Woodward−Prevost Reactions of 1,7-Dioxaspiro[5.5]undec-4-enes†

Margaret A. Brimble*,‡ and Michael R. Nairn§

School of Chemistry, University of Sydney, New South Wales 2006, Australia, and Department of Chemistry, Massey University, Palmerston North, New Zealand

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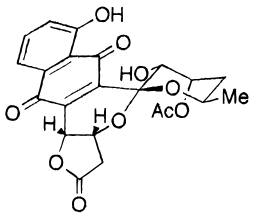
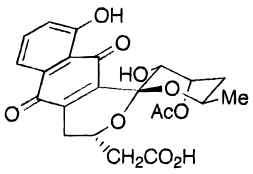
The synthesis of spiroacetals has attracted considerable synthetic interest due to their presence in a wide range of biologically active natural products such as polyether antibiotics, marine and plant toxins, and the antiparasitic agents the avermectins and milbemycins.[1] Many of these spiroacetals, notably the fruit fly pheromones[2] and the avian toxins, the talaromycins,[3] contain hydroxylated 1,7-dioxaspiro[5.5]undecane ring systems. Griseusins A (**1**) and B (**2**), produced by a strain of



Griseusin A **1**



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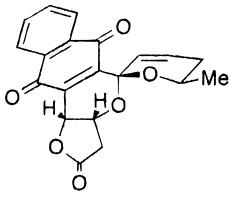

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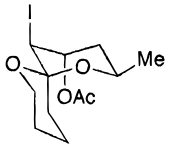

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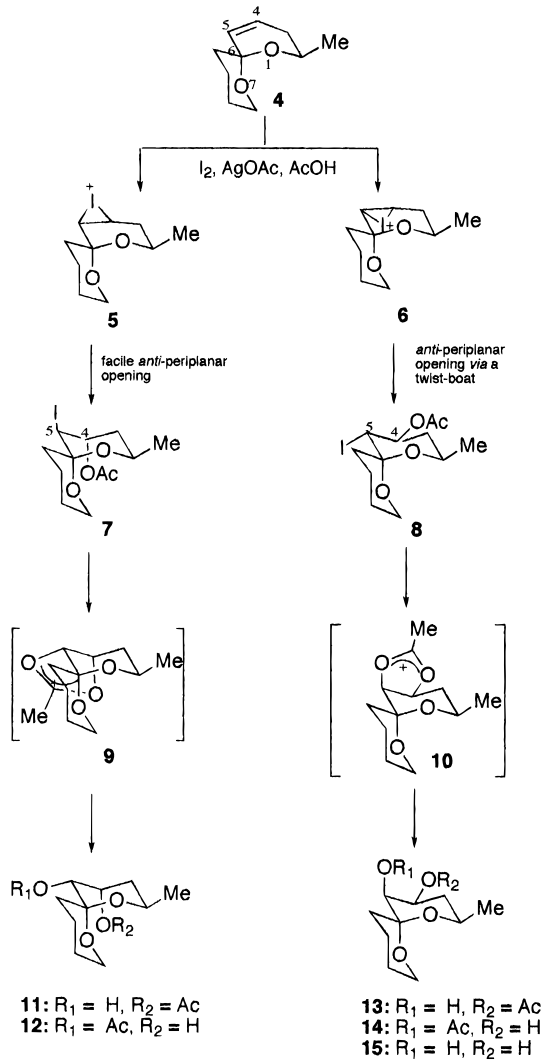
Streptomyces griseus, are members of the pyranonaphthoquinone family of antibiotics and are active against Gram-positive bacteria, pathogenic fungi, and yeasts.[4] Another distinguishing feature of these antibiotics is the presence of an oxygenated 1,7-dioxaspiro[5.5]undecane ring system. Our synthetic approach to the griseusins hinged on a stereoselective hydroxylation of unsaturated spiroacetal **3**; thus, an examination of the hydroxylation of simpler 1,7-dioxaspiro[5.5]undec-4-enes using Woodward−Prevost[5] methodology (Scheme 1) is reported herein. To date there has been no study of this reaction on a spiroacetal ring system.

Scheme 1



Our earlier work[6] focused on the *syn*-hydroxylation of a series of 1,7-dioxaspiro[5.5]undec-4-enes using osmium tetraoxide under catalytic conditions and *N*-methylmorpholine *N*-oxide as reoxidant. Hydroxylation using these reagents proceeded stereoselectively, affording diols in which the hydroxyl group at C-5 is axial and *anti* to the C−O bond of the neighboring ring; thus, olefin **4** afforded diol **15** in high yield. The stereochemical outcome of this reaction can be rationalized on steric grounds, in that the electrophile attacked the less hindered face of the olefin and is also consistent with the empirical rule proposed by Kishi *et al.*[7] for hydroxylation of allylic systems. Unfortunately, the stereochemistry obtained in this case was opposite to that required for the synthesis of griseusin A (**1**), and an alternative method was sought to effect the hydroxylation of olefin **4** from the required α-face.

Results and Discussion

Our attention therefore turned to the Woodward−Prevost[5] *syn*-hydroxylation of this spiroacetal ring system in an effort to effect stereoselective hydroxylation from the more hindered α-face (Scheme 1). It was envisaged

* To whom correspondence should be addressed. Fax: +61 2 351 3329. E-mail: brimble_m@alf.chem.su.oz.au.

† Dedicated to Clayton H. Heathcock on the occasion of his 60th birthday.

‡ University of Sydney.

§ Massey University.

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that treatment of olefin **4** with iodine and silver(I) acetate would effect iodination from the less hindered β-face followed by opening of the iodonium ion **5** by attack of acetate at C-4 to afford iodo acetate **7** which would then form a cyclic acetoxonium intermediate **9** due to anchimeric assistance from the acetate group combined with the powerful affinity of the silver ion for iodide. Addition of water cleaves the five-membered ring to the hydroxy acetates **11** and **12** resulting in overall hydroxylation of the more hindered α-face as required.

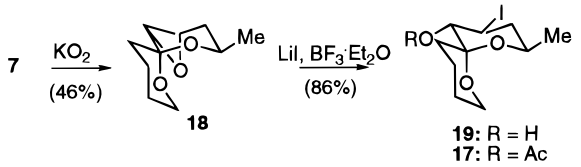
Treatment of spiroacetal **4** with iodine and silver(I) acetate in aqueous acetic acid afforded iodo acetates **7**, **8**, and **16** in the ratio 11:4:3 in 71% combined yield which were separable by flash chromatography. The major product, iodo acetate **7**, arises from approach of electrophilic iodine to the less hindered β-face of the olefin followed by *trans*-diaxial opening of the β-iodonium ion whereas iodo acetate **8** arises from attack at the more hindered α-face and subsequent cleavage of the iodonium ion **6**, presumably *via* a twist-boat conformation.

