C-Nucleosides and related compounds. XV. The synthesis of D,L-2′-*epi*-showdomycin and D,L-showdomycin

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The conversion of the Diels–Alder adduct of methyl β-nitroacrylate with furan to the title compounds and to D,L-2,5-anhydroglucose derivatives is described.

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On décrit la transformation du produit de la réaction Diels–Alder du méthyle β-nitroacrylate avec le furane en dérivés du D,L-2,5-anhydroglucose, en D,L-2′-*épi*-showdomycine, et en showdomycine.

As part of a programme to synthesize *C*-nucleosides, we were interested in developing a method to prepare an arabinose derivative **8**, bearing at the anomeric center a functionalized carbon atom, which could serve as a precursor for the synthesis of compounds such as *ara*-showdomycin (**9***b*).

Reaction of furan with methyl β-nitroacrylate gave the known adducts **1***a* and **1***b* (1). Prolonged treatment with *m*-chloroperbenzoic acid gave epoxides **2***a* and **2***b*, which upon treatment with diazabicyclo[5.4.0]undec-5-ene (DBU) gave olefinic epoxide **3**. As expected (2*a*), nmr analysis of this compound revealed that the stereochemistry of the epoxide function was *exo*, since the coupling constant between the bridgehead protons and the *endo*-protons α to the epoxide was 0 Hz (dihedral angle ~ 90° (2*b*)).

Treatment of *endo*-carbomethoxy epoxide **2***b* with acetic acid and hydrochloric acid at 95°C for 2 h gave lactone **4***a* in 60% yield. There is ample precedent that lactonizations of this type proceed in the manner depicted, and it has been recently reconfirmed in an unambiguous manner for a closely related system (12).

Attempts to acylate hydroxy lactone **4***a* with acetic anhydride or pivaloyl chloride in pyridine failed, leading to decomposition products. However, acetylation using acidic conditions gave acetate **4***b* in good yield. Tetrahydropyranyl ether **4***c* could also be easily prepared.

Attempts to transform lactone **4***c* into the α,β-unsaturated ester **5***a* using one or more equivalents of sodium methoxide in methanol, the conditions which had cleanly converted the corresponding bromolactone in the bicyclo[2.2.1]heptane series to an analogous compound (3), failed because of the formation of the sodium salt of **4***c*. However, treatment of **4***c* with DBU in methanol gave ester **5***a*, accompanied by varying amounts of **6***a*. From the relative ratios of **5***a* to **6***a* as a function of reaction time, it was obvious that **5***a* was transformed to **6***a*. Compound **5***a* was characterized as its acetate **5***b*. At this point, it became apparent that the tetrahydropyranyl protecting group obscured the nmr spectrum of **5***a* and **5***b* enough to make some of the assignments doubtful. The reaction sequence was therefore repeated with the dimethyl-*tert*-butylsilyl ether lactone **4***e*, providing **5***e* and **6***b*; **5***e* was characterized as its pivalate **5***f*. Since Just and Ouellet (3) subsequently established in the analogous carbocyclic series that the pivalate group interacted with the hydroxy group generated in the subsequent ozonolysis–reduction sequence **5** → **7**, it was decided to block the hydroxy group in **5***e* as its dimethyl-*tert*-butylsilyl ether **5***g* (4). Silylation of **5***e* proceeded in an unpredictable manner, providing the disilylation product **5***g*, except for one instance, in low yield.

Ozonolysis of the olefin **5***g*, followed by treatment with dimethyl sulfide and the reduction of the resulting keto aldehyde, obtained in part as its hydrate, with 4 equivalents of lithium tri-*tert*-butoxyaluminum hydride, gave diol ester **7***d*. Selective silylation of **7***d* gave the trisilyl ether **7***f*. That the silylation had proceeded with the desired selectivity was proven by acetylation, where only one proton was shifted downfield from 2.96 to 3.63 ppm. Oxidation (5) of **7***f* provided the relatively unstable ketoester **8***b*. Because of the low silylation yield encountered at one stage in this sequence, the methoxymethyl protecting group (6) was used in the analogous sequence **4***d* → **5***d* → **7***c* → **8***a*. In this sequence, considerable difficulty was experienced when the method worked out for the transformation **4***c* → **5***a* was applied to transformation **4***d* → **5***c*, and it had to be modified. The highest reproducible yields (40–50%) of **5***c* were obtained

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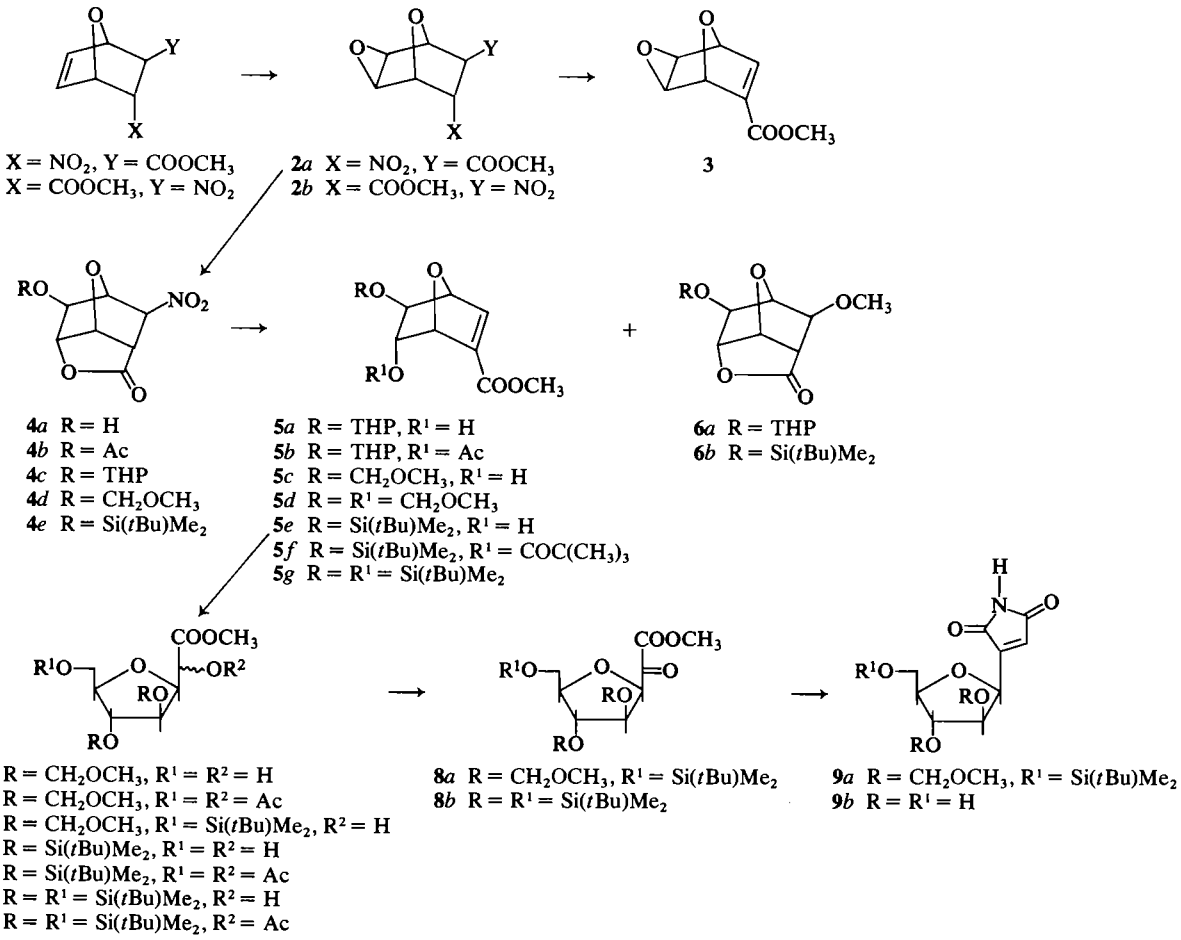


when **4***d* was boiled for 7 hours with triethylamine in dry methanol. It was transformed to its methoxymethyl ether **5***d* in high yield. The structure and stereochemistry of **5***d* follow from its mode of formation and nmr spectrum, which indicated that H4 was split by H3 (2 Hz), whereas the coupling constant H4—H5 was close to 0 Hz, indicating an *exo*-configuration of the 5-substituent. On the other hand *J*(H1—H6) was 4 Hz as expected, indicating that the 6-substituent was *endo*. This was confirmed by the fact that *J*(H5—H6) was close to 0 Hz.

Ozonolysis of **5***d*, followed by reduction with dimethylsulphide and lithium aluminum tri-*tert*-butoxyhydride, gave diol **7***a*, characterized as its diacetate **7***b*. Selective silylation with *tert*-butyldimethylsilyl chloride gave monosilyl ether **7***c*. Silyl ether **7***c* seemed to consist of one diastereomer only. The stereochemistry at C2 was of no consequence, since the next step involved oxidation (5) to ketoester **8***a*.

