394.25 (82), 371.25 (91), 55.10 (100).

(24*S*,25(26)*E*)-3α,5-Cyclo-6β-methoxy-24,26-dimethylcholest-25(26)-ene (22) from 18: ^{1}H NMR (300 MHz) 3.318 (3 H, s, OCH_3), 1.557 (3 H, d, J = 6.5 Hz, C-29), 1.483 (3 H, s, C-27), 1.016 (3 H, s, C-19), 0.947 (3 H, d, J = 6.9 Hz, C-28), 0.890 (3 H, d, J = 6.6 Hz, C-21), 0.700 (3 H, s, C-18); low-resolution mass spectrum, m/z (relative intensity) 426.40 (M^+, 30), 411.40 (41), 394.25 (37), 371.25 (70), 55.10 (100).

Jaspisterol (26), Isojaspisterol (25), and Their Isomers (23, 24). Each i-methyl ether (**19–22**) was hydrolyzed to the corresponding jaspisterol isomers (**23–26**) by a known procedure.[16]

(24*R*,25(26)*Z*)-24,26-Dimethylcholesta-5,25(26)-dien-3β-ol (23) from 19: mp 129–130 °C (MeOH); $[\alpha]^{20}_D$ −12.3° (*c* 12.5, $CHCl_3$); GC RRT (1.73); HPLC RRT (0.96); for ^{1}H NMR (300 MHz and ^{13}C NMR (400 MHz) data, see Tables I and II; low-resolution mass spectrum, m/z (relative intensity) 412.40 (M^+, 32), 379.15 (10), 328.15 (16), 314.15 (17), 299.15 (35), 271.15 (28), 255.15 (16), 213.15 (25), 55.05 (100).

(24*R*,25(26)*E*)-24,26-Dimethylcholesta-5,25(26)-dien-3β-ol (24) from 20: mp 135–136 °C (MeOH); $[\alpha]^{20}_D$ −53.8° (*c* 5.1, $CHCl_3$); GC RRT (1.77); HPLC RRT (0.96); for ^{1}H NMR (300 MHz) and ^{13}C NMR (400 MHz) data, see Tables I and II; low-resolution mass spectrum, m/z (relative intensity) 412.40 (M^+, 30), 328.15 (17), 314.15 (21), 299.15 (36), 271.15 (26), 255.15 (14), 213.10 (26), 55.05 (100).

(24*S*,25(26)*Z*)-24,26-Dimethylcholesta-5,25(26)-dien-3β-ol (Isojaspisterol, 25) from 21: mp 130–131 °C (MeOH); $[\alpha]^{20}_D$ −52.8° (*c* 8.0, $CHCl_3$); GC RRT (1.73); HPLC RRT (0.96); for ^{1}H NMR (300 MHz) and ^{13}C NMR (400 MHz) data, see Tables I and II; low-resolution mass spectrum, m/z (relative intensity) 412.40 (M^+, 35), 328.15 (21), 314.15 (19), 299.15 (28), 271.15 (35), 255.15 (14), 213.00 (28), 55.05 (100).

(24*S*,25(26)*E*)-24,26-Dimethylcholesta-5,25(26)-dien-3β-ol (Jaspisterol, 26) from 22: mp 113–114 °C (MeOH); $[\alpha]^{20}_D$ −44.1° (*c* 10.3, $CHCl_3$); GC RRT (1.74); HPLC RRT (0.96); for ^{1}H NMR (300 MHz) and ^{13}C NMR (400 MHz), see Tables I and II; high-resolution mass spectrum, m/z (relative intensity) 412.3694 (M^+, 86; calcd for $C_{29}H_{48}O$ 412.3705), 397.3486 ($C_{28}H_{45}O$, 21), 379.3361 ($C_{28}H_{43}$, 22), 328.2791 ($C_{23}H_{36}O$, 26), 314.2618 ($C_{22}H_{34}O$, 30), 299.2383 ($C_{21}H_{31}O$, 71), 271.2054 ($C_{19}H_{27}O$, 44), 255.2101 ($C_{19}H_{27}$, 23), 213.1633 ($C_{16}H_{21}$, 33), 83.0867 (C_6H_{11}, 100).

Ozonolysis of Isomeric Jaspisterol i-Methyl Ethers (19–22). A saturated solution of ozone in methylene chloride (5 mL) at −70 °C was added to each jaspisterol isomer i-methyl ether (**19–22**) at −70 °C, and the mixtures were stirred at the same temperature for 5 min. Excess ozone was destroyed by the addition of methyl sulfide. Concentration and separation by silica gel column chromatography gave the corresponding carbonyl compound (**31** or **32**), which was further purified by reverse-phase HPLC.

(24*R*)-3α,5-Cyclo-6β-methoxy-24-methyl-27-norcholestan-25-one (31)[13] from 19 and 22: ^{1}H NMR (300 MHz) δ 3.320 (3 H, s, OCH_3), 2.128 (3 H, C-26), 1.065 (3 H, d, J = 6.9 Hz, C-28), 1.017 (3 H, s, C-19), 0.917 (3 H, d, J = 6.6 Hz, C-21), 0.708 (3 H, s, C-18); low-resolution mass spectrum, m/z (relative intensity 414.50 (M^+, 29), 399.25 (42), 382.25 (100), 367.25 (24), 359.25 (71), 213.10 (34).

(24*S*)-3α,5-Cyclo-6β-methoxy-24-methyl-27-norcholestan-25-one (32)[13] from 21 and 22: ^{1}H NMR (300 MHz) δ 3.320 (3 H, s, OCH_3), 2.123 (3 H, s, C-26), 1.077 (3 H, d, J = 6.9 Hz, C-28), 1.016 (3 H, s, C-19), 0.918 (3 H, d, J = 6.5 Hz, C-21), 0.705 (3 H, s, C-18); low-resolution mass spectrum, m/z (relative intensity) 414.50 (M^+, 41), 399.25 (58), 382.25 (100), 367.25 (24), 359.25 (81), 213.10 (21).

Ozonolysis of Natural Jaspisterol (26) and Isojaspisterol (25). Ozonolysis of the mixture of i-methyl ethers, which was derived from natural jaspisterol (**26**) and isojaspisterol (**25**), was performed by the same procedure as above. The 300-MHz ^{1}H NMR spectrum of the product was same as that of **32**.

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C-Nucleosides. 6. Synthesis of 5-Methoxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one and Its Ring Transformation

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Synthesis of the versatile and stable C-nucleoside precursor 5-hydroxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one (**2**) was achieved by oxidation of glycosyl furan (**1**) with Jones reagent. Treatment of **2** with triethylamine in benzene afforded the elimination product **5** in 81% yield. Methoxylation of **2** with hydrochloric acid in methanol afforded (5*R*)- and (5*S*)-5-methoxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-furan-2(5*H*)-one (**6a** and **6b**). The conversion of the furanone ring into pyridazinone and *N*-aminopyrrolinone was performed by treatment of **6a,b** with hydrazine hydrate to give **11** and **12**. Deblocking of **11** and **12** gave **13** and **17**. Compounds **6a,b** were reacted with hydroxylamine-*O*-sulfonic acid (HOSA) in methanol to form **18** in 72% yield. Deblocking of **18** gave 3-β-D-ribofuranosyl-6*H*-1,2-oxazin-6-one (**20**). Finally, reaction of **6a,b** with ammonia in dioxane gave the known epimers of protected pyrrolinone **22**.