The third iodo acetate **16** arises from ring opening of the spiroacetal ring of iodo acetate **7** to form a planar carbocation followed by ring closure onto the opposite face of C-6. The transformation of **7** to **16** results in the loss of a stabilizing anomeric effect at the spiro center. However, 4-OAc and O-7 are no longer 1,3-diaxial in **16**; thus, a possible driving force may well be the decrease in overall dipole moment upon conversion of **7** to **16**. Variation in the reaction time (15 min to 24 h) did not alter the 11:4:3 ratio of **7**:**8**:**16**.

The *trans*-diaxial coupling between 4-H and 5-H in iodo acetate **8** allowed assignment of the relative stereochemistry between these two protons. 4-H resonated as a double double doublet at δ_H 5.31 ($J_{4ax,5ax}$ = 11.0 Hz, $J_{4ax,3ax}$ = 11.0 Hz, and $J_{4ax,3eq}$ = 5.1 Hz) and 5-H as a doublet at δ_H 3.77 ($J_{5ax,4ax}$ = 11.0 Hz). Thus, the magnitude of these coupling constants clearly established that 4-H and 5-H adopted axial positions. The C*H*OAc proton (4-H) in **8**, being 1,3-diaxial to O-7 of the neighboring ring, appeared further downfield than in **7** and **16**. The vicinal coupling constants for 4-H and 5-H in **7**, however, were all 2.2 Hz, thereby allowing assignment of these protons to equatorial positions. 5-H in **7** resonated as a double doublet at δ_H 4.27 further downfield from the same proton in **8** (δ_H 3.77) due to its proximity to both 4-OAc and O-7. The observation of a double doublet for 5-H (versus a doublet in **8**) was due to additional long-range W-coupling between 5eq-H and 3eq-H, further confirming the equatorial position of 5-H. 2-H in **7** (δ_H 4.11) resonated substantially downfield from the same proton in **8** and **16** (δ_H 3.81−3.96), consistent with 2-H in **7** being 1,3-diaxial to both 4-OAc and O-7.

In all three iodo acetates **7**, **8**, and **16**, carbons resonating in the range δ_C 71.6−74.1, which were clearly bonded to an acetoxy group, exhibited a correlation to double double doublets at δ_H 5.22−5.31 in the HETCOR spectra. The methine carbons resonating at δ_C 31.8−39.5, however, correlated with the doublets at δ_H 3.77−4.27. These two connections clearly established that the CHI proton was located at C-5 and the C*H*OAc proton at C-4. The regioselectivity of the reaction can be accounted for by steric hindrance from the saturated ring to approach of the nucleophile at C-5 and the inductive electron-withdrawing effect of O-1 and O-7 which favors development of a positive charge at C-4 rather than C-5. Chlorohydroxylation of related 1,7-dioxaspiro[5.5]undec-4-enes has been reported and proceeds similarly, with high regioselectivity and modest stereoselectivity.[8]

Scheme 2



In the Woodward−Prevost reaction of a related cyclohexane system,[9] the iodo acetates underwent facile hydrolysis to the hydroxy acetates, and the iodo acetates themselves were not isolated. Our work suggested there was some hindrance to formation of acetoxonium ion **9** because iodo acetate **7** was isolated, rather than the expected hydroxy acetates **11** and **12**.

Iodo acetate **7** was treated further with silver(I) acetate and silver(I) tetrafluoroborate in various solvents (acetic acid, methanol, DMF, DMSO) under reflux in an effort to form hydroxy acetates **11** and **12**. These conditions resulted in decomposition of the starting material and formation of a complex mixture of products for which the crude ^{1}H NMR spectrum suggested the presence of a CHI proton. It therefore appeared that the attempted displacement of iodine from **7** resulted in isomerization without loss of iodine. This suggested that the iodine at C-5 may be sterically hindered toward displacement. Alternatively, development of a partial positive charge at C-5 in the transition state for displacement may be unfavourable due to the adverse effect of the neighboring electronegative acetate group and spiroacetal oxygen atoms. It was therefore decided to attempt to form acetoxonium ion **9** from iodo acetate **17** in which the positions of the iodine and acetate groups were reversed.

Iodo acetate **17** was prepared from iodo acetate **7** *via* ring opening of epoxide **18** with lithium iodide to iodohydrin **19** followed by acetylation (Scheme 2). Treatment of **7** with potassium superoxide in DMSO/THF, in the presence of 18-crown-6, afforded epoxide **18** in modest yield. Regio- and stereoselective ring opening of epoxide **18** to iodohydrin **19** was then effected in 86% yield using lithium iodide and $BF_3{\cdot}Et_2O$. (The multiplicity and magnitude of the coupling constants for the resonances assigned to 4-H and 5-H in the ^{1}H NMR spectrum allowed assignment of the relative stereochemistry of the iodine and hydroxyl substituents in iodohydrin (**19**). Thus, 4-H resonated at $^{\delta}_H$ 4.39 as a double double doublet ($J_{4ax,5ax}$ = 10.4 Hz, $J_{4ax,3ax}$ = 12.7 Hz, and $J_{4ax,3eq}$ = 4.8 Hz) and 5-H as a double doublet at δ_H 3.39 ($J_{5ax,4ax}$ = 10.4 Hz and $J_{5ax,OH}$ = 9.2 Hz), thereby confirming that the iodine and hydroxyl groups occupied equatorial positions. The chemical shifts observed for C-4 and C-5 (32.2 and 78.3, respectively) also supported the location of the hydroxyl group at C-5 and the iodine at C-4.)