Whereas the ozonolysis, reduction, and oxidation sequence should not have affected the stereochemistry at $C2^1$, $C3^1$ and $C4^1$, there was some doubt about the stereochemistry at $C1^1$ especially in ketoester **8***a*. The following spectral and chemical data support the assignment of stereochemistry made: whereas the nmr spectrum of **7***c* in deuterochloroform or benzene was uninformative, addition of $Eu(fod)_3$ to the deuterobenzene solution of **7***c* allowed an assignment of most signals. The lowest-field signal (1H, C2) appeared as a doublet (J = 8 Hz). The $C1^1$-proton appeared at somewhat higher field as a doublet of doublets ($J_{2,1^1}$ = 8 Hz, $J_{1^1,2^1}$ = 4 Hz). This latter coupling constant is indicative of a *cis* relation (8, 20) for $H1^1$—$H2^1$. The $H3^1$ proton consisted of a 4-line system (J_a, $J_b \simeq$ 2 Hz, 2.5 Hz). The $C4^1$-proton consisted of complex signal which did not permit first order interpretation. The appearance of the protons corresponding to $C1^1$, $C2^1$, $C3^1$, $C4^1$, and $C5^1$ was similar in ketoester **8***a* and in showdomycin analogs **9***a* and **9***b*, except

for the absence of C2—C1[1] coupling in **8***a* and for the appearance of a 2 Hz long-range coupling between the olefinic proton of the heterocycle and C1[1]—H. The stereochemical assignment was confirmed by the following conversion. Compound **5***d* was ozonized at −78°C and the ozonide reduced with borohydride to the corresponding triol (**7***a*, $COOCH_3$=CH_2OH). Without purification, the triol was oxidized with periodate to give 2,5-anhydroglucose **10**, which existed predominantly in the hemiacetal form shown, as indicated by spectral and microanalytical data. The formation of a hemiacetal proves that triol **7***a* ($COOCH_3$=CH_2OH) and therefore triol derivative **7***c* had most likely the same *cis* configuration at C1[1] and C4[1].

Compound **10** was transformed to the thiazolidine acetate **11***b* and the α,β-unsaturated ester **12***b*, using the methods described for the analogous anhydroallose (1). Both types of compounds have been shown to be versatile precursors to *C*-nucleosides (10).

Compound **8***a* was obtained from nitroacrylate adduct **1***b* in an overall yield of 6.5% in 8 steps.

Following procedures used for the synthesis of showdomycin (21) and showdomycin analogues (13, 14), the ketoester **8***a* was reacted with 1 equivalent of carbamoylmethylenetriphenylphosphorane (7) in chloroform at room temperature for 2 h. The reaction gave a single major product together with considerable amounts of polar by-products. Purification of the crude product by flash chromatography (19) using petroleum ether – ethylacetate (3:1) gave the maleimide **9***a* in an overall yield of 40% from the hydroxy ester **7***c*. The nmr spectrum of this substance clearly showed the disappearance of the methyl ester group, the presence of a single NH proton at δ 8.08 and a vinyl proton at δ 6.39. The ir spectrum showed characteristic absorptions at 1790 and 1740 cm^{-1} for the carbonyl function and at 1665 cm^{-1} for the olefinic bond. In the mass spectrum, the molecular ion peak was found at *m/e* 431 and other major peaks at *m/e* 400 ($M^+ - OCH_3$) and 374 ($M^+ - C(CH_3)_3$). Furthermore, the uv spectrum revealed the typical maleimide chromophore having absorption maximum at 222 nm ($\log \varepsilon = 4.2$).

Completion of the synthesis of 2′-*epi*-showdomycin then only required removal of the protecting groups. Treatment of **9***a* with 80% aqueous trifluoroacetic acid led to the simultaneous removal of both *tert*-butyldimethylsilyl and methoxymethyl groups. Subsequent purification on silica gel plates gave crystalline D,L-2′-*epi*-showdomycin **9***b*, mp 170–171°C, in 60% yield. The uv spectrum of the product showed an absorption at 222 nm and the molar extinction coefficient ($\log \varepsilon$ 4.36) was also in accord with that of the known showdomycin (8), thus confirming the structure of the aglycon moiety of **9***b*. The ir data and elemental analysis were consistent with the structure of **9***b*. Furthermore, this compound was fully identified by its mass spectrum.

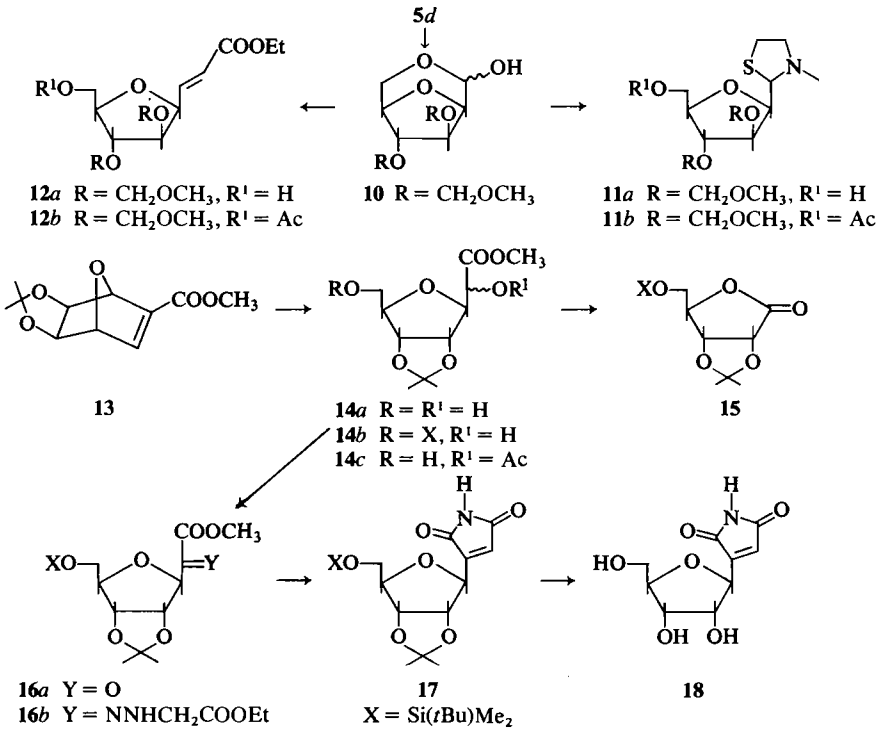
The mass spectrum of 2′-*epi*-showdomycin **9***b* was quite typical of other *C*-nucleosides (9) and showed a minor molecular ion peak at *m/e* 229 and an abundant peak at *m/e* 211 corresponding to loss of water from the molecular ion. The base peak was found at *m/e* 126 (B + 30) where B was the heterocyclic aglycon. The B + 30 peak is strongly suggestive of a formyl type residue attached to the base. Comparison of the major peaks of showdomycin with those of 2′-*epi*-showdomycin **9***b* revealed considerable similarity in the fragmentation pattern.

The nmr spectrum of **9***b* showed clearly H4 as a doublet coupled to H1[1] ($J_{1',4} = 2$ Hz), and H1[1] as a doublet of doublets ($J_{1',4} = 2$ Hz, $J_{1',2'} = 4$ Hz). A coupling constant of 4 Hz indicates *cis*-related protons. Comparison of spectra (8, 20) of *C*-nucleosides and sugars having a β-configuration at the anomeric centre to related compounds having the α-configuration shows that the chief difference is that the coupling constant corresponding to $J_{1',2'}$ in the α-anomers, having otherwise identical stereochemistry, is close to 0 Hz. We are therefore quite convinced that the stereochemistry of **9***b* is as indicated.

The overall yield for the formation of 2′-*epi*-showdomycin, based on the *exo*-nitro adduct **1***b*, was 1.6%.

The synthesis of D-showdomycin **18**, first accomplished by Kalvoda *et al.* (11) and improved by Trümmlitz and Moffatt (21), was carried out in a similar manner for the racemate, and is described below.

The readily available bicyclic ester **13** (1) was ozonolysed at −78°C, and the resulting ozonide reduced with dimethyl sulphide. The resulting ketoester aldehyde, which, when freshly prepared, seems to contain 60% of the expected aldehyde (by nmr), was normally obtained as its hydrate. Its reduction with 2.5 equivalents of lithium aluminum tri-*tert*-butoxy hydride gave diol **14***a*, presumably as a mixture of diastereoisomers, in 60–78% yield, based on **13**. It was characterized as its diacetate **14** (R = R[1] = Ac). When treated with one equivalent of *tert*-butyldimethylsilyl chloride, **14***b* was obtained. Its structure followed from the fact that acetylation gave **14***c*, in which the proton α to the acetate



function had shifted downfield by 1 ppm with respect to the same proton in **14***b*. Further confirmation was derived from the fact that the di-*tert*-butyldimethylsilyl ether of **14***a* could be selectively hydrolysed to an isomeric monosilylether **14** (R = H, R^1 = Si (tBu)Me_2), acetylation of which gave **14** (R = Ac, R^1 = Si (tBu)Me_2) in which two protons shifted downfield by 0.8 ppm. Oxidation of alcohol **14***b* with a variety of reagents such as ruthenium tetroxide (5), *N*-bromosuccinimide (15), or Collins reagent (16) resulted in either decomposition, formation of lactone **15**, or formation of the desired ketoester **16** in an irreproducible manner. However, with acetic anhydride – dimethylsulfoxide (17), the unstable ketoester **16** could be obtained in 80% yield. The analogous oxidation of related compounds such as the carbocyclic analog of **14***b* (13, 14) had never given rise to this type of erratic behaviour.

Treatment of the crude ketoester **16** with carbamoylmethylenetriphenylphosphorane (7) gave D,L-showdomycin derivative **17**, in 35% yield. The nmr spectrum of **17** was fully consistent with the structure assigned. In particular, the isopropylidene group gave two well-spaced singlets (18) indicating that only the desired "β-anomer" was obtained. Hydrolysis gave D,L-showdomycin, mp 143–144°C. Its mass spectrum was identical to that of naturally occurring showdomycin (9*a*).

Attempts to prepare pyrazomycin by cyclization of **16***a*, which had been successful for analogous compounds in the carbocyclic (13) and other series, was unsuccessful, and no pure D,L-pyrazomycin could be obtained from **16***a*, although the uv spectrum of a purified sample indicated that it had been formed in very low yield.

