afforded the triflate (**23**) (718 mg, 87%) as an oil; $[\alpha]_D^{20}$ − 32° (*c* 1.0 in CH_2Cl_2); R_f 0.55 [hexane–ethyl acetate (3:1)]; δ (60 MHz) 5.86 (1 H, d, $J_{1.2}$ 4 Hz, 1-H), 5.16 (1 H, d, $J_{3.4}$ 3 Hz, 3-H), 4.66 (1 H, d, $J_{2.1}$ 4 Hz, 2-H), 3.93 (1 H, dd, $J_{4.5}$ 6, $J_{4.3}$ 3 Hz, 4-H), 3.1 (1 H, m, 5-H), 2.83 (2 H, t, 6-H_2), and 1.5 and 1,35 (6 H, together 2 s, 2 × Me) (CIMS, NH_3) *m/z* 352 (100, MNH_4^+) (HR, EIMS) *m/z* 319.0094 (21, M^+ − Me. $C_9H_{10}F_3O_7S$ requires *m/z* 319.0099).

5,6-*Anhydro*-3-*deoxy*-1,2,O-*isopropylidene*-α-D-erythro-*hex*-3-*enofuranose* (**24**).—This was prepared from the triflate (**23**) by the method previously described [see compound (**8**)]; the *vinyl oxirane* (**24**) was obtained in 94% yield as an oil; $[\alpha]_D^{20}$ + 9° (*c* 1.0 in $CHCl_3$); R_f 0.35 [pentane–diethyl ether (3:1)]; δ 6.05 (1 H, d, $J_{1.2}$ 4 Hz, 1-H), 5.28 (2 H, m, $J_{2.1}$ 4 Hz, 2- and 3-H), 3.38 (1 H, t, $J_{5.6}$ 3 Hz, 5-H), 2.93 (2 H, d, $J_{6.5}$ 3 Hz, 6-H_2), and 1.37 (6 H, s, 2 × Me); δ_C(15.08 MHz) 158.06 (C-4), 112.72 (CMe_2), 106.63 (C-1), 101.70 (C-3), 83.50 (C-2), 46.98 and 46.05 (C-5 and -6), 28.24 (Me), and 27.94 (Me) (HR, EIMS) *m/z* 184.0742 (6, M^+. $C_9H_{12}O_4$ requires *M*, 184.0736).

3,5-*Dideoxy*-1,2-O-*isopropylidene*-α-D-glycero-*hex*-3-*enofuranose* (**27**).—A stirred solution of the allylic epoxide (**24**) (72 mg, 0.39 mmol) in dry benzene (3 ml) was refluxed under nitrogen. To this solution was added AIBN (5 mg) and (dropwise) a solution of Bu_3SnH (238 mg, 0.82 mmol) in dry benzene (1 ml). After 2 h at reflux temperature the reaction mixture was evaporated to dryness. Purification by column chromatography [hexane–ethyl acetate (4:1)] furnished *compound* (**27**) (23 mg, 32%) as an oil; $[\alpha]_D^{20}$ 0° (*c* 1.0 in $CHCl_3$); R_f 0.27 [hexane–ethyl acetate (3:1)]; δ 6.05 (1 H, d, $J_{1.2}$ 4 Hz, 1-H), 5.27 (1 H, dd, $J_{2.1}$ 4, $J_{2.3}$ 2 Hz, 2-H), 5.02 (1 H, d, $J_{3.2}$ 2 Hz, 3-H), 3.80 (2 H, t, $J_{6.5}$ 6 Hz, 6-H_2), 2.45 (2 H, t, $J_{5.6}$ 6 Hz, 5-H_2), 2.0 (1 H, br s, OH), and 1.47 (6 H, s, 2 × Me); δ_C(15.08 MHz) 160.07 (C-4), 112.17 (CMe_2), 106.14 (C-1), 99.27 (C-3), 83.93 (C-2), 59.65 (C-6), 31.83 (C-5), 28.12 (Me), and 27.87 (Me) (HR, EIMS) *m/z* 186.0915 (2, M^+. $C_9H_{14}O_4$ requires *M*, 186.0892).