(In the ^{1}H NMR spectrum recorded for **25**, 4-H resonated as a double doublet ($J_{4,3eq}$ = 5.6 Hz and $J_{4,5}$ = 3.6 Hz) and long range W-coupling (0.6 Hz) was observed between 5-H and 3eq-H thereby supporting the assignment of the epoxide ring as being *anti* to the C-6/O-7 bond.) Iodohydrin **19**, in which the iodine and hydroxyl groups are diequatorial, presumably forms *via anti*-periplanar ring opening of a twist-boat conformation of

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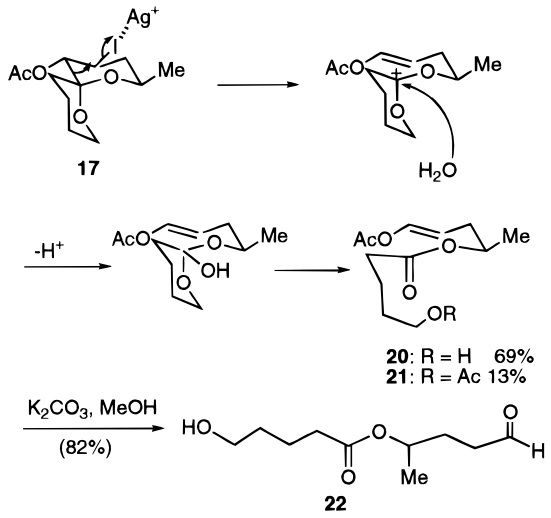
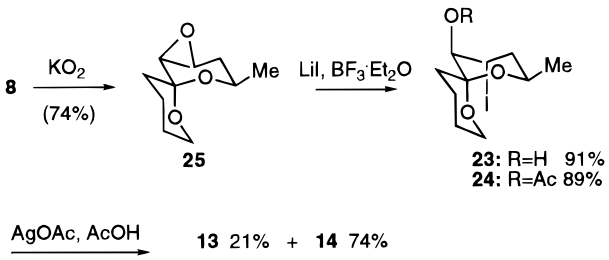
Scheme 3



Scheme 4



epoxide **18**, followed by reversion of the ring-opened product to a more stable chair conformation.

Acetylation of iodohydrin **19** under standard conditions gave iodo acetate **17** where the iodine was now attached to the less hindered carbon (C-4 versus C-5). Subsequent treatment of **17** with silver(I) acetate in aqueous acetic acid under reflux afforded two less polar products which were identified as the ring fragmentation products, *acyclic* esters **20** (69%) and **21** (13%) (Scheme 3). Hydrolysis of **21** with K_2CO_3 in methanol afforded aldehyde **22**.

The observed fragmentation of iodo acetate **17**, rather than formation and subsequent hydrolysis of acetoxonium ion **9**, suggested that steric and electronic factors precluded displacement of the iodine at C-4. The driving force for this fragmentation reaction is provided by the affinity of the silver ion for iodine and the cleavage of the C-5/C-6 bond, giving rise to a stabilized carbocation. The antiperiplanar arrangement of the C-5/C-6 and C-4/I bonds in iodo acetate **17** ensures correct alignment of the molecular orbitals for formation of the double bond.

In iodo acetates **7** and **17** the acetate group is *syn* to the neighboring ring, and this may provide steric hindrance toward formation of the acetoxonium ion **9** required for formation of hydroxy acetates **11** and **12**. It was therefore decided to investigate the silver-assisted hydrolysis of iodo acetate **24** in which the acetate group is *anti* to the neighboring ring.

In a similar manner, iodohydrin **23** and iodo acetate **24** were prepared from iodo acetate **8** (Scheme 4). Treatment of iodo acetate **8** with potassium superoxide in THF/DMSO in the presence of 18-crown-6 afforded epoxide **25** in 74% yield. Lithium iodide opening of epoxide **25** at −50 °C in THF assisted by $BF_3{\cdot}Et_2O$ proceeded regio- and stereoselectively to give diaxial iodohydrin **23** in 91% yield. Formation of **23** is accounted for by *trans*-diaxial opening of the epoxide ring in which the nucleophile attacks C-4. (The stereochemistry assigned to **23** was evident from the ^1H NMR spectrum. Thus, 2-H resonated at δ_H 4.07−4.19 and was deshielded compared to the same proton in iodohydrin (**19**) which resonated at δ_H 3.77 and is therefore consistent with being 1,3-diaxial to both 4-I and O-7. 4-H in iodohydrin (**23**) is not 1,3-diaxial to O-7 and therefore resonated further upfield at δ_H 4.29−4.33 compared to δ_H 4.39 in iodohydrin (**19**). Due to its close proximity to 4-I and O-7, 5-H in iodohydrin (**23**) resonated as a double doublet at δ_H 3.76 ($J_{5eq,OH}$ = 8.4 Hz and $J_{5eq,4eq}$ = 2.9 Hz), further downfield from 5-H in iodohydrin (**19**) (δ_H 3.39, $J_{5ax,4ax}$ = 10.4 Hz and $J_{5ax,OH}$ = 9.2 Hz).) Acetylation of **23** under standard conditions (Ac_2O, Et_3N, DMAP, CH_2Cl_2) afforded iodo acetate **24** cleanly in 89% yield. Iodo acetate **24** was then treated with silver(I) acetate in acetic acid under reflux for 0.25 h, resulting in formation of hydroxy acetates **13** and **14** in 21% and 74% yield, respectively. The structures of these hydroxy acetates were confirmed by comparison with a sample of the same compound prepared by hydroxylation of **4** to the diol **15** using osmium tetraoxide followed by acetylation.

Conclusion

In summary, a study of the Woodward−Prevost reaction of the 1,7-dioxaspiro[5.5]undec-4-ene **4** has provided valuable information concerning the stereoelectronic requirements necessary to effect satisfactory silver-assisted hydrolysis of the iodo acetates formed. Thus, iodo acetates **7** and **17** in which the acetate group is *syn* to the neighboring ring failed to undergo clean hydrolysis to hydroxy acetates **11** and **12**. Due to the antiperiplanar arrangement of the C-5/C-6 and C-4/I bonds in iodo acetate **17**, ring fragmentation to acyclic esters **20** and **21** rather than hydrolysis is observed. Iodo acetate **24**, in which the acetate group is *anti* to the neighboring ring, undergoes smooth hydrolysis to hydroxy acetates **13** and **14** as expected. These results suggest that formation of cyclic acetoxonium ion **9** which is *syn* to the neighboring ring is sterically and/or electronically unfavored compared to formation of acetoxonium ion **10** which is *anti* to the neighboring ring. Similar effects may be operating in the formation of an epoxide at C-4/C-5 in that epoxide **25** which is *anti* to the C-6/O-7 bond is readily prepared from iodo acetate **8** in good yield whereas the epoxide **18** was only prepared from iodo acetate **7** in moderate yield under the same conditions. The work described herein precludes a synthesis of griseusins A (**1**) or B (**2**) *via* Woodward−Prevost hydroxylation of an alkene such as **4**; thus, alternative synthetic strategies have been developed and will be reported in due course.