Experimental

Melting points were determined on a Gallenkamp block and are uncorrected. Preparative thin layer chromatography was performed using Merck HF-254 and Brinkmann HF-254 silica gel on 20 cm × 20 cm plates. Merck silica gel 60 and Woelm neutral alumina were used for column chromatography. Woelm silica gel 32–63 μ was used for flash chromatography. Mass spectra were obtained on AE1-MS-902 or LKB-900 mass spectrometers at 70 eV using a direct-insertion probe. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60, T60A, HA-100, or Bruker FT90 spectrometers. Infrared spectra were obtained on a Unicam SP1000 and Perkin–Elmer 257 and 297 ir spectrophotometers. Ultraviolet spectra were determined with a Unicam SP-800 or a Cary 17 spectrophotometer. Microanalyses were carried out by Dr. C. Daessle, Montreal.

3-Exo-*carbomethoxy*-*2*-endo-*nitro*-*5,6*-exo-*epoxido*-*7*-*oxabicyclo*[*2.2.1*]*heptane* (2a)

To a solution of **1***a* (2.02 g, 10 mmol) in methylene chloride (40 mL) was added by portions a solution of 85% *m*-chloroperbenzoic acid (2.49 g, 14 mmol) in methylene chloride (40 mL). The mixture was stirred for 2 days at room temperature. Excess peracid was then destroyed by addition of 10% sodium sulfite solution. The organic phase was washed with 5% aqueous sodium bicarbonate and water and dried ($MgSO_4$). Solvent removal left an oil which was crystallized from ethyl ether. Recrystallization from chloroform–hexane gave 1.31 g

(60%) of **2***a*, mp 100–101°C; ir (KBr) ν_{max}: 1745 (C=O), 1550 (C—NO_2) cm^{-1}; nmr (DMSO-d_6) δ: 3.52 (m, 2H), 3.69–3.76 (s + m, 4H), 4.83 (s, 1H), 4.94 (d, 1H, J = 5 Hz), 5.53 (t, 1H, J = 4 Hz); mass spectrum (70 eV) *m/e*: 215 (M^+), 184 ($M^+ - OCH_3$), 169 ($M^+ - NO_2$), 109 ($M^+ - COOCH_3 - HNO_2$). *Anal.* calcd. for $C_8H_9NO_6$: C 44.65, H 4.17, N 6.51; found: C 44.54, H 4.44, N 6.77.

2-Endo-*carbomethoxy-3*-exo-*nitro-5,6*-exo-*epoxido-7-oxabicyclo[2.2.1]heptane* (**2**b)

To a solution of **1***b* (3.03 g, 15 mmol) in methylene chloride (50 mL) was added dropwise a solution of 85% *m*-chloroperbenzoic acid (3.66 g, 17 mmol) in methylene chloride (50 mL). Stirring was continued for 2 days at room temperature. The reaction mixture was washed with 10% sodium sulfite (3 × 30 mL) and 5% sodium bicarbonate solution, water, and finally with brine. Drying over sodium sulfate and evaporation gave 2.44 g (74.4%) of **2***b* as an oil which was crystallized from methanol and recrystallized from chloroform, mp 109–110°C; ir (KBr) ν_{max}: 1745 (C=O), 1550 (C—NO_2) cm^{-1}; nmr (DMSO-d_6) δ: 3.66 (m, 2H), 3.73 (s, 3H), 3.93 (t, 1H, J = 4 Hz), 4.88 (d, 1H, J = 5 Hz), 5.10 (s, 1H), 5.25 (d, 1H, J = 4 Hz); mass spectrum (70 eV) *m/e*: 215 (M^+), 169 ($M^+ - NO_2$), 109 ($M^+ - COOCH_3 - HNO_2$). *Anal.* calcd. for $C_8H_9NO_6$: C 44.65, H 4.17, N 6.51; found: C 44.66, H 4.34, N 6.68.

5-Carbomethoxy-2,3-exo-*epoxido-7-oxabicyclo[2.2.1]-hept-5-ene* (**3**)

A solution of **2***a* (319 mg, 1.48 mmol) and DBU (281 mg, 1.77 mmol) in methylene chloride (10 mL) was refluxed for 40 min. The mixture was diluted with methylene chloride, washed with 0.1 *N* hydrochloric acid three times, with water, then evaporated to dryness, leaving a syrup which was purified by eluting it through a column of silicic acid using chloroform. Crystallization of the major product from carbon tetrachloride – hexane gave 152 mg (61%) of **3**, mp 76–77°C; ir (KBr) ν_{max}: 1700 (C=O), 1595 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 3.48 (d, 1H, J = 3.5 Hz), 3.62 (d, 1H, J = 3.5 Hz), 3.75 (s, 3H), 4.88 (d, 1H, J = 2 Hz), 5.00 (s, 1H), 7.26 (d, 1H, J = 2 Hz); mass spectrum (70 eV) *m/e*: 168 (M^+), 153 ($M^+ - CH_3$), 139, 136 ($M^+ - CH_3OH$). *Anal.* calcd. for $C_8H_8O_4$: C 57.14, H 4.80; found: C 57.37, H 4.85. Using the conditions described above, **2***b* was transformed to **3**, identical in all respects with **3** obtained from **2***a*.

5-Exo-*6*-endo-*dihydroxy-3*-exo-*nitro-7-oxabicyclo-[2.2.1]heptane-2*-endo-*carboxylic Acid γ-Lactone* (**4**a)

A solution of **2***b* (3.12 g, 15 mmol) in acetic acid (60 mL), hydrochloric acid (30 mL), and water (30 mL) was heated at 95–100°C for 2 h. After cooling to room temperature, the solvents were evaporated *in vacuo* to dryness and the residue was coevaporated with ethanol. The black residue was dissolved in hot acetone and treated with charcoal. The filtrate was concentrated to afford a yellow oil. Crystallization from acetone–chloroform gave 2.34 g (60%) of **4***a*, mp 170–171°C; ir (KBr) ν_{max}: 3500 (OH), 1800 (lactone), 1575 (C—NO_2) cm^{-1}; nmr ($(CD_3)_2CO$) δ: 3.36 (bs, 1H), 3.63 (d, 1H, J = 5 Hz), 4.10 (s, 1H), 4.60 (d, 1H, J = 5 Hz), 5.25 (s, 1H), 5.33 (s, 1H), 5.60 (t, 1H, J = 5 Hz); mass spectrum (70 eV) *m/e*: 201 (M^+), 155 ($M^+ - NO_2$). *Anal.* calcd. for $C_7H_7NO_6$: C 41.79, H 3.48, N 6.96; found: C 41.66, H 3.75, N 7.17.

5-Exo-*acetoxy-6*-endo-*hydroxy-3*-exo-*nitro-7-oxabicyclo-[2.2.1]heptane-2*-endo-*carboxylic Acid γ-Lactone* (**4**b)

A mixture of **4***a* (165 mg) and acetic anhydride (2 mL) containing one equivalent of *p*-toluenesulfonic acid monohydrate was stirred at room temperature for 30 min. The resulting solid was collected by filtration and washed with cold water to give 139 mg (70%) of analytically pure **4***b*, mp 198–200°C; ir (KBr) ν_{max}: 1800 (lactone), 1745 (C=O), 1560 (C—NO_2) cm^{-1}; nmr (DMSO-d_6) δ: 2.08 (s, 3H), 3.62 (d, 1H, J = 5 Hz), 4.82 (d, 1H, J = 5 Hz), 4.98 (s, 1H), 5.36 (s, 1H), 5.62 (t, 1H, J = 5 Hz), 5.83 (s, 1H); mass spectrum (70 eV) *m/e*: 243 (M^+), 196 ($M^+ - NO_2$), 155, 109. *Anal.* calcd. for $C_9H_9NO_7$: C 44.44, H 3.70, N 5.76; found: C 44.24, H 3.73, N 5.41.

6-Endo-*hydroxy-3*-exo-*nitro-5*-exo-*tetrahydropyranyl-oxy-7-oxabicyclo[2.2.1]heptane-2*-endo-*carboxylic Acid γ-Lactone* (**4**c)

To a solution of **4***a* (1.0 g, 5 mmol) and *p*-toluenesulfonic acid (10 mg) in acetone was added dihydropyran (2 mL). The mixture was stirred at room temperature for 4 h and then evaporated, leaving a solid residue. Recrystallization from acetone–hexane gave 1.21 g (85%) of **4***c*, mp 123–124°C; ir (KBr) ν_{max}: 1800 (lactone), 1560 (C—NO_2), 1040 cm^{-1}; nmr ($(CD_3)_2CO$) δ: 1.57 (m, 6H), 3.33–3.57 (m, 3H), 3.90 (s, 1H), 4.36–4.70 (m, 2H), 5.03 (bs, 2H), 5.23 (t, 1H, J = 4 Hz). *Anal.* calcd. for $C_{12}H_{15}NO_7$: C 50.53, H 5.26, N 4.91; found: C 50.43, H 5.47, N 5.12.

6-Endo-*hydroxy-3*-exo-*nitro-5*-exo-*methoxy-methyloxy-7-oxabicyclo[2.2.1]heptane-2*-endo-*carboxylic Acid γ-Lactone* (**4**d)

To a stirred solution of **4***a* (1.33 g, 6.6 mmol) and methylal (5 mL) in tetrahydrofuran (30 mL) was added phosphorus pentoxide (about 5 g). After standing for 1.5 h at room temperature the mixture was filtered and the residue was washed with tetrahydrofuran. The filtrate was evaporated to dryness. The residue was dissolved in ethyl acetate and washed with 5% sodium bicarbonate solution, water, and brine. Evaporation of the dried organic phase gave 1.53 g (93%) of **4***d* as an analytically pure solid, mp 154–155°C; ir (KBr) ν_{max}: 1800 (lactone), 1560 (C—NO_2) cm^{-1}; nmr ($(CD_3)_2CO$) δ: 3.06 (s, 3H), 3.36 (d, 1H, J = 5 Hz), 3.86 (s, 1H), 4.40 (d, 1H, J = 5 Hz), 4.43 (s, 2H), 5.23 (s, 2H), 5.50 (t, 1H, J = 5 Hz); mass spectrum (70 eV) *m/e*: 245 (M^+), 199 ($M^+ - NO_2$). *Anal.* calcd. for $C_9H_{11}NO_7$: C 44.08, H 4.52, N 5.71; found: C 44.22, H 4.75, N 5.54.