3,5-*Dideoxy*-1,2-O-*isopropylidene*-α-D-glycero-*hex*-4-*enodialdofuranose*-(1,4) (**33**).—A solution of the allylic epoxide (**24**) (600 mg, 3.26 mmol) in dry dichloromethane (20 ml) was cooled to 0 °C under nitrogen. To this solution was added $Pd(PPh_3)_4$ (20 mg, 0.018 mmol) and the mixture was stirred overnight at room temperature. The solvent was then evaporated off under reduced pressure and the residue was filtered over a short pad of silica gel (diethyl ether) to afford the isomeric *aldehydes* (**33**) (512 mg, 85%) as an oil, in a 3:1 ratio (^{1}H NMR); R_f 0.40 and 0.37 (diethyl ether); ν_{max}(neat) 1 660–1 640 cm^{-1} (CHO); δ 9.8 [0.3 H, d, $J_{6.5}$ 9 Hz, (*Z*) 6-H], 9.5 [0.7 H, d, $J_{6.5}$ 8 Hz, (*E*) 6-H], 6.17 [d $J_{1.2}$ 3 Hz, (*Z*) 1-H], 6.10 [d, $J_{1.2}$ 3 Hz, (*E*) 1-H], 5.65 [m, $J_{5E.6E}$ 8 Hz, (*E*) 5-H], 5.12 [m, $J_{5Z.6Z}$ 9 Hz, (*Z*) 5-H], 4.95–4.72 [m, $J_{2.1}$ 3, $J_{2.3\beta}$ 4 Hz, (*Z*) and (*E*) 2-H], 3.53 [d, $J_{3\alpha.3\beta}$ 18 Hz, (*E*) 3-H^α], 3.22–2.87 [ddd, $J_{3\beta.3\alpha}$ 18, $J_{3\beta.2}$ 4, $J_{3\beta.5}$ 2 Hz, (*E*) 3-H^β], 3.0 [d, $J_{3Z.2}$ 4 Hz, (*Z*) 3-H_2], and 1.47 and 1.45 (2 s,

2 × Me). Assignment of protons 1-H (*E*) and 1-H (*Z*) and 2-H (*Z*) resulted from decoupling experiments; (HR, EIMS) *m/z* 184.0743 (100, M^+. $C_9H_{12}O_4$ requires *M*, 184.0736), 169 (65, M^+ − Me), 155 (15, M^+ − CHO), 127 (43, 169 − CH_2CO), 126 (35, M^+ − Me_2CO), and 109 (52, 127 − H_2O).

3,5-*Dideoxy*-1,2-O-*isopropylidene*-α-D-glycero-*hex*-4-*enofuranose* (**34**).—Aldehydes (**33**) (110 mg, 0.59 mmol) were dissolved in dry THF (5 ml) under an inert atmosphere. The solution was cooled to −78 °C and DIBAH (102 mg, 0.72 mmol) was added dropwise. The reaction mixture was warmed to −30 °C and the mixture was stirred at this temperature for 0.5 h; excess of hydride was then destroyed by addition of dry methanol (2 ml). After 1 h at room temperature the suspension was filtered through a short pad of Celite and the filtrate was evaporated to dryness. Silica gel chromatography of the residue (105 mg) (diethyl ether) afforded each of the (*E*) and (*Z*) isomeric alcohols (**34**) in 82% total yield: (Z)-*isomer*; $[\alpha]_D^{20}$ −83° (*c* 1.1 in CH_2Cl_2); R_f 0.48 (diethyl ether); δ 5.94 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.68 (1 H, t, $J_{2,1} = J_{2,3\beta}$ = 4 Hz, 2-H), 4.6 (1 H, br t, $J_{5,6}$ 8 Hz, 5-H), 4.16 (2 H, d, $J_{6,5}$ 8 Hz, 6-H_2), 2.68 (2 H, m, $J_{3\beta,2}$ 4 Hz, 3-H_2), 1.74 (1 H, br s, OH), and 1.41 and 1.32 (6 H, together 2 s, 2 × Me); (HR, EIMS) *m/z* 186.0886 (50, M^+. $C_9H_{14}O_4$ requires *M*, 186.0892), 171 (100, M^+ − Me), 153 (7, 171 − H_2O), and 111 (40, 153 − CH_2CO).

(E)-*Isomer*; $[\alpha]_D^{20}$ − 22° (*c* 2.3 in CH_2Cl_2); R_f 0.42 (Et_2O); δ 5.92 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.15 (1 H, t, $J_{5,6}$ 8 Hz, 5-H), 4.77 (1 H, t, $J_{2,1} = J_{2,3\beta}$ = 4 Hz, 2-H), 4.06 (2 H, d, $J_{6,5}$ 8 Hz, 6-H_2), 3.0 (1 H, d, $J_{3\alpha,3\beta}$ 18 Hz, 3-H^α), 2.62 (1 H, ddd, $J_{3\beta,3\alpha}$ 18, $J_{3\beta,2}$ 4, $J_{3\beta,5}$ 2 Hz, 3-H^β), 1.57 (1 H, s, OH), and 1.5 and 1.4 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 186.0889 (52, M^+), 171 (100, M^+ − Me), 153 (5, 171 − H_2O), and 111 (50, 153 − CH_2CO).