Experimental Section

General Experimental Procedures. Chemicals and reagents were purchased from the Aldrich Chemical Co. and used without further purification. Melting points were determined on a Kofler hotstage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were obtained at 270 and 67.8 MHz, respectively. All ^{13}C NMR spectra were assigned with the aid of DEPT and HETCOR experiments. Mass spectra were recorded under electron impact using an ionization potential of 70 eV, using chemical ionization with ammonia as the reagent gas, or using liquid secondary ionization mass spectrometry (LSIMS) with either a nitrobenzyl alcohol (NBA) or 5:1 dithiothreitol:dithioerythritol (DTDE) matrix. Flash chromatography was per-

formed using Merck Kieselgel 60 (230−400 mesh) with the solvents indicated. Analytical TLC was performed using precoated silica gel plates (Merck Kieselgel 60 F_{254}). THF was distilled from sodium benzophenone ketyl before use. (2*R**,6*S**)-2-Methyl-1,7-dioxaspiro[5.5]undec-4-ene (**4**) was prepared according to the published procedure.[10]

5-Iodo-2-methyl-1,7-dioxaspiro[5.5]undec-4-yl Acetate (7, 8, and 16). To a stirred suspension of **4** (94 mg, 0.56 mmol), silver acetate[11] (280 mg, 1.68 mmol), and water (0.11 mL, 6 mmol) in glacial acetic acid (10 mL) was added iodine (171 mg, 0.67 mmol) portionwise over 10 min. The resultant yellow mixture was stirred for 18 h and then filtered through a cotton wool plug to remove insoluble material. The filtrate was poured into ether (40 mL) and washed with water (2 × 7 mL) and saturated aqueous sodium hydrogen carbonate (7 mL). The aqueous washings were extracted with ether (10 mL) and the combined ethereal fractions washed with brine (7 mL) and then dried (Na_2SO_4). Removal of the solvent under reduced pressure gave an orange residue that was purified by flash chromatography, using hexane−EtOAc (95:5) as eluent, to afford (2*R**,4*S**,5*R**,6*S**)-iodo acetate **8** (32 mg, 16%); [R_f 0.39 [hexane−EtOAc (9:1)] as colorless rods; mp 49.5−52.5 °C; IR (film) 1748 (C=O), 1239 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.21 (3 H, d, J = 6.2 Hz, Me), 1.47−1.90 (6 H, m, 3-, 9-, 10-CH_2), 2.02−2.06 (1 H, m, 11_{eq}-H), 2.09 (3 H, s, OAc), 2.27 (1 H, ddd, J_{gem} = 13.0 Hz, $J_{11ax,10ax}$ = 13.0 Hz, $J_{11ax,10eq}$ = 4.4 Hz, 11_{ax}-H), 3.51−3.74 (2 H, m, 8-CH_2), 3.77 (1 H, d, $J_{5ax,4ax}$ = 11.0 Hz, CHI), 3.81−3.96 (1 H, m, C*H*Me), 5.31 (1 H, ddd, $J_{4ax,5ax}$ = 11.0 Hz, $J_{4ax,3ax}$ = 11.0 Hz, $J_{4ax,3eq}$ = 5.1 Hz, C*H*OAc); ^{13}C NMR ($CDCl_3$) 18.6 (CH_2, C-10), 20.7, 21.2 (CH_3, 2 × Me), 24.4 (CH_2, C-9), 33.9 (CH_2, C-11), 39.5 (CH, C-5), 40.6 (CH_2, C-3), 61.2 (CH_2, C-8), 63.0 (CH, C-2), 72.5 (CH, C-4), 97.9 (C, C-6), 169.8 (C, *C*OMe); MS (EI) *m*/*z* 354 (M^+, 14). Anal. Calcd for $C_{12}H_{19}O_4I$: C, 40.7; H, 5.4; I, 35.8. Found: C, 41.1; H, 5.7; I, 36.0.], (2*R**,4*R**,5*S**,6*S**)-iodo acetate **7** (85 mg, 43%): R_f 0.34 [hexane−EtOAc (9:1)] as colorless rods; mp 73.0−81.0 °C; IR (film) 1739 (C=O), 1242 (CO), 1083 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (3 H, d, J = 6.2 Hz, Me), 1.28−1.87 (6 H, m, 3-, 9-, 10-CH_2), 2.05 (3 H, s, OAc), 2.08−2.17 (1 H, m, 11_{eq}-H), 2.28 (1 H, ddd, J_{gem} = 14.7 Hz, $J_{11ax,10ax}$ = 11.6 Hz, $J_{11ax,10eq}$ = 3.3 Hz, 11_{ax}-H), 3.56−3.63 (2 H, m, 8-CH_2), 4.11 (1 H, qdd, $J_{2ax,Me}$ = 6.2 Hz, $J_{2ax,3ax}$ = 12.4 Hz, $J_{2ax,3eq}$ = 2.0 Hz, C*H*Me), 4.27 (1 H, dd, $J_{5eq,4eq}$ = 2.2 Hz, $J_{5eq,3eq}$ = 2.2 Hz, CHI), 5.23 (1 H, ddd, $J_{4eq,5eq}$ = 2.2 Hz, $J_{4eq,3ax}$ = 2.2 Hz, $J_{4eq,3eq}$ = 2.2 Hz, C*H*OAc); ^{13}C NMR (67.8 MHz; $CDCl_3$) 19.6 (CH_2, C-10), 21.0, 21.2 (CH_3, 2 × Me), 24.3 (CH_2, C-9), 31.2 (CH_2, C-11), 31.8 (CH, C-5), 38.9 (CH_2, C-3), 60.6 (CH_2, C-8), 61.8 (CH, C-2), 74.1 (CH, C-4), 96.2 (C, C-6), 170.5 (C, *C*OMe); MS (EI) *m*/*z* 354 (M^+, 5). Anal. Calcd for $C_{12}H_{19}O_4I$: C, 40.7; H, 5.4; I, 35.8. Found: C, 40.5; H, 5.5; I, 35.9.], and (2*R**,4*R**,5*S**,6*R**)-iodo acetate **16** (24 mg, 12%): R_f 0.29 [hexane−EtOAc (9:1)] as colorless rods; mp 95.5−98.5 °C; IR (film) 1746 (C=O), 1242 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.27 (3 H, d, J = 6.2 Hz, Me), 1.42−2.11 (7 H, m, 3-, 9-, 10-CH_2,11_{ax}-H), 2.14 (3 H, s, OAc), 2.24−2.33 (1 H, m, 11_{eq}-H), 3.66−3.74 (1 H, m, 8_{eq}-H), 3.91−4.05 (2 H, m, C*H*Me, 8_{ax}-H), 4.27 (1 H, d, $J_{5eq,4eq}$ = 3.7 Hz, CHI), 5.22 (1 H, ddd, $J_{4eq,5eq}$ = 3.7 Hz, $J_{4eq,3ax}$ = 3.7 Hz, $J_{4eq,3eq}$ = 3.7 Hz, C*H*OAc); ^{13}C NMR (67.8 MHz; $CDCl_3$) 18.6 (CH_2, C-10), 21.2, 21.4 (CH_3, 2 × Me), 24.7 (CH_2, C-9), 29.0 (CH_2, C-11), 37.8 (CH_2, C-3), 38.0 (CH, C-5), 62.2 (CH_2, C-8), 65.1 (CH, C-2), 71.6 (CH, C-4), 97.8 (C, C-6), 169.7 (C, *C*OMe); MS (EI) *m*/*z* 354 (M^+, 12). Anal. Calcd for $C_{12}H_{19}O_4I$: C, 40.7; H, 5.4; I, 35.8. Found: C, 40.5; H, 5.2; I, 36.0.