6-Endo-*hydroxy-3*-exo-*nitro-5*-exo-*tert-butyldimethylsilyloxy-7-oxabicyclo[2.2.1]-heptane-2*-endo-*carboxylic Acid γ-Lactone* (**4**e)

To a solution of **4***a* (2.01 g, 10 mmol) in tetrahydrofuran (20 mL) and dimethylformamide (20 mL) was added dimethyl-*tert*-butylsilyl chloride (2.26 g, 15 mmol) and imidazole (1.70 g, 25 mmol). The reaction mixture was stirred at room temperature for one day. After evaporation of the solvents the residue was dissolved in ethyl acetate, washed with water, dried, and evaporated. The residue was chromatographed on a column of silicic acid (40 g) using methylene chloride. Crystallization from hexane gave 2.84 g (90%) of **4***e*, mp 112–113°C; ir (Nujol) ν_{max}: 1800 (lactone), 1560 (C—NO_2) cm^{-1}; nmr ($CDCl_3$) δ: 0.16 (s, 6H), 0.95 (s, 9H), 3.76 (d, 1H, J = 5 Hz), 4.00 (s, 1H), 4.58 (d, 1H, J = 5 Hz), 4.84 (s, 1H), 5.14 (s, 1H), 5.51 (t, 1H, J = 5 Hz); mass spectrum (70 eV) *m/e*: 315 (M^+), 258 ($M^+ - C(CH_3)_3$). *Anal.* calcd. for $C_{13}H_{21}NO_6Si$: C 49.52, H 6.67, N 4.44; found: C 49.77, H 6.87, N 4.56.

5-Carbomethoxy-3-endo-*hydroxy-2*-exo-*tetrahydro-pyranyloxy-7-oxabicyclo[2.2.1]hept-5-ene* (**5**a) *and* *6*-Endo-*hydroxy-3*-exo-*methoxy-5*-exo-*tetrahydro-pyranyloxy-7-oxabicyclo[2.2.1]heptane-2*-endo-*carboxylic Acid γ-Lactone* (**6**a)

A solution of **4***c* (336 mg, 1.18 mmol) and DBU (205 mg, 0.13 mmol) in methanol – methylene chloride (1:1) was refluxed for 45 min. The solvents were then evaporated and the residue was dissolved in chloroform, washed with 0.1 *N* hydrochloric acid (3×) and water, dried (Na_2SO_4), and evaporated. The residue was applied on silica gel plates using chloroform. Elution

of the major, more polar, band gave 220 mg (70%) of **5***a* as an oil; ir ($CHCl_3$) ν_{max}: 3480 (OH), 1720 (C=O), 1625 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 1.68 (m, 6H), 2.70 (bs, 1H), 3.65 (m, 2H), 3.76 (s, 4H), 4.25 (d, 1H, J = 4 Hz), 4.76 (m, 1H), 5.00–5.08 (m, 2H), 7.17 (d, 1H, J = 2 Hz). *Anal.* calcd. for $C_{13}H_{18}O_6$: C 57.77, H 6.71; found: C 57.65, H 6.58. Elution of the minor, less polar, band gave 45 mg (14%) of **6***a*, mp 134–136°C; ir (KBr): 1800 (lactone) cm^{-1}; nmr ($CDCl_3$) δ: 1.66 (m, 6H), 2.73 (d, 1H, J = 4 Hz), 3.40 (s, 3H), 3.50–4.00 (m, 4H), 4.56 (d, 1H, J = 4 Hz), 4.67–4.90 (m, 2H), 5.36 (t, 1H, J = 5 Hz); mass spectrum (70 eV) *m/e*: 270 (M^+), 238 ($M^+ - CH_3OH$). *Anal.* calcd. for $C_{13}H_{18}O_6$: C 57.71, H 6.71; found: C 57.82, H 6.71.

*3-*Endo-*acetoxy-5-carbomethoxy-2-*exo-*tetrahydropyranyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5b)*

A solution of **5***a* (91 mg) and acetic anhydride (1 mL) in pyridine (2 mL) was stirred overnight at room temperature. The mixture was then evaporated to dryness *in vacuo*. The residue was dissolved in chloroform and washed with water. The dried organic phase was evaporated and purified by chromatography on a silica gel plate using ethyl ether, giving 70 mg (67%) of **5***b* as an oil which solidified on standing, mp 81–82°C; ir ($CHCl_3$) ν_{max}: 1740 (C=O), 1625 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 1.69 (m, 6H), 1.96 (s, 3H), 3.47 (m, 1H), 3.76 (s + m, 5H), 4.76 (bs, 1H), 5.05 (m, 2H), 5.16 (d, 1H, J = 4 Hz), 7.17 (d, 1H, J = 2 Hz); mass spectrum (70 eV) *m/e*: 312 (M^+), 281 ($M^+ - OCH_3$), 228 ($M^+ - O(CH_2)_4CH$). *Anal.* calcd. for $C_{15}H_{20}O_7$: C 57.68, H 6.46; found: C 57.47, H 6.49.

*5-Carbomethoxy-3-*endo-*hydroxy-2-*exo-*methoxymethyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5c)*

A solution of **4***d* (1.2 g, 4.89 mmol) and triethylamine (510 mg, 3 mmol) in dry methanol (60 mL) was refluxed for 8 h. Then the solution was filtered to remove small amounts of precipitate and the filtrate was evaporated to dryness. The residue was dissolved in chloroform, washed twice with water, dried over sodium sulfate, and evaporated. The oil obtained was chromatographed on a column of alumina using 3:1 chloroform – ether and slowly increasing the polarity to pure ethyl ether. Compound **5***c* was obtained as a colourless oil in 40% yield (500 mg); ir ($CHCl_3$) ν_{max}: 3500 (alcohol), 1730 (ester), 1625 (olefin) cm^{-1}; nmr ($CDCl_3$) δ: 2.89 (bs, 1H, OH), 3.20 (s, 3H, CH_2OCH_3), 3.51 (d, 1H, $CHOCH_2OCH_3$, J = 1 Hz), 3.73 (s, 3H, $COOCH_3$), 4.22 (dd, 1H, $CHOH$, J = 1, 4 Hz), 4.71 (s, 2H, CH_2OCH_3), 4.92–5.04 (m, 2H, bridgeheads), 7.06 (d, 1H, J = 2 Hz, C=CH) ppm. *Anal.* calcd. for $C_{10}H_{14}O_6$: C 52.17, H 6.13; found: C 52.08, H 6.28.

*5-Carbomethoxy-2-*exo-*3-*endo-*dimethoxymethyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5d)*

To a stirred solution of **5***c* (1.3 g, 5.6 mmol) in dry chloroform (50 mL) were added methylal (10 mL) and approximately 3 g of phosphorus pentoxide. After 2 h at room temperature, the mixture was poured into 5% sodium bicarbonate solution. The organic layer was washed with water, dried over sodium sulfate, and evaporated to dryness. The residue was purified on a column of silicic acid using chloroform–hexane – ethyl ether (10:6:1), giving 1.3 g (84%) of **5***d* as a homogeneous syrup; ir ($CHCl_3$) ν_{max}: 1730 (ester), 1625 (olefin) cm^{-1}; nmr ($CDCl_3$) δ: 3.36 (2s, 3H + 3H, CH_2OCH_3), 3.66 (d, 1H, CH_3OCH_2OCH, J = 0.8 Hz), 3.76 (s, 3H, $COOCH_3$), 4.20 (dd, 1H, CH_3OCH_2OCH, J = 0.8, 4 Hz), 4.66 (q, 2H, OCH_2, J = 3, 6 Hz), 4.76 (s, 2H, OCH_2), 4.99 (d, 1H, CH=CH—CH, J = 2 Hz), 5.12 (d, 1H, CH=C—CH, J = 4 Hz), 7.15 (d, 1H, C=CH, J = 2 Hz); ms (70 eV) *m/e*: 259 ($M^+ - CH_3$), 243 ($M^+ - OCH_3$), 213 ($M^+ - CH_3OCH_2O$), 148. *Anal.* calcd. for $C_{12}H_{18}O_7$: C 52.55, H 6.62; found: C 52.38, H 6.53.

*5-Carbomethoxy-3-*endo-*hydroxy-2-*exo-*tert-butyldimethylsilyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5e) and 6-*Endo-*hydroxy-3-*exo-*methoxy-5-*exo-*tert-butyldimethylsilyloxy-7-oxabicyclo[2.2.1]heptane-2-*endo-*carboxylic Acid γ-Lactone (6b)*

To a stirred refluxing solution of DBU (635 mg) in methylene chloride – methanol (15:15 mL) was added dropwise a solution of **4***e* (1.22 g, 3.8 mmol) in methylene chloride (15 mL). The mixture was kept refluxing for an additional 15 min. After evaporation of the cooled solution the residue was dissolved in chloroform, washed with dilute hydrochloric acid and water, dried over sodium sulfate, and evaporated. The residue was chromatographed on a column of silicic acid using chloroform, giving 976 mg (84%) of the more polar **5***e* as a colorless syrup; ir ($CHCl_3$) ν_{max}: 3500 (OH), 1725 (C=O), 1620 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 0.13 (s, 6H), 0.97 (s, 9H), 3.37 (bs, 1H), 3.66 (s, 1H), 3.76 (s, 3H), 4.13 (d, 1H, J = 5 Hz), 4.75 (d, 1H, J = 2 Hz), 5.01 (d, 1H, J = 5 Hz), 7.08 (d, 1H, J = 2 Hz). The less polar compound **6***b* (62 mg) was also obtained; ir ($CHCl_3$): 1800 (lactone) cm^{-1}; nmr ($CDCl_3$) δ: 0.15 (s, 6H), 0.85 (s, 9H), 2.67 (d, 1H, J = 5 Hz), 3.33 (s, 3H), 3.62 (s, 1H), 3.68 (s, 1H), 4.30–4.50 (m, 2H), 5.63 (m, 1H).