It has been demonstrated that certain five- and six-membered α,β-unsaturated lactone derivatives possess, in addition to other pharmacological properties,[1] tumor-inhibitory activity.[2] Moreover, they have proven to be versatile synthetic intermediates, suitable for the elaboration of other heterocyclic systems.[3] We were interested

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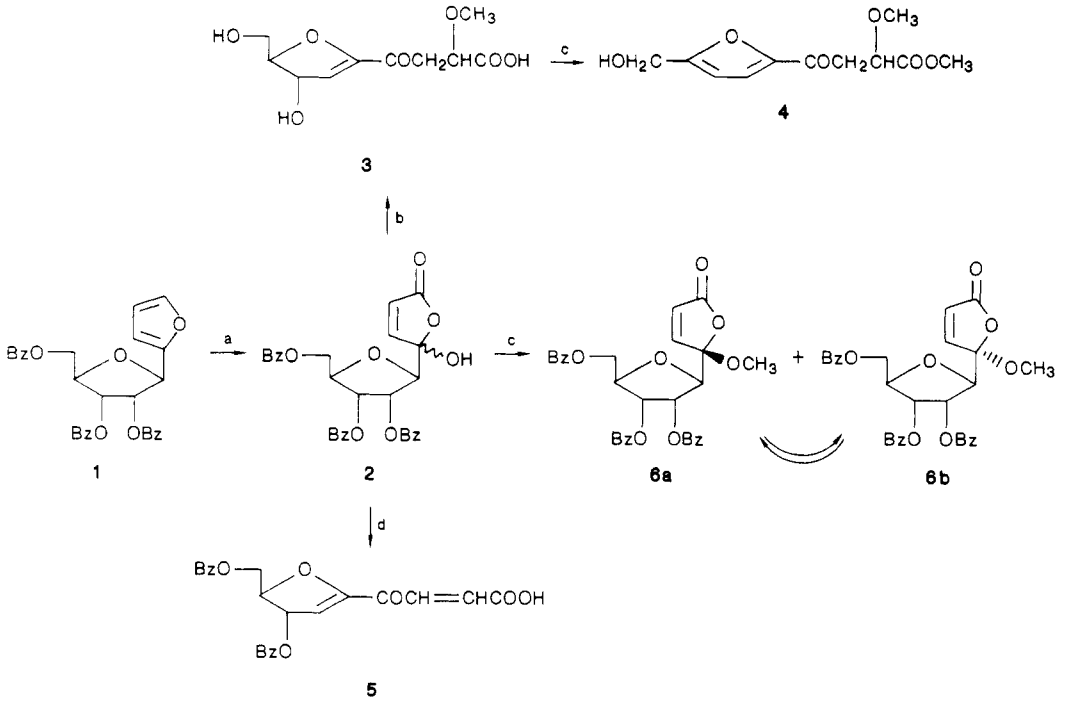
Scheme I[a]



[a] Reagents: (a) CrO_3–H_2SO_4, acetone; (b) Na_2CO_3–H_2O, MeOH; (c) HCl, MeOH; (d) Et_3N, benzene.

in the synthesis and antitumor properties of C-nucleoside analogues. In previous publications[4] from our laboratory, we described the synthesis of C-nucleoside analogues starting from 2-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan (**1**). In this paper, we describe the preparation of α,β-unsaturated lactone glycosides (5*R*)- and (5*S*)-5-methoxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one (**6a** and **6b**) from **1** and demonstrate the utility of **6a,b** through the construction of pyridazin-6(1*H*)-one, 5-hydroxypyrrolin-2-one, and a hitherto unknown 6*H*-1,2-oxazin-6-one C-nucleoside.

The key synthetic intermediate furanone glycoside **2** can be obtained from **1** by oxidation of its furan ring. It is well known that 5-hydroxyfuran-2(5*H*)-one was prepared by the sensitized photooxygenation of furan,[5] furfural,[6] or 2-furoic acid,[7] and the oxidation of furan derivatives by *m*-chloroperbenzoic acid (MCPBA)[8] or pyridinium chlorochromate (PCC)[9] resulted in formation of enedione systems. Oxidation of **1** by photolysis or PCC under a variety of conditions proved unsuccessful. Compound **1** oxidized by MCPBA in chloroform afforded the desired compound **2** in 11% yield. Variation in the reaction temperature, time, reactant proportions, and solvent did not improve the above yield. Next, treatment of **1** in acetone with chromium trioxide in sulfuric acid and water at 0 °C afforded **2** in 93% yield after purification by silica gel column chromatography. Compound **2** is an inseparable mixture of diastereoisomers (differing in configuration only at C-5). Debenzoylation of **2** with sodium carbonate in methanol did not afford the deprotected furanone glycoside but instead gave the dihydrofuran **3** in 62% yield. This assignment was supported by the ^1H NMR spectrum, which contained a chemical shift for the olefinic proton at δ 6.70 ($J_{2',3'}$ = 4.0 Hz). The ^{13}C NMR spectrum and elemental analysis are consistent with the structure of **3** being 4-(1,4-anhydro-2-deoxy-D-*erythro*-pent-1-enofuranosyl)-2-methoxy-4-oxobutyric acid. Treatment of **3** with hydrochloric acid in methanol afforded the corresponding furan derivative **4**. Several instances of C-glycosyl compounds containing a dihydrofuran moiety have been reported where side reactions gave furan derivatives.[10] When **2** was stirred in benzene with triethylamine, the elimination product **5** was obtained in 81% yield. The formation of **5** occurs at room temperature and undoubtedly results from abstraction by base of the H-1′ rendered more acidic by the carbonyl group in the ring-opened system. Compounds **3** and **5** should prove to be very useful synthetic intermediates in future deoxy C-glycoside work.