6-O-*Benzyl*-3,5-*dideoxy*-1,2-O-*isopropylidene*-α-D-glycero-*hex*-4-*enofuranose* (**35**).—Sodium hydride (120 mg of a 55% dispersion in oil; 2.75 mmol) in a two-necked flask was washed with dry hexane under nitrogen. Anhydrous DMF (1.5 ml) was added and the suspension was cooled to 0 °C; a solution of alcohols (**34**) (100 mg, 0.54 mmol) in dry DMF (2 × 1 ml) was then added dropwise. The reaction mixture was stirred for 10 min and benzyl bromide (290 mg, 1.7 mmol) was added dropwise. The cooling bath was removed and the mixture was stirred overnight at room temperature. Dilution with diethyl ether (20 ml) followed by usual work-up furnished a residue, which was purified by silica gel chromatography [hexane–ethyl acetate (85:15)] to afford the isomeric *benzyl ethers* (**35**) (119 mg, 80%); R_f 0.27 [hexane–ethyl acetate (85:15)]; δ 7.4 (5 H, s, Ph), 6.0 (1 H, t, $J_{1,2}$ 4 Hz, 1-H), 4.85–4.7 (2 H, m, $J_{2,1}$ 4 Hz, 2- and 5-H), 4.6 (2 H, s, CH_2Ph), 4.23 (1 H, d, $J_{6,5}$ 8 Hz, 6-H), 4.0 (1 H, d, $J_{6',5}$ 8 Hz, 6-H'), 2.8 (2 H, m, 3-H), and 1.5 and 1.37 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 276.1367 (6, M^+. $C_{16}H_{20}O_4$ requires *M*, 276.1362), 261 (28, M^+ − Me), 247 (5, M^+ − CHO), 218 (22, M^+ − Me_2CO), 170 (95, M^+ − PhCHO), 169 (60, M^+ − $PhCH_2O$), 155 (45, 170 − Me), and 91 (100, $C_7H_7^+$).

5-*Deoxy*-5-*iodo*-1,2-O-*isopropylidene*-α-D-*xylofuranose* (**37**).—Compound (**36**) (73 mg, 0.38 mmol) and triphenylphosphine (300 mg, 1.14 mmol) were dissolved in dry pyridine (5 ml) under a stream of nitrogen. To the vigorously stirred solution at 0 °C was added tetraiodomethane (300 mg, 0.6 mmol) portionwise. The resulting yellow suspension was heated at 60 °C for 1.5 h. Anhydrous methanol (3 ml) was added to the resulting solution and the mixture was heated for a further 30 min; after cooling to room temperature the reaction mixture was filtered and the filtrate was evaporated to dryness. Silica gel column chromatography of the residue (535 mg) [hexane–acetone (3:1)] afforded *compound* (**37**) (105 mg, 91%) as a powder; $[\alpha]_D^{20}$ −38° (*c* 1.07 in $CHCl_3$) (Found: C, 31.8; H, 4.5. $C_8H_{13}IO_4$ requires C, 32.01; H, 4.36%); δ (60 MHz) 5.86 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.50 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.33 (2 H, m, $J_{4,5}$ 6 Hz, 4-H), 3.23 (2 H, d, $J_{5,4}$ 6 Hz, 5-H_2), 2.17 (1 H, br s, OH), and 1.47 and 1.27 (6 H, together 2 s, 2 × Me) (EIMS) *m/z* 300 (5, M^+), 285 (82, M^+ − Me), 267 (15, 285 − H_2O), and 159 (10, oxonium).