(2*R,4*R**,5*R**,6*S**)-4,5-Epoxy-2-methyl-1,7-dioxaspiro-[5.5]undecane (18).** To a solution of iodo acetate **7** (152 mg, 0.43 mmol) in dry DMSO (10 mL) and dry THF (3 mL) under an atmosphere of nitrogen was added 18-crown-6 (227 mg, 0.86 mmol) followed by potassium superoxide (92 mg, 1.29 mmol). After being stirred for 4 h the mixture was poured into ether (83 mL) and washed with water (3 × 17 mL). The aqueous washings were extracted with a further volume of ether (33 mL) and the combined ethereal phases dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a clear oil that was purified by flash chromatography, using hexane−EtOAc (4:1) as eluent, to give epoxide **18** (36 mg, 46%) as a colorless oil: IR (film) cm^{-1} 1080 (CO), 793 (epoxide CO); ^1H NMR ($CDCl_3$) 1.16 (3 H, d, J = 6.2 Hz, Me), 1.49−1.93 (7 H, m, 3-, 9-, 10-CH_2, 11_{ax}-H), 2.03 (1 H, ddd, J_{gem} = 14.3 Hz, $J_{11eq,10ax}$ = 2.2 Hz, $J_{11eq,10eq}$ = 2.2 Hz, 11_{eq}-H), 3.09 (1 H, d, $J_{5,4}$ = 4.0 Hz, 5-H), 3.33−3.38 (1 H, m, 4-H), 3.66−3.72 (1 H, m, 8_{eq}-H), 3.77−3.89 (2 H, m, C*H*Me, 8_{ax}-H); ^{13}C NMR ($CDCl_3$) 18.3 (CH_2, C-10), 20.6 (CH_3, Me), 25.1 (CH_2, C-9), 32.6 (CH_2, C-11), 34.7 (CH_2, C-3), 51.7 (CH, C-4), 55.1 (CH, C-5), 59.7 (CH, C-2), 60.9 (CH_2, C-8), 93.5 (C, C-6); MS (LSIMS, DTDE matrix) *m*/*z* 185 (M + H, 100). Anal. Calcd for $C_{10}H_{16}O_3$: C; 65.2; H, 8.75. Found: C, 65.1; H, 8.7.

(2*R,4*S**,5*S**,6*S**)-4,5-Epoxy-2-methyl-1,7-dioxaspiro[5.5]-undecane (25).** Using the procedure described above for the preparation of epoxide **18**, epoxide **25** (23 mg, 74%) was prepared from iodo acetate **8** (60 mg, 0.17 mmol), 18-crown-6 (90 mg, 0.34 mmol), and potassium superoxide (36 mg, 0.51 mmol) as a colorless oil: IR (film) 1097 (CO), 891 (epoxide CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.15 (3 H, d, J = 6.3 Hz, Me), 1.48−1.97 (8 H, m, 3-, 9-, 10-, 11-CH_2), 2.80 (1 H, dd, $J_{5,4}$ = 3.6 Hz, $J_{5,3eq}$ = 0.6 Hz, 5-H), 3.32 (1 H, dd, $J_{4,3eq}$ = 5.6 Hz, $J_{4,5}$ = 3.6 Hz, 4-H), 3.59−3.94 (3 H, m, 8-CH_2, C*H*Me); ^{13}C NMR ($CDCl_3$) 17.7 (CH_2, C-10), 20.8 (CH_3, Me), 25.3 (CH_2, C-9), 30.4 (CH_2, C-11), 32.2 (CH_2, C-3), 50.9 (CH, C-4), 52.8 (CH, C-5), 61.0(2) (CH_2, C-8; CH, C-2), 94.5 (C, C-6); MS (LSIMS, DTDE matrix) *m*/*z* 185 (M + H, 45). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.2; H, 8.75. Found: C, 65.2; H, 8.6.

(2R*,4S*,5S*,6S*)-4-Iodo-2-methyl-1,7-dioxaspiro[5.5]-undecan-5-ol (19). A suspension of lithium iodide (294 mg, 2.20 mmol) in dry THF (15 mL) was cooled to −50 °C under an atmosphere of nitrogen. To this was added a solution of epoxide **18** (270 mg, 1.47 mmol) in dry THF (28 mL), followed after 0.25 h by boron trifluoride etherate (1.90 mL, 15.4 mmol). The reaction was stirred at this temperature for 0.5 h, water (0.7 mL) was added, and the mixture was warmed to room temperature. Removal of the solvent under reduced pressure and purification of the residue by flash chromatography, using hexane−EtOAc (95:5 → 4:1) as eluent, gave iodohydrin **19** (393 mg, 86%) as colorless needles: mp 82.0−83.0 °C; IR (film) 3556−3212 (OH), 1092 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.18 (3 H, d, J = 6.2 Hz, Me), 1.46−1.64 (4 H, m, 9-CH_2, 10_{eq}-H, 11_{eq}-H), 1.73−1.92 (1 H, m, 10_{ax}-H), 1.98−2.16 (1 H, m, 11_{ax}-H), 2.04−2.22 (1 H, m, 3_{ax}-H), 2.22 (1 H, d, J = 9.2 Hz, OH), 2.41 (1 H, ddd, J_{gem} = 13.2 Hz, $J_{3eq,4ax}$ = 4.8 Hz, $J_{3eq,2ax}$ = 2.2 Hz, 3_{eq}-H), 3.39 (1 H, dd, $J_{5ax,4ax}$ = 10.4 Hz, $J_{5ax,OH}$ = 9.2 Hz, C*H*OH), 3.58−3.72 (2 H, m, 8-CH_2), 3.77 (1 H, qdd, $J_{2ax,Me}$ = 6.2 Hz, $J_{2ax,3ax}$ = 12.4 Hz, $J_{2ax,3eq}$ = 2.2 Hz, C*H*Me), 4.39 (1H, ddd, $J_{4ax,5ax}$ = 10.4 Hz, $J_{4ax,3ax}$ = 12.7 Hz, $J_{4ax,3eq}$ = 4.8 Hz, CHI); ^{13}C NMR ($CDCl_3$) 18.3 (CH_2, C-10), 20.3 (CH_3, Me), 24.9 (CH_2, C-9), 31.0 (CH_2, C-11), 32.2 (CH, C-4), 46.4 (CH_2, C-3), 61.0 (CH_2, C-8), 66.3 (CH, C-2), 78.3 (CH, C-5), 97.9 (C, C-6); MS (LSIMS, DTDE matrix) *m*/*z* 313 (M + H, 40). Anal. Calcd for $C_{10}H_{17}O_3I$: C, 38.5; H, 5.5; I, 40.65. Found: C, 38.65; H, 5.6; I, 40.8.