Methoxylation of **2** with hydrochloric acid in methanol at room temperature afforded two major products in a combined yield of 94% and in a 1:1 ratio. These were readily separable by preparative TLC and assumed to be (5*R*)- and (5*S*)-5-methoxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one (**6a** and **6b**). Isomerization (**6a** ⇌ **6b**) was observed during the methoxylation experiments (Scheme I). In order to confirm the β configuration of **6a,b** by comparison with the α anomer, the α anomer **7** was also oxidized by using similar reaction conditions to give

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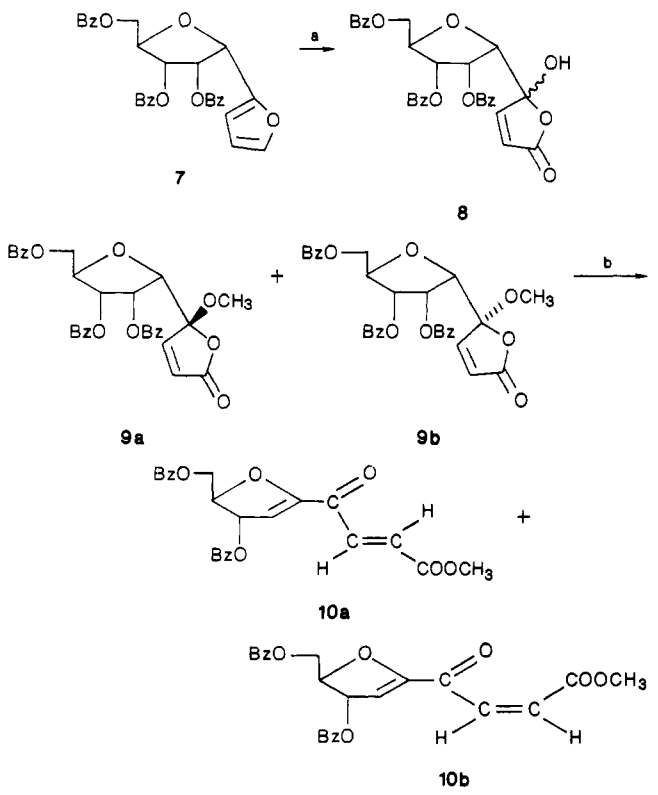
Scheme II[a]



[a] Reagents: (a) CrO_3–H_2SO_4, acetone; (b) HCl, MeOH.

furanone 8. Attempts to purify 8 on preparative TLC plates were not practical owing to appreciable decomposition of this product. The furanone 8 was treated with hydrochloric acid in methanol to obtain four products, (5*R*)- and (5*S*)-5-methoxy-5-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)furan-2(5*H*)-one (**9a** and **9b**) in 21% yield and olefinic material (**10a** and **10b**) in 24% yield. The assignments of the anomeric configuration at C-1′ to **6a,b** and **9a,b** were based on comparison of their ^{1}H NMR spectra. The chemical shift of the anomeric proton in compound **9a** and **9b** (δ 4.80 and 4.66) appeared downfield from that of compound **6a** and **6b** (δ 4.29 and 4.54) since the β face location of this anomeric proton placed it out of the shielding influence of the 2′-oxygen. This is in agreement with the general trend seen for most nucleoside anomeric pairs.[11] Although Schemes I and II depict **6a,b** and **9a,b** as each possessing an absolute configuration about the hydroxy carbon (furanone C) that connects the furanone and sugar moieties, this is merely illustrative since the actual stereochemical assignment (*R* or *S*) was not readily obtainable from available spectral data. The olefinic products (**10a,b**) were assumed to be trans/cis mixture of dihydrofuran products in which the lactone moiety was ring-opened. This assignment was supported by its 270-MHz ^{1}H NMR spectrum, which contained chemical shifts for the olefinic protons at δ 6.93 and 7.51 for the trans isomer (J = 15.8 Hz) and at δ 6.28 and 6.68 for the cis isomer (J = 12.1 Hz) (Scheme II).

Reaction of the β isomers **6a,b** with hydrazine hydrate in methanol gave two products, pyridazinone **11** and a mixture of diastereomeric *N*-aminopyrrolinones **12** that could not be separated, in yields of 26% and 71%, respectively. Debenzoylation of **11** with 1 N sodium hydroxide solution at room temperature afforded **13** in 97% yield. In order to determine the anomeric configuration, the isopropylidene acetal **14** was synthesized by using ethyl orthoformate in acidic condition. The ^{1}H NMR spectrum showed two singlets at δ 1.35 and 1.55 with Δδ = 0.20 ppm; a value of less than 0.10 ppm would be expected in the case of an α anomer. The proton at C-4′ showed a quartet at δ 4.12, the coupling of H-3′ and H-4′ was about 3 Hz. In α anomers this coupling constant should be zero, resulting in an apparent triplet for H-4′. The *N*-amino compound **12** was characterized as its azomethine derivative **15**. The oxidation of *N*-amino heterocycles with lead tetraacetate,[12] *tert*-butyl hypochlorite,[13] or silica gel[14] in chloroform–methanol leading to ring expansion of the presumed nitrene intermediate is well known. However, when **12** was refluxed in benzene without any oxidizing agents, the product of ring expansion **11** was obtained in quantitative yield. The reaction does not proceed well when methanol is used as the solvent. We propose the mechanism of this ring expansion involving the formation of an intermediate diaziridine **16**, which subsequently evolves into a six-membered pyridazinone derivative. These results indicate that the configuration of **12** is β. Debenzoylation of **12** with 1 N sodium hydroxide solution afforded **17**, which was chromatographically inseparable. Acetonization of **17** was unsuccessful owing to the lability of the *N*-amino function (Scheme III).

A general synthesis of the 1,2-oxazinones system is the cyclization of the monooximes of α,β-unsaturated 1,4-dicarbonyl compounds.[15] We found a novel synthesis of 1,2-oxazinone involving a ring expansion from furanones **6a,b** by reaction with hydroxylamine-*O*-sulfonic acid (HOSA). Compounds **6a,b** were reacted with HOSA in methanol to form 3-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-6*H*-1,2-oxazin-6-one (**18**) in 72% yield, the structure of which was confirmed by ^{1}H NMR and ^{13}C NMR and mass spectra. The mechanism of this reaction is presumed to be as follows: As the first step, a nucleophilic attack of HOSA takes place on the 5-position of **6a,b** and is followed by formation of **19**,[16] which is converted to **18** by the ring expansion. Deprotection of **18** with 1 N sodium hydroxide solution affords **20**. For the assignment of the anomeric configuration of **20**, the data obtained from the 2′,3′-*O*-isopropylidene derivative **21** is used as a basis for the determination (See the Experimental Section).

The versatility of intermediates **6a,b** was further demonstrated by the synthesis of pyrrolinone **22** (Scheme IV). Treatment of **6a,b** with ammonia in dioxane at room temperature gave the known epimers of protected pyrrolinone **22**, which were found to be identical with the products previously prepared by the reported procedure.[17] The overall yield of **22** by this method is greater than the yield by our earlier method.