5,6,7,8-*Tetradeoxy*-1,2-*isopropylidene*-α-D-xylo-*oct*-7-*enofuranose* (**38**).—Compound (**37**) (250 mg, 1 mmol) was dissolved in dry toluene (1.5 ml) and the solution was degassed by nitrogen bubbling for 30 min. Allylstannane (660 mg, 2 mmol) and AIBN (25 mg, 0.15 mmol) were successively added and the mixture was stirred overnight at 80 °C. After evaporation of the solvent the residue was taken up in acetonitrile (10 ml) and the tin by-products were removed by extraction with hexane (2 × 10 ml). The acetonitrile phase was decanted and evaporated to dryness; purification by silica gel chromatography [diethyl ether–hexane (1:1)] afforded compound (**38**) (96 mg, 45%) as a powder; starting material (**37**) and the reduced product (**39**) were also isolated in 18 and 24% yield respectively; *compound* (**38**) had m.p. 57–58 °C (Found: C, 61.5; H, 8.35. $C_{11}H_{18}O_4$ requires C, 61.66; H, 8.47%); $[\alpha]_D^{20}$ −25° (*c* 1.0 in $CHCl_3$); R_f 0.5 [diethyl ether–hexane (1:1)]; δ (400 MHz) 5.88 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.88–5.77 (1 H, m, 7-H), 5.07 (1 H, ddd, $J_{8',7}$ 18, $J_{8',8}$ 3, $J_{8',6}$ 1.5 Hz, 8-H'), 4.98 (1 H, ddd, $J_{8,7}$ 10 Hz, 8-H), 4.5 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.11 (1 H, dt, $J_{4,5}$ 4, $J_{4,3}$ 3 Hz, 4-H), 4.04 (1 H, d, $J_{3,4}$ 3 Hz, 3-H), 2.25–2.06 (3 H, m, 6-H_2, and OH), and 1.43 and 1.26 (6 H, together 2 s, 2 × Me); δ_C(15.08 MHz) 138.04 (C-7), 115.39 (C-8), 111.62 (CMe_2), 104.38 (C-1), 85.51 (C-2), 79.91 (C-4), 75.41 (C-3), 30.19 (C-6), 26.90 (C-5), 26.66 (Me), and 26.33 (Me) (CIMS, isobutane) *m/z* 215 (100, MH^+) and 157 (30, MH^+ − Me_2CO) (HR, EIMS) *m/z* 199.0962 (45, M^+ − Me. $C_{10}H_{15}O_4$ requires *m/z*, 199.0970), 172 (15, M^+ − C_3H_6), and 159 (20, oxonium).

5,6,7,8-*Tetradeoxy*-1,2-O-*isopropylidene*-3-O-*trifluoromethylsulphonyl*-α-D-xylo-*oct*-7-*enofuranose* (**40**).—The procedure described for the preparation of compound (**7**) was employed with compound (**38**) to afford *compound* (**40**) (90%) after silica gel column chromatography [hexane–ethyl acetate (4:1)] as an oil; $[\alpha]_D^{20}$ − 10° (*c* 5.5 in CH_2Cl_2); R_f 0.54 [hexane–acetone (9:1)]; δ 5.95 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 6.0–5.55 (1 H, m, $J_{7,8'}$ 18, $J_{7,8}$ 10 Hz, 7-H), 5.26–4.83 (3 H, m, $J_{8',7}$ 18, $J_{8,7}$ 10, $J_{8,8'}$ 2 Hz, 8-H_2 and 3-H), 4.7 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 4.56–4.23 (1 H, m, 4-H), 2.53–2.10 (2 H, m, 6-H_2), 2.0–1.56 (2 H, m, 5-H_2), and 1.5 and 1.32 (6 H, together 2 s, 2 × Me) (HR, EIMS) *m/z* 346.0693 (5, M^+. $C_{12}H_{17}F_3O_6S$ requires *M*, 346.0698), 331 (100, M^+ − Me) 304 (15, M^+ − C_3H_6), 291 (50, oxonium), 281 (18, 331 − C_3H_6), and 233 (oxonium − Me_2CO).

3,5,6,7,8-*Pentadeoxy*-1,2-O-*isopropylidene*-α-D-glycero-*octa*-3,7-*dienofuranose* (**41**).—Elimination of trifluoromethanesulphonic acid was carried out as previously described; silica gel chromatography [hexane–ethyl acetate (95:5)] furnished the *unsaturated sugar* (**41**) (93%) as an oil; $[\alpha]_D^{20}$ − 2° (*c* 2.4 in CH_2Cl_2); R_f 0.58 [hexane–ethyl acetate (92:8)]; δ 6.0 (1 H, d, $J_{1,2}$ 5 Hz, 1-H), 5.95–5.60 (1 H, m, $J_{7,8'}$ 18, $J_{7,8}$ 10 Hz, 7-H), 5.22 (1 H, dd, $J_{2,1}$ 5, $J_{2,3}$ 2 Hz, 2-H), 5.0 (1 H, dd, $J_{8',7}$ 18, $J_{8',8}$ 2 Hz, 8-H'), 4.95 (1 H, dd, $J_{8,7}$ 10, $J_{8,8'}$ 2 Hz, 8-H), 4.87 (1 H, d, $J_{3,2}$ 2 Hz, 3-H), 2.25 (4 H, m, 5- and 6-H_2), and 1.42 (6 H, s, 2 × Me) (HR, EIMS) *m/z* 196.1102 (2, M^+. $C_{11}H_{16}O_3$ requires *M*, 196.1099), 181 (75, M^+ − Me), 167 (100, M^+ − CHO), and 139 (30, 181 − CH_2CO).