(2*R,4*R**,5*R**,6*S**)-4-Iodo-2-methyl-1,7-dioxaspiro[5.5]-undecan-5-ol (23).** Iodohydrin **23** (63 mg, 91%) was prepared using the following modification of the procedure described above for the preparation of iodohydrin **19**, from epoxide **25** (41 mg, 0.22 mmol), lithium iodide (44 mg, 0.33 mmol), and boron trifluoride etherate (0.30 mL, 2.44 mmol). After addition of water and warming to room temperature, the reaction mixture was poured into ether (28 mL) and washed with water (5 mL). and the aqueous washings were then extracted with ether (12 mL). The combined organic fractions were dried over Na_2SO_4 and passed through a silica gel pad before the solvent was removed under reduced pressure. The resultant pale yellow solid was purified by flash chromatography using hexane−EtOAc (95:5 → 4:1) as eluent to give iodohydrin **23** (63 mg, 91%) as colorless needles: mp 104.0 °C dec; IR (film) 3420 (OH), 1082 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.26 (3 H, d, J = 6.2 Hz, Me), 1.41−2.08 (8 H, m, 3-, 9-, 10-, 11-CH_2), 2.25 (1 H, d, J = 8.4 Hz, OH), 3.57−3.72 (2H, m, 8-CH_2), 3.76 (1H, dd, $J_{5eq,OH}$ = 8.4 Hz, $J_{5eq,4eq}$ = 2.9 Hz, C*H*OH), 4.07−4.19 (1 H, m, C*H*Me), 4.29−4.33 (1 H, m, CHI); ^{13}C NMR ($CDCl_3$) 18.1 (CH_2, C-10), 20.7 (CH_3, Me), 21.4 (CH, C-4), 24.6 (CH_2, C-9), 31.4 (CH_2, C-3), 37.1 (CH_2, C-11), 60.2 (CH_2, C-8), 61.7 (CH, C-2), 71.6 (CH, C-5), 98.4 (C, C-6); MS (CI, NH_3) *m*/*z* 330 (MH + NH_3, 4). Anal. Calcd for $C_{10}H_{17}O_3I$: C, 38.5; H, 5.5; I, 40.65. Found: C, 38.45; H, 5.5; I, 40.7.

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(2*R,4*S**,5*S**,6*S**)-4-Iodo-2-methyl-1,7-dioxaspiro[5.5]-undec-5-yl Acetate (17).** To a solution of iodohydrin **19** (235 mg, 0.75 mmol) in dichloromethane (11 mL) was added acetic anhydride (0.50 mL, 3.55 mmol), triethylamine (0.40 mL, 2.87 mmol), and a catalytic amount of DMAP (*ca.* 5 mg). The solution was stirred at room temperature until no starting material was visible (TLC). The solvent was removed under reduced pressure and the residue purified by flash chromatography using hexane−EtOAc (4:1) as eluent to give the iodo acetate **17** (252 mg, 95%) as colorless needles: mp 105.5−107.5 °C; IR 1747 (C=O), 1230 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.20 (3 H, d, J = 6.2 Hz, Me), 1.42−1.63 (5H, m, 9-, 11-CH_2, 10_{eq}-H), 1.73−1.88 (1 H, m, 10_{ax}-H), 2.12−2.26 (1 H, m, 3_{ax}-H), 2.20 (3 H, s, OAc), 2.48 (1 H, ddd, J_{gem} = 13.3 Hz, $J_{3eq,4ax}$ = 4.8 Hz, $J_{3eq,2ax}$ = 2.2 Hz, 3_{eq}-H), 3.57−3.76 (2 H, m, 8-CH_2), 3.83 (1 H, qdd, $J_{2ax,Me}$ = 6.2 Hz, $J_{2ax,3ax}$ = 12.4 Hz, $J_{2ax,3eq}$ = 2.2 Hz, C*H*Me), 4.53 (1 H, ddd, $J_{4ax,3ax}$ = 12.7 Hz, $J_{4ax,5ax}$ = 11.0 Hz, $J_{4ax,3eq}$ = 4.8 Hz, CHI), 4.96 (1 H, d, $J_{5ax,4ax}$ = 11.0 Hz, C*H*OAc); ^{13}C NMR ($CDCl_3$) 18.1 (CH_2, C-10), 20.2, 21.3 (CH_3, 2 × Me), 24.4 (CH, C-4), 24.7 (CH_2, C-9), 31.3 (CH_2, C-3), 46.4 (CH_2, C-11), 61.1 (CH_2, C-8), 66.1 (CH, C-2), 77.5 (CH, C-5), 97.5 (C, C-6), 170.3 (C, *C*OMe); MS (LSIMS, DTDE matrix) *m*/*z* 355 (M + H, 100). Anal. Calcd for $C_{12}H_{19}O_4I$: C, 40.7; H, 5.4; I, 35.8. Found: C, 40.9; H, 5.6; I, 35.8.