Experimental Section

Melting points were determined on a Yanagimoto apparatus and are uncorrected. Infrared (IR) spectra were measured with a JASCO IRA-1 spectrometer. ^{1}H NMR spectra were measured with a JNM-GX-270 spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 Fourier transform spectrometer operating at 25.00

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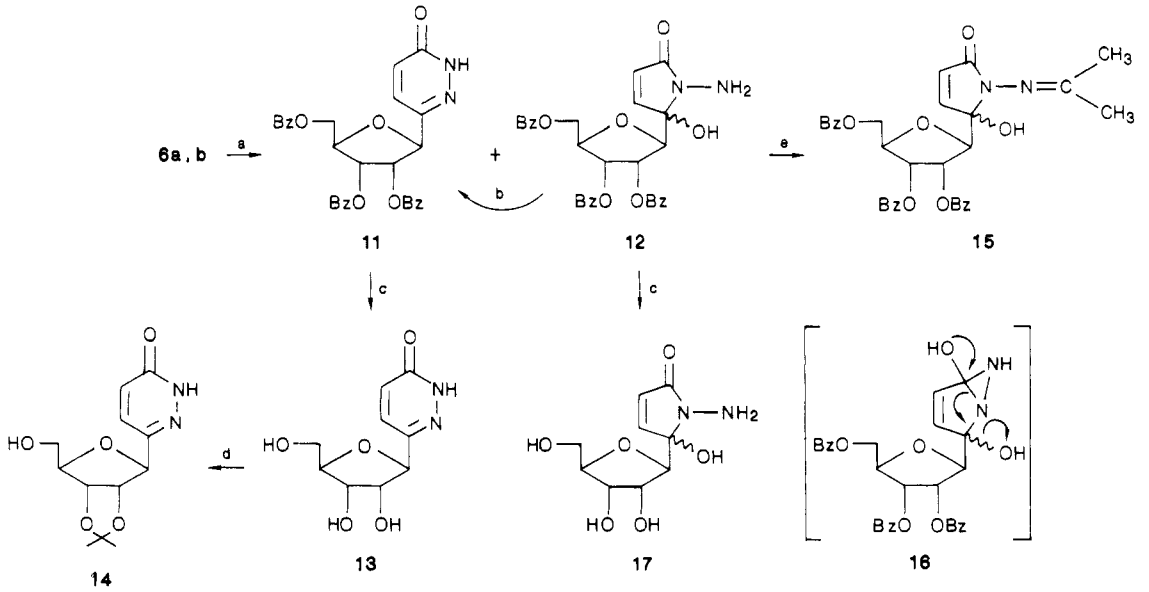
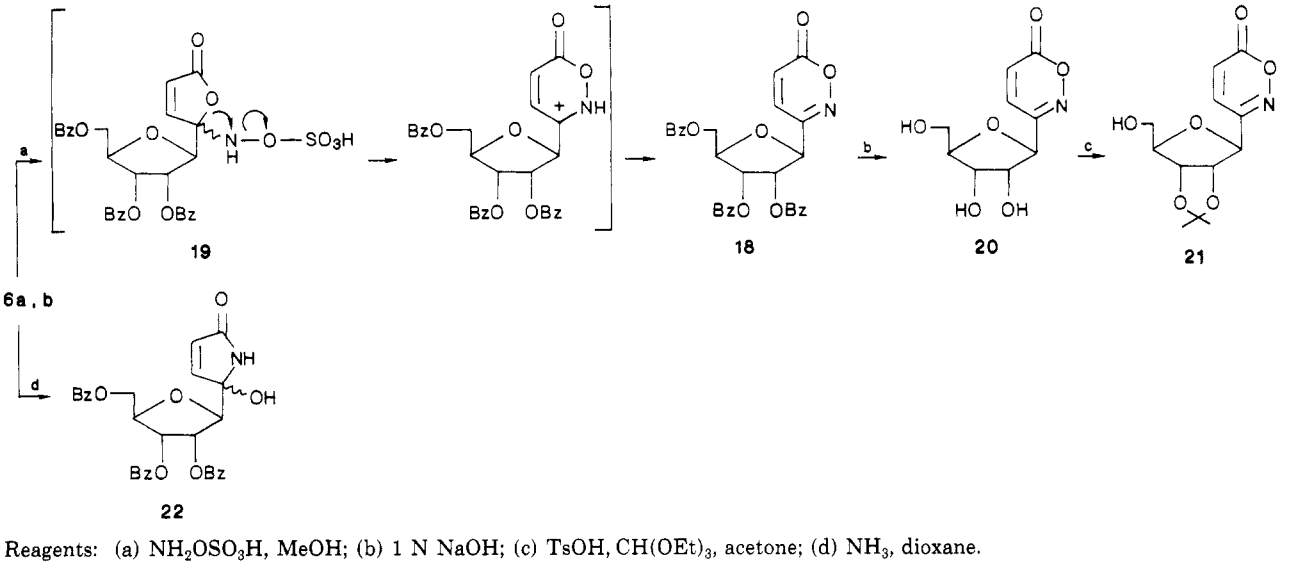
Scheme III[a]



[a] Reagents: (a) NH_2NH_2, MeOH; (b) benzene, Δ; (c) 1 N NaOH; (d) TsOH, $CH(OEt)_3$, acetone; (e) acetone.

Scheme IV[a]



[a] Reagents: (a) NH_2OSO_3H, MeOH; (b) 1 N NaOH; (c) TsOH, $CH(OEt)_3$, acetone; (d) NH_3, dioxane.

MHz with tetramethylsilane as an internal standard. Analytical thin-layer chromatography was performed on glass plates coated with a 0.5-mm layer of silica gel GF_{254} (Merck). The compounds were detected with a UV light (254 nm). Column chromatography was performed on silica gel C-200 (74–149 μm, Wakogel). Spectroscopic data are reported on materials of >95% purity (by ^1H and ^{13}C NMR).

(5*R*)- and (5*S*)-5-Hydroxy-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one (2). A solution of chromium trioxide (5.34 g) in concentrated sulfuric acid (4.6 mL) and water (15 mL) was cautiously added to a stirred solution of **1** (1.37 g, 2.7 mmol) in acetone (15 mL) at 0 °C until an orange-yellow color persisted. The solution was stirred for an additional 4 h at room temperature. Water was added, and the mixture was extracted with chloroform (3 × 100 mL). The extracts were combined, washed with water, dried over magnesium sulfate, and evaporated in vacuo to a syrup. The residue was chromatographed over a column of silica gel with chloroform as the eluent. This afforded 1.07 g of **2** (93%) as a colorless foam. Despite multiple elutions, the diastereomers were not separated: IR ($CHCl_3$) 3450–3200 cm^{-1} (OH), 1770, 1720 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 4.11 (d, $^2/_3$, H-1′, $J_{1',2'}$ = 4.7 Hz), 4.28 (d, $^1/_3$, H-1′, $J_{1',2'}$ = 3.4 Hz), 4.31–4.48 (m, 3, H-4′, H-5′), 5.51–5.65 (m, 2, H-3, H-3′), 5.98 (t, $^1/_3$, H-2′, $J_{1',2'}$ = $J_{2',3'}$ = 3.4 Hz), 6.02 (dd, $^2/_3$, H-2′, $J_{1',2'}$ = 4.7 Hz, $J_{2',3'}$ = 5.7 Hz), 6.51 (d, $^2/_3$, H-4, $J_{3,4}$ = 5.7 Hz), 6.69 (d, $^1/_3$, H-4, $J_{3,4}$ = 5.7 Hz), 6.85–8.27 (m, 15, Ar H); ^{13}C NMR ($CDCl_3$) δ 63.86 (C-5′), 72.35, 75.85, 79.45, 84.60 (C-1′, C-2′, C-3′, C-4′), 105.54 (C-5), 124.74 (C-3), 128.37–133.33 (Ar C), 151.70 (C-4), 165.21, 166.15, 171.18 (C=O). Anal. Calcd for $C_{30}H_{24}O_{10}\cdot{}^1/_6H_2O$: C, 65.81; H, 4.48. Found: C, 65.74; H, 4.36.