*5-Carbomethoxy-3-*endo-*pivaloyloxy-2-*exo-*tert-butyldimethylsilyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5f)*

A mixture of **5***e* (320 mg, 1 mmol) and pivaloyl chloride (1 mL) in dry pyridine (5 mL) was stirred overnight at room temperature and then evaporated to dryness *in vacuo*. The mixture was coevaporated with toluene as a chaser, dissolved in chloroform, and washed with 5% hydrochloric acid and water. The dried organic phase was chromatographed on a column of silicic acid (act. III) using ethyl ether – hexane (1:1), giving 300 mg (89%) of **5***f* as a syrup that solidified on standing, mp 48–49°C; ir (neat) ν_{max}: 1760, 1750 (C=O), 1630 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 0.10 (s, 6H), 0.87 (s, 9H), 1.13 (s, 9H), 3.72 (s, 3H), 3.80 (bs, 1H), 4.80 (bs, 1H), 4.88 (d, 1H, J = 5 Hz), 5.25 (d, 1H, J = 5 Hz), 7.28 (d, 1H, J = 2 Hz); mass spectrum (70 eV) *m/e*: 369 ($M^+ - CH_3$), 353 ($M^+ - OCH_3$), 327 ($M^+ - C(CH_3)_3$), 258, 201. *Anal.* calcd. for $C_{19}H_{32}O_6Si$: C 59.35, H 8.39; found: C 59.66, H 8.28.

*5-Carbomethoxy-2-*exo-*3-*endo-*di-O-*tert-*butyldimethylsilyloxy-7-oxabicyclo[2.2.1]hept-5-ene (5g)*

The mixture of **5***e* (1.14 g, 3.8 mmol), dimethyl-*tert*-butylsilyl chloride (1.44 g, 9.5 mmol) and imidazole (610 mg, 8.9 mmol) in dimethylformamide (20 mL) was stirred at room temperature for 6 h and then evaporated to dryness. The residue was dissolved in ethyl acetate, washed with water and with brine, dried over sodium sulfate, and evaporated. The resulting syrup was chromatographed on a column of silicic acid using ethyl ether – hexane (1:1), giving 600 mg (51%) of **5***g* as an oil which solidified on standing, mp 90–91°C; ir (KBr) ν_{max}: 1738 (C=O), 1630 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 0.10 (s, 12H), 0.83 (s, 9H), 0.90 (s, 9H), 3.54 (bs, 1H), 3.64 (s, 3H), 4.02 (d, 1H, J = 4 Hz), 4.62 (d, 1H, J = 1 Hz), 4.85 (d, 1H, J = 4 Hz), 7.02 (d, 1H, J = 2 Hz). *Anal.* calcd. for $C_{20}H_{38}O_5Si_2$: C 57.97, H 9.18; found: C 57.88, H 9.27.

Methyl 2-(2¹,3¹-Di-O-methoxymethyl-β-D,L-arabinofuranosyl) Glycolate (7a)

Through a solution of **5***d* (327 mg, 1.19 mmol) in dry methylene chloride at −78°C was bubbled ozone until a faintly blue color was observed. Excess ozone was flushed with dry nitrogen while the system was kept at −78°C and dimethyl sulfide (0.5 mL) was added. The mixture was allowed to rise to room temperature over a period of 5 h. The solution was then evaporated to dryness. To a precooled solution of the residue in freshly distilled tetrahydrofuran (50 mL) at 0°C was added lithium tri-*tert*-butoxyaluminum hydride (0.91 g, 3.57 mmol).

The resulting clear solution was then allowed to warm to room temperature and stirred overnight under dry nitrogen. A solution of ammonium sulfate (2 g) in water (2 mL) and Celite (1 g) were added to the reaction at 0°C. The mixture was stirred for 30 min and finally filtered over a layer of Celite. Following evaporation of the solvent the residue was dissolved in ethyl acetate, washed with water, dried ($MgSO_4$), and evaporated. The crude clear oil was crystallized from chloroform–hexane giving 222 mg (60%) of **7***a* as white crystals, mp 70–71°C; ir ($CHCl_3$) ν_{max}: 3500 (alcohol), 1745 (ester) cm^{-1}; nmr ($CDCl_3$) δ: 3.33 (s, 3H), 3.36 (s, 3H), 3.67–3.96 (m, 6H), 4.06–4.56 (m, 5H), 4.56–4.83 (m, 5H) ppm. *Anal.* calcd. for $C_{12}H_{22}O_9$: C 46.45, H 7.15; found: C 46.28, H 7.28.

Methyl 2-O-acetyl-2-(5¹-O-acetyl-2¹,3¹-di-O-methoxymethyl-β-D,L-arabinofuranosyl) Glycolate (7b)

The compound 7*a* (73 mg) was acetylated using acetic anhydride (1 mL) and pyridine (1 mL) with stirring overnight. After evaporation to dryness the residue was chromatographed on a column of silicic acid using ethyl ether – hexane (1:1) giving 84 mg (92%) of 7*b* as an oil; ir (neat) ν_{max}: 1745, 1755 (C=O) cm^{-1}; nmr ($CDCl_3$) δ: 2.00 (s, 3H), 2.03 (s, 3H), 3.21 (s, 3H), 3.24 (s, 3H), 3.26 (s, 3H), 3.90–4.13 (m, 5H), 4.13–4.30 (m, 1H), 4.32 (d, 2H, J = 1 Hz), 4.40 (s, 2H), 4.86 (s, 0.5H), 5.0 (s, 0.5H); mass spectrum (70 eV) *m/e*: 363 ($M^+ - OCH_3$), 317, 289 ($M^+ - COCH_3 - CH_3OCH_2OH$). *Anal.* calcd. for $C_{16}H_{26}O_{11}$: C 48.73, H 6.60; found: C 48.63, H 6.88.

*Methyl 2-(2¹,3¹-Di-O-methoxymethyl-5¹-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glycolate (7c)*

A mixture of **7***a* (169 mg, 0.54 mmol), dimethyl-*tert*-butylsilyl chloride (82 mg, 0.54 mmol), and imidazole (92 mg, 1.35 mmol) in dimethylformamide (5 mL) was stirred at room temperature for 18 h. Then the reaction mixture was added to 60 mL of ethyl ether and washed three times with water, dried, and evaporated, leaving a syrup. The latter was chromatographed on a column of silicic acid eluting with ethyl ether – hexane (2:1) giving 197 mg (85%) of **7***c* as an oil which crystallizes below room temperature; ir ($CHCl_3$) ν_{max}: 3500 (alcohol), 1745 (ester) cm^{-1}; nmr ($CDCl_3$) δ: 0.10 (s, 6H), 0.96 (s, 9H), 3.32 (s, 3H), 3.36 (s, 3H), 3.48 (m, 1H), 3.60–4.00 (m, 6H), 4.08–4.43 (m, 4H), 4.62 (bs, 4H) ppm. *Anal.* calcd. for $C_{18}H_{36}O_9Si$: C 50.94, H 8.94; found: C 50.68, H 8.37.

*Methyl 2-(2¹,3¹-Di-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glycolate (7d)*

After reductive ozonolysis of **5***g* (386 mg, 0.93 mmol) in methylene chloride, the solution was washed with brine twice, dried, and evaporated. To a solution of the residue in dry tetrahydrofuran (40 mL) was added lithium tri-*tert*-butoxyaluminum hydride (945 mg, 3.72 mmol) at 0°C. The resulting clear mixture was allowed to warm to room temperature and stirred overnight under nitrogen. A solution of ammonium sulfate (2 g) in water (2 mL) and Celite (1 g) were added to the reaction mixture at 0°C. The mixture was stirred for 30 min and finally filtered over a layer of Celite. The residue was washed with tetrahydrofuran. Following evaporation of the solvent the residue was dissolved in ethyl acetate, washed with water, dried, and evaporated. The residue was purified on silica gel plates using ethyl ether – hexane (2:1), giving 250 mg (59%) of 7*d* as an oil; ir ($CHCl_3$) ν_{max}: 3500 (OH), 1745 (C=O) cm^{-1}; nmr ($CDCl_3$) δ: 0.10 (m, 12H), 0.86 (s, 9H), 0.90 (s, 9H), 1.96 (bs, 1H), 2.70 (bs, 1H), 3.53–4.36 (m, 10H). *Anal.* calcd. for $C_{20}H_{42}O_7Si_2$: C 53.33, H 9.33; found: C 53.00, H 9.17.