(2*R,4*R**,5*R**,6*S**)-4-Iodo-2-methyl-1,7-dioxaspiro[5.5]-undec-5-yA acetate (24).** Using the procedure described above for the preparation of iodo acetate **17,** iodo acetate **24** (76 mg, 89%) was prepared from iodohydrin **23** (75 mg, 0.24 mmol), acetic anhydride (0.16 mL, 1.21 mmol), and triethylamine (0.13 mL, 0.96 mmol) as colorless rods; mp 107.5−110.0 °C; IR (film) 1749 (C=O), 1232 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.29 (3 H, d, J = 6.2 Hz, Me), 1.33−2.04 (8 H, m, 3-, 9-, 10-, 11-CH_2), 2.09 (3 H, s, OAc), 3.58−3.76 (2 H, m, 8-CH_2), 4.09−4.23 (1 H, m, C*H*Me), 4.24−4.27 (1 H, m, CHI), 4.96 (1 H, d, $J_{5eq,4eq}$ = 2.2 Hz, C*H*OAc); ^{13}C NMR ($CDCl_3$) 17.2 (CH, C-4), 17.9 (CH_2, C-10), 20.6, 20.8 (CH_3, 2 × Me), 24.6 (CH_2, C-9), 31.2 (CH_2, C-3), 37.6 (CH_2, C-11), 60.1 (CH_2, C-8), 61.7 (CH, C-2), 71.3 (CH, C-5), 97.3 (C, C-6), 169.5 (C, *C*OMe); MS (LSIMS, NBA matrix) *m*/*z* 355 (M + H, 35). Anal. Calcd for $C_{12}H_{19}O_4I$: C, 40.7; H, 5.4; I, 35.8. Found: C, 40.8; H, 5.7; I, 36.0.

(4′*E*)-5′-Acetoxypent-4′-en-2′-yl 5-Acetoxypentanoate (21) and (4′*E*)-5′-Acetoxypent-4′-en-2′-yl 5-Hydroxypentanoate (20). A mixture of iodo acetate **17** (166 mg, 0.47 mmol), silver acetate (157 mg, 0.94 mmol), and water (0.4 mL, 23 mmol) in glacial acetic acid (13 mL) was heated at reflux for 0.25 h, at the end of which time two products were visible (TLC). The suspension was filtered through a Celite pad, the pad washed with dichloromethane (20 mL), and the filtrate dried over Na_2SO_4. Removal of the solvent at reduced pressure gave a clear oil that was purified by flash chromatography using hexane−EtOAc (1:1) as eluent to give diacetate **21** (18 mg, 13%) [R_f 0.46 [hexane−EtOAc (1:1)] as a colorless oil; IR (film) 3082 (=*CH*), 1763−1720 (C=O), 1676m (C=*C*, *trans*), 1226 (CO, acetate) cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) 1.22 (3 H, d, J = 6.2 Hz, Me), 1.59−1.75 (4 H, m, 3-, 4-CH_2), 2.05 (3 H, s, CH_2OAc), 2.12 (3 H, s, =C*H*O*Ac*), 2.22−2.27 (2 H, m, =C*H*CH_2), 2.30−2.35 (2 H, m, CH_2COO), 4.07 (2 H, t, J = 6.2 Hz, CH_2OAc), 4.94 (1 H, qt, $J_{2',Me}$ = 6.2, Hz $J_{2',3'}$ = 6.2 Hz, C*H*Me), 5.36 (1 H, dt, $J_{4',5'}$ = 12.5 Hz, $J_{4',3'}$ = 7.7 Hz, =*CH*CH$_2$), 7.11 (1 H, dt, $J_{5',4'}$ = 12.5 Hz, $J_{5',3'}$ = 1.3 Hz, =*CH*OAc); ^{13}C NMR (67.8 MHz; $CDCl_3$) 19.4 (CH_3, C-1′), 20.7 (CH_3, 5′-CO*Me*), 21.0 (CH_2, C-3), 21.5 (CH_3, 5-CO*Me*), 28.0 (CH_2, C-4), 33.8 (CH_2, C-3′), 34.0 (CH_2, C-2), 64.0 (CH_2, C-5), 69.9 (CH, C-2′), 109.7 (CH, C-4′), 137.4 (CH, C-5′), 167.4 (C, 5′-*C*OMe), 171.4 (C, 5-*C*OMe), 172.8 (C, C-1); MS (LSIMS, NBA matrix) *m*/*z* 287 (M + H, 52). Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.7; H, 7.7. Found: C, 58.9; H, 7.8.] and acetate **20** (79 mg, 69%): R_f 0.32 [hexane−EtOAc (1:1)] as a colorless oil; IR (film) 3082 (=*CH*), 3670−3116 (OH), 1755, 1732 (C=O), 1676 (C=*C*, *trans*), 1221 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.22 (3 H, d, J = 6.2 Hz, Me), 1.55−1.74 (4 H, m, 3-, 4-CH_2), 2.12 (3 H, s, OAc), 2.24 (2 H, ddd, $J_{3',4'}$ = 7.7 Hz, $J_{3',2'}$ = 6.2 Hz, $J_{3',5'}$ = 1.3 Hz, =C*H*CH_2), 2.33 (2H, t, J = 7.1 Hz, CH_2COO), 3.65 (2 H, t, J = 6.2 Hz, CH_2-OH), 4.94 (1 H, qt, $J_{2',Me}$ = 6.2 Hz, $J_{2',3'}$ = 6.2 Hz, C*H*Me), 5.36 (1 H, dt, $J_{4',5'}$ = 12.5 Hz, $J_{4',3'}$ 7.7 Hz, =*CH*CH$_2$), 7.10 (1 H, dt, $J_{5',4'}$ = 12.5 Hz, $J_{5',3'}$ = 1.3 Hz, =*CH*OAc); ^{13}C NMR ($CDCl_3$) 19.5 (CH_3, C-1′), 20.7 (CH_3, CO*Me*), 21.1 (CH_2, C-3), 32.1 (CH_2, C-4), 33.8 (CH_2, C-3′), 34.2 (CH_2, C-2), 62.2 (CH_2, C-5), 69.8 (CH, C-2′), 109.8 (CH, C-4′), 137.4 (CH, C-5′), 168.2 (C, *C*OMe), 173.2 (C, C-1); MS (LSIMS, DTDE matrix) *m*/*z* 245 (MH^+, 94). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.0; H, 8.0. Found: C, 59.1; H, 8.3.