Oxidation of 1 with MCPBA. To a solution of **1** (100 mg, 0.2 mmol) in chloroform (3 mL) was slowly added 80% MCPBA (84 mg, 0.4 mmol) in chloroform (1 mL) at 0–5 °C, and the mixture was allowed to stand at room temperature for 12 h. Solvent was removed under reduced pressure and the residue was separated by preparative TLC to afford 10.3 mg of **2** (10.7%) identical in all respects with that obtained by Jones oxidation.

4-(1,4-Anhydro-2-deoxy-D-*erythro*-pent-1-enofuranosyl)-2-methoxy-4-oxobutyric Acid (3). To a solution of **2** (324 mg, 0.6 mmol) in methanol (10 mL) was added 500 mg of sodium carbonate in water (5 mL). The suspension was cooled in an ice bath for 2 h. After evaporation of the solvent, the residue was chromatographed over a column of silica gel with chloroform–methanol (11:9) as the eluent. This afforded 90 mg of **3** (62%) as a syrup: ^1H NMR (D_2O) δ 3.54 (d, 2, H-3, $J_{2,3}$ = 6 Hz), 3.76 (s, 3, OCH_3), 4.08–4.32 (m, 2, H-5′), 4.51 (t, 1, H-2), 4.90 (q, 1, H-4′, $J_{3',4'}$ = $J_{4',5'}$ = 4 Hz), 5.38 (t, 1, H-3′); ^{13}C NMR (D_2O) δ 43.00 (C-3), 58.62 (OCH_3), 62.83 (C-5′), 75.94, 79.62 (C-3′, C-4′),

90.21 (C-2), 115.66 (C-2'), 156.26 (C-1'), 179.66, 194.58 (C=O). Anal. Calcd for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.94; H, 5.59.

Methyl 4-[5-(Hydroxymethylene)-2-furyl]-2-methoxy-4-oxobutyrate (4). A solution of **3** (12 mg, 0.05 mmol) in methanol (1 mL) containing 1 drop of concentrated hydrochloric acid was allowed to stir at room temperature for 12 h. The reaction mixture was neutralized with sodium bicarbonate. After evaporation of the solvent, the residue was chromatographed over a column of silica gel with chloroform–methanol (99:1) as the eluent. This afforded 11 mg of **4** (98%) as an oil: MS, *m/e* 242 (M^+); ^1H NMR ($CDCl_3$) δ 3.08–3.29 (m, 2, H-3), 3.44 (s, 3, $COOCH_3$), 3.76 (s, 3, OCH_3), 4.28–4.46 (m, 1, H-2), 4.66 (s, 2, CH_2OH), 6.42 (d, 1, H-4 furan, $J_{3,4}$ = 4 Hz), 7.14 (d, 1, H-3 furan). Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.38; H, 5.66.

4-(3,5-Di-*O*-benzoyl-1,4-anhydro-2-deoxy-D-*erythro*-pent-1-enofuranosyl)-4-oxo-2-butenoic Acid (5). To a solution of **2** (2.09 g, 3.8 mmol) in absolute benzene (15 mL) was added 1.2 g (11.8 mmol) of triethylamine in absolute benzene (5 mL), and the mixture was allowed to stand at room temperature for 4 h. Water was added, and the resultant mixture was neutralized with hydrochloric acid solution. The mixture was extracted with chloroform (3 × 50 mL), washed with water, dried over magnesium sulfate, and evaporated in vacuo to a syrup. The residue was chromatographed over a column of silica gel with chloroform as the eluent. This afforded 1.31 g of **5** (80.6%) as a colorless syrup. Due to the lability of this compound good elemental analysis could not be obtained: ^1H NMR ($CDCl_3$) δ 4.68 (d, 2, H-5', $J_{4',5'}$ = 4.7 Hz), 5.12 (m, 1, H-4'), 6.18 (t, 1, H-3', $J_{2',3'} = J_{3',4'}$ = 3.4 Hz), 6.34 (d, 1, H-2'), 6.92 (d, 1, H-3, $J_{2,3}$ = 15.5 Hz), 7.36–8.05 (m, 11, H-2, Ar H); ^{13}C NMR ($CDCl_3$) δ 63.83 (C-5'), 78.74, 84.83 (C-3', C-4'), 109.46 (C-2'), 128.53–136.37 (C-2, C-3, Ar C), 158.25 (C-1'), 166.21, 169.31, 180.72 (C=O).

(5*R*)- and (5*S*)-5-Methoxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)furan-2(5*H*)-one (6a and 6b). A solution of **2** (1.1 g, 2 mmol) in methanol (20 mL) containing 5 drops of concentrated hydrochloric acid was allowed to stir at room temperature for 48 h. The reaction mixture was neutralized with a saturated sodium bicarbonate solution, and the mixture was extracted with chloroform (3 × 100 mL). The extracts were combined, washed with water, dried over magnesium sulfate, and evaporated in vacuo to a syrup. TLC (chloroform–methanol, 100:1) showed that the syrup contained two major components (R_f 0.44 and 0.38). The residue was chromatographed over a column of silica gel with chloroform–benzene (11:9) as the eluent. The first compound eluted, **6a** (491 mg, 47.1%, corresponding to R_f 0.44 on TLC), was obtained as a colorless syrup: IR ($CHCl_3$) 1765, 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.08 (s, 3, OCH_3), 4.29 (d, 1, H-1', $J_{1',2'}$ = 3.0 Hz), 4.47 (dd, 1, H-5'a, $J_{4',5'a}$ = 4.4 Hz, $J_{5'a,5'b}$ = 11.8 Hz), 4.55 (m, 1, H-4'), 4.83 (dd, 1, H-5'b, $J_{4',5'b}$ = 2.1 Hz), 5.85 (dd, 1, H-3', $J_{2',3'}$ = 5.4 Hz, $J_{3',4'}$ = 7.1 Hz), 6.07 (dd, 1, H-2'), 6.37 (d, 1, H-3, $J_{3,4}$ = 5.7 Hz), 7.37 (d, 1, H-4), 7.29–8.14 (m, 15, Ar H); ^{13}C NMR ($CDCl_3$) δ 51.48 (OCH_3), 63.24 (C-5'), 72.30, 75.88, 79.67, 85.53 (C-1', C-2', C-3', C-4'), 108.29 (C-5), 126.37 (C-3), 128.37–133.33 (Ar C), 152.05 (C-4), 164.98, 165.15, 166.03, 168.78 (C=O).