*Methyl 2-O-acetyl-2-(5¹-O-acetyl-2¹,3¹-di-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glycolate (7e)*

The compound 7*d* (126 mg) was acetylated with acetic anhydride (1 mL) and pyridine (1.5 mL). After the usual work-up, the crude product was purified by column chromatography (aluminum oxide act. III) using ethyl ether – hexane (1:2) to give 136 mg (91%) of **7***e* as an oil which solidified on standing, mp 74–77°C; ir (KBr) ν_{max}: 1755 (C=O), 1240, 1080 cm^{-1}; nmr ($CDCl_3$) δ: 0.13 (m, 12H), 0.96 (s, 18H), 2.03 (s, 3H), 2.10 (s, 3H), 3.76 (s, 3H), 3.90–4.33 (m, 6H), 4.70, 4.96 (bs, 0.5H each); mass spectrum (60 eV) *m/e*: 519 ($M^+ - CH_3$), 503 ($M^+ - OCH_3$), 477 ($M^+ - C(CH_3)_3$). *Anal.* calcd. for $C_{24}H_{46}O_9Si_2$: C 53.93, H 8.61; found: C 54.12, H 8.84.

*Methyl 2-(2¹,3¹,5¹-Tri-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glycolate (7f)*

To a solution of 7*d* (106 mg, 0.24 mmol) in dimethylformamide (5 mL) was added dimethyl-*tert*-butylsilyl chloride (36 mg, 0.24 mmol) and imidazole (40 mg, 0.6 mmol). The mixture was stirred at room temperature for 21 h. The solvent was evaporated *in vacuo* and the residue was coevaporated several times with ethyl acetate. The residue was dissolved in chloroform, washed with water, dried, and evaporated. The resulting syrup was chromatographed on a column of alumina using ethyl ether – hexane (1:2) to give 125 mg (94%) of 7*f* as an oil; ir ($CHCl_3$) ν_{max}: 3500 (OH), 1730 (C=O) cm^{-1}; nmr ($CDCl_3$) δ: 0.10 (m, 18H), 0.92 (m, 27H), 2.96 (bs, 1H), 3.30–3.90 (m, 5H), 3.90–4.45 (m, 5H). *Anal.* calcd. for $C_{26}H_{56}O_7Si_3$: C 55.32, H 9.93; found: C 55.59, H 9.84.

*Methyl 2-O-acetyl-2-(2¹,3¹,5¹-tri-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glycolate (7g)*

The compound **7***f* (125 mg, 0.22 mmol) was acetylated with acetic anhydride (1.5 mL) and pyridine (1.5 mL). After the usual work-up the crude product was chromatographed on a column of alumina using ethyl ether – hexane (1:1) to give 134 mg (100%) of **7***g* as an oil which solidified on standing, mp 68–72°C; ir (KBr) ν_{max}: 1760 (C=O), 1080, 840 cm^{-1}; nmr ($CDCl_3$) δ: 0.05 (m, 18H), 0.87 (bs, 27H), 2.06 (s, 3H), 3.63 (m, 1H), 3.71 (s, 3H), 3.85–4.33 (m, 5H), 4.70, 4.85 (two bs, 1H). *Anal.* calcd. for $C_{28}H_{58}O_8Si_3$: C 55.45, H 9.55; found: C 55.16, H 9.32.

*Methyl 2-(2¹,3¹-Di-O-methoxymethyl-5¹-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glyoxylate (8a)*

To a solution of **7***c* (424 mg, 1 mmol) in carbon tetrachloride (40 mL) were added ruthenium dioxide dihydrate (20 mg) and a solution of sodium periodate (856 mg, 4 mmol) in water (40 mL). The pH of the reaction mixture was controlled between 6 and 7 by the addition of a 5% sodium bicarbonate solution. After 6 h, stirring at room temperature or until a yellow color persisted, the reaction was terminated by adding a few drops of isopropyl alcohol. After collection of the black precipitated solid (RuO_2) on Celite, the organic phase was washed with water and brine, dried over magnesium sulfate, and evaporated, leaving 359 mg of crude **8***a* as a low mp white solid (less than 25°C). Attempted purification by chromatography on silicic acid led to partial decomposition and accordingly the material was used directly in the next step; ir (neat) ν_{max}: 1750, 1775 (ketone, ketoester) cm^{-1}; nmr ($CDCl_3$) δ: 0.08 (s, 6H), 0.86 (s, 9H), 3.13 (s, 3H), 3.25 (s, 3H), 3.36–3.58 (m, 2H), 3.72 (s, 3H), 3.76 (m, 1H), 4.13 (bs, 1H), 4.30 (m, 1H), 4.40–4.70 (m, 4H), 5.06 (d, 1H, J = 5 Hz) ppm.

*Methyl 2-(2¹,3¹,5¹-Tri-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl) Glyoxylate (8b)*

To the mixture of **7***e* (416 mg, 0.74 mmol) in carbon tetrachloride (40 mL) and ruthenium dioxide dihydrate (20 mg) was added a solution of sodium periodate (633 mg) in water (40 mL). The pH of the mixture was controlled between 6 and 7 by the addition of a 5% sodium bicarbonate solution. After vigorously stirring at room temperature until a yellow color persisted, a few drops of isopropyl alcohol were added to terminate the reaction. Ruthenium dioxide was removed on Celite and the organic

phase was washed with water and brine, dried ($MgSO_4$), and evaporated, giving 353 mg of crude **8***b*; ir ($CHCl_3$) ν_{max}: 1750, 1730 (C=O) cm^{-1}; nmr ($CDCl_3$) δ: 0.13 (m, 18H), 0.86 (m, 27H), 3.76–4.00 (m, 5H), 4.13 (m, 1H), 4.33 (m, 1H), 4.53 (bs, 1H), 4.66 (d, 1H, J = 4 Hz).

*2-(2¹,3¹-Di-O-methoxymethyl-5¹-O-*tert*-butyldimethylsilyl-β-D,L-arabinofuranosyl)maleimide (9*a*)*

A solution of carbamoylmethylenetriphenylphosphorane (400 mg, 1.2 mmol) and the crude ketoester **8***a* (450 mg, 1.07 mmol) in freshly distilled chloroform (20 mL) was stirred at room temperature for 2 h. The solvent was then evaporated and the residue was purified by chromatography on a silica gel column using petroleum ether – ethyl acetate (3:1), giving 216 mg (47%) of solid **9***a*, mp 49–50°C; ir ($CHCl_3$) ν_{max}: 3460, 3250 (alcohol, amine), 1740, 1790 (maleimide), 1655 (olefin) cm^{-1}; nmr ($CDCl_3$, D_2O), 100 MHz δ: 0.10 (s, 6H, $Si(CH_3)_2$), 0.82 (s, 9H, $C(CH_3)_3$), 3.20 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.53–3.70 (m, 2H, $SiOCH_2CH$), 3.70–4.10 (m, 1H, $SiOCH_2CH$), 4.30 (d, 1H, OCH_2OCH, J = 2 Hz), 4.50 (d, 1H, OCH_2OCH, J = 4 Hz), 4.65 (q, 2H, CH_3OCH_2), 4.80 (q, 2H, CH_3OCH_2), 5.0 (q, 1H, "anomeric" proton, J_1 = 4 Hz, J_2 = 3 Hz), 6.39 (d, 1H, C=CH, J = 2 Hz); ms (70 eV) *m/e*: 431 (M^+), 400 (M^+ – OCH_3), 374 (M^+ – $C(CH_3)_3$), 328. *Anal.* calcd. for $C_{19}H_{33}NO_8Si$: C 52.90, H 7.66, N 1.62; found: C 52.68, H 7.76, N 1.49.

*2¹-*Epi*-showdomycin (9*b*)*

A solution of **9***a* (212 mg, 0.5 mmol) in a mixture of trifluoroacetic acid – water–tetrahydrofuran (4:1:1) (12 mL) was stirred at room temperature for 4 h. After evaporation to dryness *in vacuo* the residue was crystallized from acetone–hexane to give 68 mg (60%) of **9***b* with mp 170–171°C; ir (KBr) ν_{max}: 3470, 3110 (alcohol, amine), 1775, 1720 (maleimide), 1625 (olefin) cm^{-1}; uv (λ_{max}^{EtOH}): 222 nm (log ε 4.36); nmr (D_2O), 100 MHz δ: 3.8–3.9 (m, 2H, $HOCH_2$—CH), 4.1–4.25 (m, 1H, $HOCH_2CHO$), 4.28 (q, 1H, J_1 = 2 Hz, J_2 = 3 Hz), 4.55 (q, 1H, J_1 = 2 Hz, J_2 = 4 Hz), 5.1 (q, 1H, "anomeric" H, J_1 = 2 Hz, J_2 = 4 Hz), 6.85 (d, 1H, C=CH, J = 2 Hz); ms (70 eV) *m/e*: 229 (M^+), 211 (M^+ – H_2O), 180, 140 (M^+ – $HOCHCH_2B$), 127 (B + 31), 126 (B + 30), 110, 87, 85, 69, 57, 55, 45, 44, 43, 32, 31, 28 (B is maleimide). *Anal.* calcd. for $C_9H_{11}NO_6$: C 47.16, H 4.80, N 6.15; found: C 47.05, H 4.75, N 6.08.

3,4-Di-O-methoxymethyl-2,5-anhydro-D,L-glucose (10)

To a solution of **5***d* (230 mg, 0.84 mmol) in methylene chloride was bubbled ozone until a faintly blue color was observed. Excess ozone was flushed with dry nitrogen and evaporation of solvent left a white foam. The ozonide in isopropanol was treated with sodium borohydride (500 mg) at 0°C and then refluxed for 4 h. The solution was then cooled in an ice-bath and stirred with 50% aqueous acetic acid (10 mL) for 30 min and evaporated *in vacuo*. The residue was coevaporated with ethanol and dissolved in water and stirred with sodium periodate (300 mg) for 1 h at room temperature. The resulting precipitate was removed by filtration on cotton and the filtrate extracted with chloroform three times. The organic phase was dried and evaporated, giving 77 mg (37%) of **10** as a colorless syrup; ir ($CHCl_3$) ν_{max}: 3500, 3420 (OH), 2840, 2800 cm^{-1}; nmr ($CDCl_3$) δ: 3.36 (bs, 6H), 3.56 (bs, 1H), 3.90 (m, 1H), 3.93–4.27 (m, 3H), 4.36 (m, 2H), 4.72 (m, 4H), 4.98 (bs, 1H). *Anal.* calcd. for $C_{10}H_{18}O_7$: C 47.99, H 7.25; found: C 47.65, H 7.51.