2-*Hydroxy*-4-*oxo*-*oct*-7-*enal* (**42**).—The title compound and its hydrated form were obtained in 72% yield from the enol

ether (**41**) following the procedure previously described [see compound (**9**)]; R_f 0.37 and 0.34 [hexane–ethyl acetate (3:5)] (EIMS) *m/z* 127 (90, $M^+ - CHO$), 101 (40, $C_4H_5O_3^+$), 85 (100, $C_5H_7O^+$), 73 (80, $C_3H_5O_2^+$), 55 (85, $C_4H_7^+$), and 41 (85, $C_3H_5^+$).

(R)-2-*Allyl*-4-*benzoyloxycyclopent*-2-*enone* (**44**).—A solution of the keto aldehyde (**42**) (40 mg) and hydroquinone (2 mg) in absolute ethanol (15 ml) was stirred at ambient temperature under dry nitrogen. 0.1M-Aqueous sodium hydroxide (8 ml) was added slowly (15 min) and the mixture was stirred for 5 h. The reaction mixture was cooled to 0 °C and acidified to pH 3 (2M-HCl). Extraction with diethyl ether (2 × 25 ml) and usual work-up furnished a residue (34 mg), which was dissolved in dry pyridine (3 ml) and treated overnight with benzyloyl chloride (1.2 mol equiv.). The reaction mixture was diluted with diethyl ether (20 ml): usual work-up followed by silica gel chromatography [hexane–ethyl acetate (4:1)] afforded *compound* (**44**) [13 mg, 20% from (**41**)] as an oil; $[\alpha]_D^{20}$ + 50° (*c* 0.5 in CH_2Cl_2); R_f 0.57 [hexane–ethyl acetate (4:1)]; ν_{max}(neat) 1 710 (CO) and 1 260 cm^{-1} (CO ester); δ(400 MHz) 8.0 (2 H d, $J_{2'',3''} = J_{6'',5''}$ = 8 Hz, 2″- and 6″-H), 7.56 (1 H, t, $J_{4'',3''} = J_{4'',5''}$ = 8 Hz, 4″-H), 7.43 (2 H, t, $J_{3'',4''} = J_{3'',2''} = J_{5'',3''} = J_{5'',6''}$ = 8 Hz, 3″- and 5″-H), 7.3 (1 H, d, $J_{3,4}$ 2 Hz, 3-H), 6.0 (1 H, m, $J_{4,5\beta}$ 6, $J_{4,5\alpha} = J_{4,3}$ = 4 Hz, 4-H), 5.86 (1 H, m, $J_{7,8'}$ 17, $J_{7,8}$ 10, $J_{7,6}$ 7 Hz, 7-H), 5.14 (1 H, dd, $J_{8',7}$ 17, $J_{8',8}$ 2 Hz, 8-H′), 5.12 (1 H, dd, $J_{8,7}$ 10, $J_{8',8}$ 2 Hz, 8-H), 3.0 (3 H, m, $J_{5\beta,5\alpha}$ 18, $J_{5\beta,4}$ 6, $J_{6,7}$ 7 Hz, 5-H^β and 6-H_2), and 2.54 (1 H, dd, $J_{5\alpha,5\beta}$ 18, $J_{5\alpha,4}$ 2 Hz, 5-H^α); δ_C(100.62 MHz) 166.33 (ester CO), 152.56 (C-3), 148-54 (C-2), 133.51 and 133.45 (C-4″, and -7), 129.85 (C-2″ and -6″), 129.75 (C-1″), 128.62 (C-3″ and -5″), 117.82 (C-8), 71.06 (C-4), 41.76 (C-5), and 29.24 (C-7) (HR, EIMS) *m/z* 242.0934 (100, M^+. $C_{15}H_{14}O_3$ requires *M*, 242.0943).

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