Compound **6b** was eluted as the second fraction (492 mg, 47.1%, corresponding to R_f 0.38 on TLC) as a colorless syrup: IR ($CHCl_3$) 1765, 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.28 (s, 3, OCH_3), 4.54 (d, 1, H-1', $J_{1',2'}$ = 4.0 Hz), 4.45–4.65 (m, 3, H-4', H-5'), 5.70 (t, 1, H-3', $J_{2',3'} = J_{3',4'}$ = 5.7 Hz), 5.98 (dd, 1, H-2'), 6.29 (d, 1, H-3, $J_{3,4}$ = 5.7 Hz), 7.18 (d, 1, H-4), 7.27–8.06 (m, 15, Ar H); ^{13}C NMR ($CDCl_3$) δ 51.48 (OCH_3), 64.00 (C-5'), 71.96, 72.25, 79.33, 83.02 (C-1', C-2', C-3', C-4'), 108.82 (C-5), 126.83 (C-3), 128.30–133.34 (Ar C), 150.53 (C-4), 165.00, 166.03, 168.84 (C=O). Anal. Calcd for $C_{31}H_{26}O_{10}$: C, 66.66; H, 4.69. Found for **6a**: C, 66.49; H, 4.60. Found for **6b**: C, 66.54; H, 4.71.

Epimerization of 6a ⇌ 6b by Hydrochloric Acid. To a solution of 20 mg of **6a** in 1 mL of methanol was added 1 drop of concentrated hydrochloric acid, and the resulting solution was stored at room temperature for 3 days and then worked up as above for **6a** and **6b**. The syrup was shown by ^1H NMR spectrum to consist of **6a** and **6b** in a ratio of 1:1.

(5*R*)- and (5*S*)-5-Hydroxy-5-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)furan-2(5*H*)-one (8). The same procedure was used as the reaction of **1** with Jones reagent: yield 86.6%; colorless foam; IR ($CHCl_3$) 3300 cm^{-1} (OH), 1770, 1720 cm^{-1} (C=O); ^1H NMR (C_6D_6) δ 4.27–4.53 (m, 4, H-1', H-4', H-5'), 5.52–5.54 (m, 1 H-3), 5.60–5.64 (m, 1, H-3'), 5.91–5.95 (m, 1, H-2'), 6.85–8.14 (m, 16, H-4, Ar H); ^{13}C NMR ($CDCl_3$) δ 63.89 (C-5'), 71.96, 72.72, 78.51, 80.50 (C-1', C-2', C-3', C-4'), 124.86 (C-3), 128.36–133.74 (Ar C), 151.81 (C-4), 165.33, 166.26, 170.18 (C=O). Anal. Calcd for $C_{30}H_{24}O_{10}$: C, 66.17; H, 4.44. Found: C, 66.35; H, 4.69.

(5*R*)- and (5*S*)-5-Methoxy-5-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)furan-2(5*H*)-one (9a and 9b) and *trans*- and *cis*-Methyl 4-(3,5-Di-*O*-benzoyl-1,4-anhydro-2-deoxy-D-*erythro*-pent-1-enofuranosyl)-4-oxo-2-butenoate (10a and 10b). The same procedure was used as the reaction of **2** with methanolic acid solution. Compounds **9** and **10** were separated by preparative TLC with chloroform as the eluent after four elutions. Compound **9a**: yield 13.5%; colorless foam; R_f 0.38 ($CHCl_3$–MeOH, 200:1); IR ($CHCl_3$) 1780, 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.17 (s, 3, OCH_3), 4.50–4.61 (m, 3, H-4', H-5'), 4.80 (d, 1, H-1', $J_{1',2'}$ = 4.4 Hz), 5.77 (m, 1, H-3'), 6.24 (t, 1, H-2'), 6.34 (d, 1, H-3, $J_{3,4}$ = 6.1 Hz), 7.19–8.04 (m, 16, H-4, Ar H); ^{13}C NMR ($CDCl_3$) δ 51.25 (OCH_3), 64.00 (C-5'), 71.84, 72.84, 75.82, 80.50 (C-1', C-2', C-3', C-4'), 110.34 (C-5), 127.07 (C-3), 128.41–133.68 (Ar C), 150.47 (C-4), 164.63, 165.04, 166.09, 168.84 (C=O).

Compound **9b**: yield 7.2%; colorless foam; R_f 0.29 ($CHCl_3$–MeOH, 200:1); IR ($CHCl_3$) 1780, 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.11 (s, 3, OCH_3), 4.48 (dd, 1, H-5'a, $J_{4',5'a}$ = 4.0 Hz, $J_{5'a,5'b}$ = 11.7 Hz), 4.60–4.70 (m, 2, H-4', H-5'b), 4.66 (d, 1, H-1', $J_{1',2'}$ = 4.7 Hz), 5.77 (dd, 1, H-3', $J_{2',3'}$ = 4.7 Hz, $J_{3',4'}$ = 8.1 Hz), 6.25 (t, 1, H-2'), 6.30 (d, 1, H-3, $J_{3,4}$ = 5.7 Hz), 7.18 (d, 1, H-4), 7.29–8.11 (m, 15, Ar H); ^{13}C NMR ($CDCl_3$) δ 51.07 (OCH_3), 63.65 (C-5'), 70.96, 72.19, 78.57, 79.39 (C-1', C-2', C-3', C-4'), 108.93 (C-5), 126.37 (C-3), 128.30–133.39 (Ar C), 151.58 (C-4), 165.21, 165.33, 166.09, 169.60 (C=O). Anal. Calcd for $C_{31}H_{26}O_{10}$: C, 66.66; H, 4.69. Found for **9a**: 66.55; H, 4.47. Found for **9b**: C, 66.76; H, 4.63.

Compound **10a**: yield 20.7%; syrup; R_f 0.54 ($CHCl_3$–MeOH, 200:1); ^1H NMR ($CDCl_3$) δ 3.83 (s, 3, OCH_3), 4.67 (d, 2, H-5', $J_{4',5'}$ = 4.7 Hz), 5.10–5.40 (m, 1, H-4'), 6.18 (t, 1, H-3', $J_{2',3'} = J_{3',4'}$ = 3.0 Hz), 6.31 (d, 1, H-2'), 7.41–8.06 (m, 10, Ar H); ^{13}C NMR ($CDCl_3$) δ 52.48 (OCH_3), 63.84 (C-5'), 78.69, 84.83 (C-3', C-4'), 108.99 (C-2'), 120.28 (C-3), 128.47–135.49 (C-2, Ar C), 158.37 (C-1'), 165.91, 166.03, 180.83 (C=O).

Compound **10b**: yield 2.8% syrup; R_f 0.50 ($CHCl_3$–MeOH, 200:1); ^1H NMR ($CDCl_3$) δ 3.69 (s, 3, OCH_3), 4.63–4.65 (m, 2, H-5'), 5.08 (m, 1, H-4'), 6.11–6.14 (m, 2, H-2', H-3'), 7.41–8.07 (m, 10, Ar H). Anal. Calcd for $C_{24}H_{20}O_8$ (mixture): C, 66.05; H, 4.62. Found: C, 65.71; H, 4.83.