5′-Oxopent-2′-yl 5-Hydroxypentanoate (22). To acetate **20** (36 mg, 0.15 mmol) in methanol (2.6 mL) was added potassium carbonate (7 mg, 0.051 mmol) and the mixture stirred until no starting material was visible (TLC). The majority of the solvent was removed under reduced pressure, and the residual liquid (*ca.* 0.3 mL) was subjected to flash chromatography using hexane−EtOAc (1:1) as eluent to give aldehyde **22** (24 mg, 82%) as a colorless oil: IR (film) 3702−3060 (OH), 2727 (*HC*=O), 1735−1701 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (3 H, d, J = 6.2 Hz, Me), 1.55−1.82 (4 H, m, 3-, 4-CH_2), 1.89−1.94 (2 H, m, 3′-CH_2), 2.32 (2 H, t, J = 7.3 Hz, CH_2COO), 2.50 (2 H, td, $J_{4',3'}$ = 7.3, $J_{4',5'}$ = 1.4 Hz, CH_2CHO), 3.66 (2 H, t, J = 6.2 Hz, CH_2OH), 4.94 (1 H, qt, $J_{2',Me}$ = 6.2, $J_{2',3'}$ = 6.2 Hz, C*H*Me), 9.77 (1 H, t, $J_{5',4'}$ = 1.4 Hz, CHO); ^{13}C NMR ($CDCl_3$) 20.0 (CH_3, C-1′), 21.1 (CH_2, C-3), 28.1 (CH_2, C-3′), 32.0 (CH_2, C-4), 34.1 (CH_2, C-2), 40.0 (CH_2, C-4′), 62.2 (CH_2, C-5), 70.0 (CH, C-2′), 173.3 (C, C-1), 201.5 (C, C-5′); MS (CI, NH_3) *m*/*z* 220 (MH + NH_3, 2), 203 (M + H, 3). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.4; H, 9.0. Found: C, 59.2; H, 8.8.

(2*R,4*S**,5*S**,6*S**)-4-Hydroxy-2-methyl-1,7-dioxaspiro-[5.5]undec-5-yl Acetate (14) and (2*R**,4*S**,5*S**,6*S**)-5-Hydroxy-2-methyl-1,7-dioxaspiro[5.5]undec-4-yl Acetate (13).** Using the procedure described for the preparation of esters **20** and **21**, hydroxy acetate **14** (31 mg, 74%), R_f 0.50 [hexane−EtOAc (1:1)], was prepared from iodo acetate **24** (61 mg, 0.17 mmol) and silver acetate (58 mg, 0.35 mmol). Purification by flash chromatography using hexane−EtOAc (1:1) as eluent afforded a colorless solid: mp 81.0−82.5 °C; IR (film) 3647−3107 (OH), 1743 (C=O), 1245 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.27 (3 H, d, J = 6.4 Hz, Me), 1.33−1.90 (8 H, m, 3-, 9-, 10-, 11-CH_2), 1.99−2.06 (1 H, OH), 2.14 (3 H, s, OAc), 3.59 (2 H, dd, $J_{8,9ax}$ = 8.3 Hz, $J_{8,9eq}$ = 3.1 Hz, 8-CH_2), 3.80 (1 H, qdd, $J_{2ax,Me}$ = 6.4 Hz, $J_{2ax,3ax}$ = 12.8 Hz, $J_{2ax,3eq}$ = 2.4 Hz, C*H*Me), 4.18−4.29 (1 H, m, C*H*OH), 4.93 (1 H, d, $J_{5eq,4ax}$ = 3.3 Hz, C*H*OAc); ^{13}C NMR ($CDCl_3$) 18.0 (CH_2, C-10), 21.0(2) (CH_3, 2 × Me), 24.9 (CH_2, C-9), 31.4 (CH_2, C-11), 35.8 (CH_2, C-3), 60.3 (CH_2, C-8), 64.2 (CH, C-2), 65.6 (CH, C-4), 73.1 (CH, C-5), 97.2 (C, C-6), 171.6 (C, *C*OMe); MS (LSIMS, NBA matrix) *m*/*z* 245 (M + H, 100). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.0; H, 8.25. Found: C, 58.7; H, 8.1. Hydroxy acetate **13** (9 mg, 21%), R_f 0.60 [hexane−EtOAc (1:1)], was also isolated as colorless prisms: mp 129−130 °C (lit.[6] mp 129−130 °C). Acetylation of an approximately 1:1 mixture of the two hydroxy acetates **13** and **14** (9 mg, 0.037 mmol) using acetic anhydride (10 μL, 0.052 mmol), triethylamine (11 μL, 0.037 mmol), and DMAP (*ca.* 1 mg) afforded the diacetate derivative (9 mg, 85%). Purification by flash chromatography using hexane−EtOAc (4:1) as eluent gave colorless needles: mp 112.5−113.0 °C; IR (film) 1749 (C=O), 1247, 1227 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) 1.28 (3 H, d, J = 6.2 Hz, Me), 1.49−1.81 (8 H, m, 3-, 9-, 10-, 11-CH_2), 1.98 (3 H, s, 4- or 5-OAc), 2.13 (3 H, s, 5- or 4-OAc), 3.58−3.63 (2 H, m, 8-CH_2), 3.88 (1 H, qdd, $J_{2ax,Me}$ = 6.2 Hz, $J_{2ax,3ax}$ = 12.4 Hz, $J_{2ax,3eq}$ = 2.9 Hz, C*H*Me), 5.05 (1 H, d, $J_{5eq,4ax}$ = 2.9 Hz, 5_{eq}-H), 5.32 (1 H, ddd, $J_{4ax,3ax}$ = 11.9 Hz, $J_{4ax,3eq}$ = 5.3 Hz, $J_{4ax,5eq}$ = 2.9 Hz, 4_{ax}-H); ^{13}C NMR ($CDCl_3$) 18.0 (CH_2, C-10), 20.9, 21.0, 21.1 (CH_3, 3 × Me), 24.8 (CH_2, C-9), 31.1 (CH_2, C-11), 32.9 (CH_2, C-3), 60.4 (CH_2, C-8), 64.1 (CH, C-2), 67.8 (CH, C-4), 70.2 (CH, C-5), 97.2 (C, C-6), 170.1, 170.4 (C, 2 × *C*OMe); MS (EI) *m*/*z* 286 (M, 0.3), 143 ($C_7H_{11}O_3$, 21), 126 ($C_7H_{10}O_2$, 22), 114 ($C_6H_{10}O_2$, 9), 101 ($C_5H_9O_2$, 100), 84 (C_5H_8O, 14), 43 (CH_3CO, 40). Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.7; H, 7.7. Found: C, 59.0; H, 7.8. The ^1H and ^{13}C NMR spectra recorded for this diacetate were identical to those obtained from material prepared by diacetylation of diol **15**.

Supporting Information Available: Mass spectral fragmentation data for compounds **7**, **8**, **16**, **18**, **25**, **19**, **23**, **17**, **24**, **21**, **20**, **22**, **14**, and **13** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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