*N-methyl 2-(2¹,3¹-Di-O-methoxymethyl-β-D,L-arabinofuranosyl) Thiazolidine and its 5¹-Acetate (11*b*)*

To a solution of **10** (77 mg, 0.31 mmol) in dry benzene (15 mL) was added *N*-methylthioethanolamine (31 mg, 0.34 mmol). The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent the crude product (**11***a*) was directly acetylated with acetic anhydride in pyridine. The compound (**11***b*) was purified by a column of alumina using chloroform to give 86 mg (77%) of **11***b* as a colorless oil; ir ($CHCl_3$) ν_{max}: 2870, 2830 (N—CH_3), 1755 (C=O) cm^{-1}; nmr ($CDCl_3$) δ: 2.03 (s, 3H), 2.30, 2.40 (s + s, 3H), 2.60–3.26 (m, 4H), 3.30 (s, 3H), 3.40 (s, 3H), 3.90–4.23 (m, 6H), 4.37–4.53 (m, 1H), 4.57–4.76 (m, 4H); mass spectrum (70 eV) *m/e*: 365 (M^+), 333 (M^+ – CH_3OH), 318 (M^+ – CH_2SH), 102. *Anal.* calcd. for $C_{15}H_{27}NO_7S$: C 49.32, H 7.40, N 3.84, S 8.77; found: C 49.53, H 7.60, N 4.08, S 8.53.

Ethyl trans*-3-(2¹,3¹-Di-O-methoxymethyl-β-D,L-arabinofuranosyl) Acrylate (12*a*)*

To a solution of crude **10** (144 mg, 0.58 mmol) in methylene chloride (10 mL) was added carbethoxymethylenetriphenylphosphorane (242 mg, 0.69 mmol). After 4 h at room temperature, the solvent was evaporated and the residue was partitioned between chloroform and water. The organic phase was dried over sodium sulfate and evaporated. The residue was chromatographed on a column of alumina using chloroform, eluting 143 mg (79%) of **12***a* as a chromatographically homogeneous syrup; ir ($CHCl_3$) ν_{max}: 3500 (OH), 1730 (C=O), 1680 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 1.23 (t, 3H, J = 7 Hz), 2.23 (t, 1H, J = 6 Hz), 3.26 (s, 3H), 3.30 (s, 3H), 3.53–4.30 (m, 8H), 4.52 (d, 2H, J = 2 Hz), 4.60 (s, 2H), 5.98 (d, 1H, J = 14 Hz), 6.85 (dd, 1H, J = 14 Hz, J = 4 Hz); mass spectrum (70 eV) *m/e*: 320 (M^+), 289 (M^+ – OCH_3), 243, 230 (M^+ – $2CH_3OCH_2$). *Anal.* calcd. for $C_{14}H_{24}O_8$: C 52.49, H 7.55; found: C 52.48, H 7.62.

Ethyl trans*-3-(5¹-O-acetyl-2¹,3¹-di-O-methoxymethyl-β-D,L-arabinofuranosyl) Acrylate (12*b*)*

The compound **12***a* (40 mg, 0.13 mmol) was acetylated using acetic anhydride (1 mL) and pyridine (2 mL). Evaporation to dryness and separation on a column of alumina, eluting with chloroform gave 40 mg (89%) of **12***b* as a colorless oil; ir ($CHCl_3$) ν_{max}: 1750, 1730 (C=O), 1680 (C=C) cm^{-1}; nmr ($CDCl_3$) δ: 3.27 (t, 3H, J = 6 Hz), 2.06 (s, 3H), 3.28 (s, 3H), 3.33 (s, 3H), 3.90–4.30 (m, 8H), 4.57 (d, 2H, J = 2 Hz), 4.62 (s, 2H), 6.02 (d, 1H, J = 14 Hz), 6.88 (dd, 1H, J = 14 Hz, J = 4 Hz); mass spectrum (70 eV) *m/e*: 362 (M^+), 331 (M^+ – OCH_3), 317 (M^+ – $2CH_3O$), 272 (M^+ – $2CH_3OCH_2$). *Anal.* calcd. for $C_{16}H_{26}O_9$: C 53.03, H 7.23; found: C 53.10, H 7.32.

*Diol 14*a *from Olefin 13*

The olefin **13** (452 mg, 2 mmol) in dry methylene chloride (50 mL) was treated with ozone at −78°C until the blue colour persisted. The excess ozone was removed by bubbling in dry nitrogen gas, and then 1 mL of dimethyl sulfide was added at −78°C. The solution was then allowed to warm up to room temperature with stirring, at which time it was evaporated.

To the resulting oily residue in dry tetrahydrofuran (THF), (50 mL) at 0°C under a nitrogen atmosphere was added lithium aluminum tri-(*tert*-butoxy) hydride (7.0 mmol, 1.78 g). After stirring at 0°C for 3 h, ammonium sulfate (2 g) in 10 mL of water was added, and the stirring continued for another 30 min. The mixture was then filtered, and the residue washed with 25 mL of THF, the combined filtrates were evaporated to dryness and the resulting residue was dissolved in ethyl acetate (50 mL), washed with brine (20 mL × 3), dried (Na_2SO_4), and evaporated to afford 315 mg (65%) of diol **14***a*; ir ($CHCl_3$) ν_{max}: 3650–3350 (OH), 1755 (C=O), 1395 cm^{-1}; nmr ($CDCl_3$) δ: 1.33 (s, 3H), 1.52 (s, 3H), 3.66 (d, 2H, J = 4.0 Hz, CH_2OH), 3.76 (s, 3H, $COOCH_3$), 3.78–4.85 (m, 7H, two deuterium exchangeable protons) ppm; ms (80°C) *m/e*: 262 (M^+), 247 (M^+ – CH_3), 230 (M^+ – CH_2OH), 203 (M^+ – $COOCH_3$), 201, 187, 185, 173 (M^+ – $CHOHCOOCH_3$), 169, 139, 85, 83. *Anal.* calcd. for $C_{11}H_{18}O_7$: C 50.38, H 6.91; found: C 50.59, H 6.76.

*Diacetate 14 (R = R¹ = Ac) from Diol 14*a

The diol **14***a* (131 mg, 0.5 mmol) was stirred overnight at room temperature in 5 mL pyridine – acetic anhydride (3:2). After the removal of the solvent, chloroform (25 mL) was added to the residue and the solution washed with dilute hydrochloric acid (10 mL × 2), water (10 mL × 2), dried (Na_2SO_4), and evaporated. The diacetate **14** (R = R¹ = Ac) was obtained in quantitative yield; ir ($CHCl_3$) ν_{max}: 1765 and 1755 (C=O), 1390 cm^{-1}; nmr ($CDCl_3$) δ: 1.35 (s, 3H), 1.52 (s, 3H), 2.08 (s, 3H, CO*CH*$_3$), 2.19 (s, 3H, COC*H*$_3$), 3.75 (s, 3H, COOC*H*$_3$), 4.12 (bs, 2H, C*H*$_2$OCOCH$_3$), 4.22–4.95 (m, 4H), 5.12 (d, *J* = 4 Hz, C*H*OCOCH$_3$) ppm; ms (150°C) *m/e*: 346 (M^+), 331 ($M^+ - CH_3$), 287 ($M^+ - COOCH_3$), 271, 245, 243, 229, 215, 211, 201, 179, 169. *Anal.* calcd. for $C_{15}H_{22}O_9$: C 52.03, H 6.35; found: C 52.33, H 6.75.

*Monosilylated Diol 14*b *from Diol 14*a

To the diol **14***a* (524 mg, 2 mmol) and imidazole (340 mg, 5 mmol) in *N,N*-dimethylformamide (5 mL) was added *tert*-butyldimethylchlorosilane (302 mg, 2 mmol). After stirring at room temperature for 18 h, the solvent was removed under high vacuum. To the residue was then added ethyl acetate (50 mL) and the solution was washed with water (20 mL × 3), dried (Na_2SO_4), and evaporated. The crude product was chromatographed on silica gel. Elution with ether–hexane (1:1) afforded 677 mg (90%) of the silyl ether **14***b*; ir ($CHCl_3$) ν_{max}: 3550 and 3400 (OH), 1770 (C=O), 1395 cm^{-1}; nmr ($CDCl_3$) δ: 0.13 (s, 6H, Si(C*H*$_3$)$_2$), 0.92 (s, 9H, Si—*t*Bu), 1.32 (s, 3H), 1.50 (s, 3H), 3.73 (bs, 5H, COOC*H*$_3$ and C*H*$_2$OSi), 3.86–4.82 (m, 6H) ppm; ms (180°C) *m/e*: 361 ($M^+ - CH_3$), 317 ($M^+ - COOCH_3$), 287 ($M^+ - CHOHCOOCH_3$), 261 ($M^+ - (CH_3)_2Si$—*t*Bu), 201. *Anal.* calcd. for $C_{17}H_{32}O_7Si$: C 54.25, H 8.51; found: C 54.55, H 8.72.