3-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl)-6(1*H*)-pyridazinone (11) and (5*R*)- and (5*S*)-1-Amino-5-hydroxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-3-pyrrolin-2-one (12). To a solution of **6a,b** (316 mg, 0.57 mmol) in methanol (5 mL) was slowly added hydrazine hydrate (42 mg, 0.85 mmol) in methanol (1 mL) at 0–5 °C, and the mixture was allowed to stand at room temperature for 2 h. The reaction mixture was evaporated to dryness in vacuo. TLC (chloroform–methanol, 50:1) showed that the light yellow syrup contained two major components (R_f 0.35 and 0.22). The mixture was chromatographed over a column of silica gel with chloroform–benzene (7:3) as the eluent. The first compound eluted, **11** (78.7 mg, 25.7%, corresponding to R_f 0.35 on TLC), was obtained as a foam. The best elemental analysis was consistent with 0.5 mol of water: IR ($CHCl_3$) 3350 cm^{-1}, 1720, 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 4.57 (dd, 1, H-5'a, $J_{4',5'a}$ = 3.7 Hz, $J_{5'a,5'b}$ = 12.1 Hz), 4.71 (m, 1, H-4'), 4.86 (dd, 1, H-5'b, $J_{4',5'b}$ = 3.0 Hz, $J_{5'a,5'b}$ = 12.1 Hz), 5.17 (d, 1, H-1', $J_{1',2'}$ = 5.4 Hz), 5.81–5.86 (m, 2, H-2', H-3'), 6.85 (d, 1, H-5, $J_{4,5}$ = 9.8 Hz), 7.35–8.07 (m, 16, H-4, Ar H); ^{13}C NMR ($CDCl_3$) δ 63.77 (C-5'), 72.43, 74.53, 80.85, 80.97 (C-1', C-2', C-3', C-4'), 128.41–133.50 (C-4, C-5, Ar C), 144.97 (C-3), 161.76, 165.21, 165.33, 166.03 (C=O). Anal. Calcd for $C_{30}H_{24}N_2O_8 \cdot {}^1/_2H_2O$: C, 65.57; H, 4.59; N, 5.10. Found: C, 65.71; H, 4.52; N, 4.97.

Compound **12** was eluted as the second fraction (223.3 mg, 70.7%, corresponding to R_f 0.22 on TLC) as a foam. The best elemental analysis was consistent with 0.5 mol of water: IR ($CHCl_3$) 3500–3200 cm^{-1} (OH, NH), 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.97 (br, 2, NH_2), 4.45 (m, 1, H-1'), 4.50–4.80 (m, 3, H-4', H-5'), 5.59–5.67 (m, 1, H-3'), 5.80–6.10 (m, 1, H-2'), 6.15 (d, $^1/_2$, H-3, $J_{3,4}$ = 6.4 Hz), 6.21 (d, $^1/_2$, H-3, $J_{3,4}$ = 6.4 Hz), 7.00 (d, $^1/_2$,

H-4, $J_{3,4}$ = 6.4 Hz), 7.04 (d, $^1/_2$, H-4, $J_{3,4}$ = 6.4 Hz), 7.35–8.07 (m, 15, Ar H); ^{13}C NMR ($CDCl_3$) δ 63.71 (C-5′), 72.13, 72.60, 84.53, 84.95 (C-1′, C-2′, C-3′, C-4′), 89.40, 89.98 (C-5), 126.95–133.56 (C-3, Ar C), 144.97, 145.73 (C-4), 165.39, 165.68, 166.38, 169.07, 169.66 (C=O). Anal. Calcd for $C_{30}H_{26}N_2O_9 \cdot {}^1/_2H_2O$: C, 63.49; H, 4.80; N, 4.94. Found: C, 63.29; H, 5.02; N, 5.01.

Transformation of 12 to 11. A solution of **12** (29 mg, 0.05 mmol) in benzene (2 mL) was heated under reflux for 2 h. Benzene was removed under reduced pressure, and the residue was chromatographed over a column of silica gel with chloroform–methanol (97:3) as the eluent. This afforded 25 mg of **11** (95%) as a foam. Identity was confirmed by comparing IR and ^{1}H NMR spectrum.

3-β-D-Ribofuranosyl-6(1*H*)-pyridazinone (13). To a solution of **11** (151 mg, 0.28 mmol) in methanol (10 mL) was added 1.5 mL of 1 N NaOH solution at 0 °C for 1 h, and the mixture was rendered neutral with acetic acid and evaporated. The residue was chromatographed over a column of silica gel with chloroform–methanol (1:1) as the eluent. This afforded 62.2 mg of **13** (97.4%) as a colorless syrup. This compound is hygroscopic, and best analysis was obtained as the monohydrate: $[\alpha]^{24.5}_D$ −17.0° (*c* 0.37, methanol); MS, *m/e* 228 (M^+); ^{1}H NMR (CD_3OD) δ 3.67 (dd, 1, H-5′a, $J_{4',5'a}$ = 4.0 Hz, $J_{5'a,5'b}$ = 12.1 Hz), 3.76 (dd, 1, H-5′b, $J_{4',5'b}$ = 3.4 Hz), 3.96 (m, 1, H-4′), 4.07–4.14 (m, 2, H-2′, H-3′), 4.63 (d, 1, H-1′, $J_{1',2'}$ = 6.1 Hz), 6.97 (d, 1, H-5, $J_{4,5}$ = 9.8 Hz), 7.71 (d, 1, H-4); ^{13}C NMR (CD_3OD) δ 63.30 (C-5′), 72.95, 76.81, 83.89, 86.99 (C-1′, C-2′, C-3′, C-4′), 130.75, 133.80 (C-4, C-5), 149.35 (C-3), 163.92 (C=O). Anal. Calcd for $C_9H_{12}N_2O_5 \cdot H_2O$: C, 43.90; H, 5.73; N, 11.38. Found: C, 44.11; H, 5.63; N, 11.21.

3-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)-6(1*H*)-pyridazinone (14). Ethyl orthoformate (0.1 mL, 0.6 mmol) was added to a well-stirred suspension of **13** (9 mg, 0.032 mmol) in acetone (1 mL) containing *p*-toluenesulfonic acid monohydrate (4.6 mg), and the mixture was allowed to stand at room temperature for 18 h. The sodium bicarbonate was added, and the mixture was stirred for 15 min. The solid was collected by filtration and thoroughly washed with acetone. The filtrates were combined and evaporated in vacuo to a syrup, which was purified by preparative TLC with chloroform–methanol (9:1) as the eluent: yield 66.2%; colorless syrup; ^{1}H NMR (CD_3OD) δ 1.35 (s, 3, isopropylidene CH_3), 1.55 (s, 3, isopropylidene CH_3), 3.62 (d, 2, H-5′, $J_{4',5'}$ = 5.0 Hz), 4.12 (q, 1, H-4′), 4.64–4.88 (m, 5, H-1′, H-2′, H-3′, OH, NH), 6.90 (d, 1, H-5, $J_{4,5}$ = 9.8 Hz), 7.58 (d, 1, H-4).

(5*R*)- and (5*S*)-1-(*N*-Isopropylideneamino)-5-hydroxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-3-pyrrolin-2-one (15). A solution of **12** (28 mg, 0.05 mmol) in acetone (3 mL) was heated under reflux for 2 h. Acetone was removed under reduced pressure, and the residue was chromatographed over a column of silica gel with chloroform–methanol (49:1) as the eluent. This afforded 15 mg of **15** (51%) as a colorless syrup. Due to the unstable and hygroscopic nature of this compound, good elemental analysis could not be obtained: ^{1}H NMR ($CDCl_3$) δ 1.92, 1.97, 2.08 (each s, 6, CH_3), 4.46 (d, 1, H-1′, $J_{1',2'}$ = 4 Hz), 4.64 (apparent s, 4, H-4′, H-5′, OH), 5.60–5.88 (m, 1, H-2′ or H-3′), 5.96–6.32 (m, 2, H-3, H-2′ or H-3′), 7.00–8.20 (m, 16, H-4, Ar H).

(5*R*)- and (5*S*)-1-Amino-5-hydroxy-5-β-D-ribofuranosyl-3-pyrrolin-2-one (17). The same procedure was used as for the deprotection of **11** with 1 N NaOH solution: yield 92%; chromatographically homogeneous clear foam; ^{1}H NMR (CD_3OD) δ 3.53–4.28 (m, 6, H-1′, H-2′, H-3′, H-4′, H-5′), 6.17, 6.20 (each d, 1, H-3, $J_{3,4}$ = 6.4 Hz), 7.04, 7.12 (each d, 1, H-4); ^{13}C NMR (CD_3OD) δ 63.07, 63.53 (C-5′), 72.43–87.11 (C-1′, C-2′, C-3′, C-4′), 91.79, 91.91 (C-5), 127.77, 128.18 (C-3), 147.66, 148.60 (C-4), 171.30 (C=O). Anal. Calcd for $C_9H_{14}N_2O_6 \cdot {}^1/_2H_2O$: C, 42.35; H, 5.92; N, 10.98. Found: C, 42.46; H, 5.95; N, 10.86.

3-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl)-6*H*-1,2-oxazin-6-one (18). A solution of **6a,b** (206 mg, 0.37 mmol) and hydroxylamine-*O*-sulfonic acid 334.7 mg (3.0 mmol) in methanol (10 mL) was treated under reflux for 10 h. The reaction mixture was neutralized with a saturated sodium bicarbonate solution, and the resulting mixture was extracted with chloroform (3 × 50 mL), dried over magnesium sulfate, and evaporated in vacuo to a syrup. The residue was chromatographed over silica gel with chloroform–benzene (11:9) as the eluent. This afforded 143.3 mg of **18** (71.8%) as colorless crystals: mp 147–148 °C; IR ($CHCl_3$) 1750, 1720 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 4.60 (dd, 1, H-5′a, $J_{4',5'a}$ = 3.4 Hz, $J_{5'a,5'b}$ = 12.1 Hz), 4.73 (m, 1 H-4′), 4.85 (dd, 1, H-5′b, $J_{4',5'b}$ = 3.0 Hz), 5.21 (d, 1, H-1′, $J_{1',2'}$ = 7.0 Hz), 5.81 (dd, 1, H-2′), 5.89 (dd, 1, H-3′, $J_{2',3'}$ = 5.7 Hz, $J_{3',4'}$ = 4.1 Hz), 6.58 (d, 1, H-5, $J_{4,5}$ = 9.8 Hz), 7.17–8.09 (m, 16, H-4, Ar H). Anal. Calcd for $C_{30}H_{23}NO_9$: C, 66.54; H, 4.28; N, 2.58. Found: C, 66.37; H, 4.27; N, 2.65.

3-β-D-Ribofuranosyl-6*H*-1,2-oxazin-6-one (20). The same procedure was used as for the deprotection of **11** with 1 N NaOH solution: yield 92.3%; chromatographically homogeneous clear foam; $[\alpha]^{24.5}_D$ −13.2° (*c* 0.34, methanol); MS, *m/e* 229 (M^+); ^{1}H NMR (CD_3OD) δ 3.65–3.72 (m, 2, H-5′), 4.00 (m, 1, H-4′), 4.10–4.19 (m, 2, H-2′, H-3′), 4.63 (d, 1, H-1′, $J_{1',2'}$ = 7.1 Hz), 6.81 (d, 1, H-5, $J_{4,5}$ = 9.8 Hz), 7.54 (d, 1, H-4); ^{13}C NMR (CD_3OD) δ 63.12 (C-5′), 73.19, 76.00, 81.92, 87.81 (C-1′, C-2′, C-3′, C-4′), 126.60 (C-5), 132.92 (C-4), 157.43 (C-3), 164.98 (C=O). Anal. Calcd for $C_9H_{11}NO_6 \cdot {}^1/_4H_2O$: C, 46.25; H, 4.96; N, 5.99. Found: C, 46.11; H, 5.31; N, 5.96.

3-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)-6*H*-1,2-oxazin-6-one (21). The same procedure was used as the acetonization of **13** with ethyl orthoformate: yield 58.3%; ^{1}H NMR (CD_3OD) δ 1.36 (s, 3, isopropylidene CH_3), 1.54 (s, 3, isopropylidene CH_3), 3.52–3.80 (m, 2, H-5′), 4.18 (q, 1, H-4′, $J_{3',4'} = J_{4',5'}$ = 4 Hz), 4.60–5.00 (m, 4, H-1′, H-2′, H-3′, OH), 6.76 (d, 1, H-5, $J_{4,5}$ = 9 Hz), 7.41 (d, 1, H-4).

(5*R*)- and (5*S*)-5-Hydroxy-5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-3-pyrrolin-2-one (22). To a solution of **6a,b** (550 mg, 0.98 mmol) in dioxane (11 mL) was added ammonia (5 mL) at 0–5 °C, and the mixture was allowed to stand at room temperature for 1 h. Water was added, and the resultant mixture was neutralized with acetic acid. The mixture was extracted with chloroform (3 × 100 mL), washed with water, dried over magnesium sulfate, and evaporated in vacuo to a syrup. The residue was chromatographed over a column of silica gel with chloroform–methanol (95:5) as the eluent. This afforded 450 mg of **22** (93%) as a colorless foam. Identity was confirmed by comparing the IR and ^{1}H NMR spectra with the spectra of the products previously prepared by the reported procedure.

Registry No. **1**, 86528-49-6; **2** (5*R* diastereomer), 109930-03-2; **2** (5*S* diastereomer), 110012-35-6; **3**, 109930-04-3; **4**, 109930-05-4; **5**, 109930-06-5; **6a**, 109930-07-6; **6b**, 110012-36-7; **7**, 86528-50-9; **8** (5*R* diastereomer), 110012-37-8; **8** (5*S* diastereomer), 110012-38-9; **9a**, 110012-39-0; **9b**, 110012-40-3; **10a**, 109930-08-7; **10b**, 109930-09-8; **11**, 109930-10-1; **12** (5*R* diastereomer), 109930-11-2; **12** (5*S* diastereomer), 110012-41-4; **13**, 109930-12-3; **14**, 109930-13-4; **15** (5*R* diastereomer), 109930-14-5; **15** (5*S* diasteroemer), 110012-42-5; **17** (5*R* diasteromer), 109930-15-6; **17** (5*S* diastereomer), 110012-43-6; **18**, 109930-16-7; **20**, 109930-17-8; **21**, 109930-18-9; **22** (5*R* diastereomer), 108007-65-4; **22** (5*S* diastereomer), 108100-93-2.