*Monoacetate 14*c *from Monosilylated Diol 14*b

The acetate **14***c* was prepared from the alcohol **14***b* by the usual acetylation procedure; ir ($CHCl_3$) ν_{max}: 1770 (C=O), 1395 cm^{-1}; nmr ($CDCl_3$) δ: 0.08 (s, 6H, (C*H*$_3$)$_2$), 0.8 (s, 9H, Si—*t*Bu), 1.32 (s, 3H), 1.50 (s, 3H), 2.11 (s, 3H, COC*H*$_3$), 3.60 (d, 2H, *J* = 5 Hz, C*H*$_2$OSi), 3.68 (s, 3H, COOC*H*$_3$), 3.83–4.78 (m, 4H), 5.08 (d, 1H, *J* = 5 Hz, C*H*OCOCH$_3$) ppm; ms (170°C) *m/e*: 403 ($M^+ - CH_3$), 387 ($M^+ - OCH_3$), 361 ($M^+ - t$Bu), 303 ($M^+ - (CH_3)_2Si$—*t*Bu), 261, 243, 201.

Silylated Diol 14 (R = R¹ = (CH$_3$*)*$_2$*Si*—t*Bu) from Diol 14*a

The disilyl ether **14** (R = R¹ = $(CH_3)_2Si$—*t*Bu) was prepared with two equivalents of *tert*-butyldimethylchlorosilane from **14***a* by the usual silylation procedure; nmr ($CDCl_3$) δ: 0.07 (s, 12H, 2 Si(C*H*$_3$)$_2$), 0.89, 0.92 (each s, 18H, 2 Si—*tBu*), 1.29 (s, 3H), 1.49 (s, 3H), 3.56 (m, 2H), 3.63 (s, 3H, COOC*H*$_3$), 3.80–4.72 (m, 5H) ppm.

Monosilylated Diol 14 (R = H, R¹ = (CH$_3$*)*$_2$*Si*—t*Bu) from Silylated Diol 14 (R = R¹ = (CH*$_3$*)*$_2$*Si*—t*Bu)*

Disilyl ether **14** (R = R¹ = $(CH_3)_2Si$ +) (490 mg, 1 mmol) was stirred in a solution of acetic acid – water–THF (3:1:1) (5 mL) at room temperature for 20 h. After evaporation of the solution, chloroform (40 mL) was added to the residue, which was washed with saturated sodium bicarbonate solution (15 mL × 2), water (15 mL), then dried (Na_2SO_4) and evaporated. The alcohol **14** (R = H, R¹ = $(CH_3)_2Si$ +) was obtained in 90% yield; ir ($CHCl_3$) ν_{max}: 3550 (OH), 1770 (C=O), 1400, 1395 cm^{-1}; nmr ($CDCl_3$) δ: 0.08, 0.11 (each s, 6H, Si(C*H*$_3$)$_2$), 0.95 (s, 9H, Si—*t*Bu), 1.33 (s, 3H), 1.54 (s, 3H), 2.77 (bs, 1H, O*H*), 3.66 (m, 2H, C*H*$_2$OH), 3.76 (s, 3H, COOC*H*$_3$), 3.96–4.82 (m, 5H) ppm.

Monoacetate 14 (R = Ac, R¹ = (CH$_3$*)*$_2$*Si*—t*Bu) from Monosilylated Diol 14 (R = H, R¹ = (CH*$_3$*)*$_2$*Si*—t*Bu)*.

Monoacetate **14** (R = Ac, R¹ = $(CH_3)_2Si$—*t*Bu) was prepared from alcohol **14** (R = H, R¹ = $(CH_3)_2Si$—*t*Bu) by the usual acetylation procedure; ir ($CHCl_3$) ν_{max}: 1760 (C=O), 1400, 1390 cm^{-1}; nmr ($CDCl_3$) δ: 0.08, 0.11 (each s, 6H, Si(C*H*$_3$)$_2$), 0.92 (s, 9H, Si—*t*Bu), 1.32 (s, 3H), 1.53 (s, 3H), 2.03 (s, 3H, COC*H*$_3$), 3.70 (s, 3H, COOC*H*$_3$), 4.12 (s, 2H, C*H*$_2$OCOCH$_3$), 4.16–4.85 (m, 5H) ppm.

*Lactone 15 from Monosilylated Diol 14*b

To alcohol **14***b* (94 mg, 0.25 mmol) in methylene chloride (5 mL) was added 15 equivalents of chromium trioxide – pyridine complex in methylene chloride (10 mL). After stirring for 30 min at room temperature, the solution was decanted from the black residue, and the residue was triturated with anhydrous ether (20 mL). The combined organic layers were washed with 5% HCl (15 mL), saturated sodium bicarbonate solution (15 mL), and brine (15 mL), followed by drying (Na_2SO_4) and evaporation. Recrystallization from petroleum ether (bp 30–60°C) afforded 59 mg (78%) lactone **15**; ir ($CHCl_3$) ν_{max}: 1800 (lactone C=O), 1395 cm^{-1}; nmr ($CDCl_3$) δ: 0.07 (s, 6H, Si(C*H*$_3$)$_2$), 0.86 (s, 9H, Si—*t*Bu), 1.36 (s, 3H), 1.44 (s, 3H), 3.73 (m, 2H, C*H*$_2$OSi), 4.29–4.79 (m, 4H) ppm; ms (270°C) *m/e*: 287 ($M^+ - 15$), 258, 217. *Anal.* calcd. for $C_{14}H_{26}O_5Si$: C 55.63, H 8.61; found: C 55.98, H 8.94.

*Keto-ester 16 from Monosilylated Diol 14*b

Alcohol **14***b* (320 mg, 1 mmol) was stirred in dimethyl sulfoxide – acetic anhydride (3:2) (3 mL) overnight at room temperature. The solution was further stirred for 15 min after the addition of chloroform (25 mL) and saturated Na_2CO_3 solution (15 mL). The organic layer was washed with water (10 mL × 2), dried (Na_2SO_4), and evaporated. The unstable keto-ester **16** was obtained in 80% yield; ir ($CHCl_3$) ν_{max}: 1755 and 1745 (C=O), 1400, 1390 cm^{-1}; nmr ($CDCl_3$) δ: 0.07 (s, 6H, Si(C*H*$_3$)$_2$), 0.86 (s, 9H, Si—*t*Bu), 1.37 (s, 3H), 1.52 (s, 3H), 3.67 (m, 2H, C*H*$_2$OSi), 3.80 (s, 3H, COOC*H*$_3$), 4.06–4.96 (m, 4H) ppm.

D,L-Showdomycin Derivative 17 from Keto-ester 16

To keto-ester **16** (374 mg, 1 mmol) in dry chloroform (10 mL) was added carbamoylmethylenetriphenylphosphorane (319 mg, 1 mmol). After stirring at room temperature for 3 h, the crude product was purified by silica plates to afford 134 mg (35%) of D,L-showdomycin derivative **17**; ir ($CHCl_3$) ν_{max}: 3480 (maleimide NH), 2985, 2895, 1795, 1745, 1395 cm^{-1}; uv (EtOH) λ_{max}: 222 nm (ε 13 400), shoulder ~ 275 nm (ε 1430); nmr ($CDCl_3$) δ: 0.07 (s, 6H, Si(C*H*$_3$)$_2$), 0.87 (s, 9H, Si—*tBu*), 1.35 (s, 3H), 1.57 (s, 3H), 3.66 (m, 2H, C*H*$_2$OSi), 4.13 (bm, 1H), 4.55–4.82 (m, 3H), 6.41 (t, 1H, *J* = 2 Hz), 7.99 (bm, 1H, N*H*) ppm; ms (150°C) *m/e*: 368 ($M^+ - CH_3$), 326 ($M^+ - t$Bu), 268 ($M^+ - (CH_3)_2Si$—*t*Bu).

D,L-Showdomycin 18 from D,L-Showdomycin Derivative 17

To showdomycin derivative **17** (383 mg, 1 mmol) was added 3 mL of trifluoroacetic acid – water 4:1. After stirring at room temperature for 10 min, the solution was evaporated to dryness. Recrystallization from benzene–acetone afforded 176 mg (77%) D,L-showdomycin **18**, mp 143–144°C; nmr (acetone-d_6) δ: 3.15–4.75 (m, 10H), 6.60 (t, 1H, *J* = 2 Hz); ms (180°C) *m/e*: 229 (M^+), 211 ($M^+ - H_2O$), 180, 156, 152, 140, 139, 127 (B + 31), 126 (B + 30), 123, 110, 85, 73.

*Hydrazone 16*a *from Keto-ester 16*

To keto-ester **16** (374 mg, 1 mmol) and pyridine (87 mg, 1.1 mmol) in methanol (10 mL) was added ethyl hydrazinoacetate hydrochloride (170 mg, 1.1 mmol). After stirring at room temperature overnight, the solution was evaporated to dryness. Chloroform (40 mL) was added to the residue, which was washed (2 × 15 mL H_2O), dried (Na_2SO_4), and evaporated. The crude product was purified by silica plates to afford 389 mg (82%) hydrazone **16***a* as *syn*- and *anti*-isomers. (*Syn*-isomer) ir ($CHCl_3$) ν_{max}: 3300 (NH), 2985, 2890, 1760 (C=O), 1700 (C=N), 1400, 1390 cm^{-1}; uv (EtOH) λ_{max}: 294 nm (ε 13 800);

nmr ($CDCl_3$) δ: 0.05 (s, 6H, $Si(CH_3)_2$), 0.89 (s, 9H, Si—*t*Bu), 1.26 (t, 3H, $J = 7$ Hz, CH_2CH_3), 1.34 (s, 3H), 1.52 (s, 3H), 3.57 (d, 2H, $J = 5$ Hz, CH_2OSi), 3.73 (s, 3H, $COOCH_3$), 3.86–5.05 (m, 8H), 10.21 (bm, 1H, NH); ms (140°C) *m/e*: 474 (M^+), 459 ($M^+ - CH_3$), 417 ($M^+ - t$Bu).

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