in 50ml of $CHCl_3$ in the presence of a catalytic amount of pyridine. The reaction mixture was stirred overnight at room temperature. Without separation of the brominated product, 14ml (100mmol) of triethylamine in 10ml of $CHCl_3$ was added and stirred additionally for 3 hrs.. The colorless triethylammonium bromide was filtered off and $CHCl_3$ solvent was removed under reduced pressure. The reaction product was distilled under reduced pressure to give 3.3g (48% yield) of a mixture of 1,1,3,4-tetramethyl-1-sila-2,4-cyclopentadiene monomer (dominated at 77—80°C, 60mmHg) and a dimer (dominated at 90-98°C, 30mmHg). Mass spectrum, m/e, calcd. for $(C_8H_{14}Si)_2$, 276.56, found 276, ir (neat) ν Si-CH_3 = 1250cm^{-1}(s), δ Si-CH_3 = 820cm^{-1}(m), ^{1}H-nmr. ^{13}C-nmr and C/H-correlation two dimensional nmr (see Table 3).

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Synthetic Studies Related to Ezomycins and Octosyl Acids. Synthesis of Heptofuranose Nucleosides

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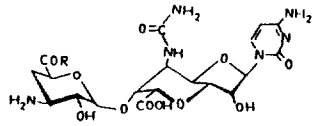
1-[Ethyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hept-5-enofuranosyluronate] uracil (**12**) was synthesized. Other various heptofuranose nucleosides were also synthesized from uridine and adenosine by two-carbon chain extension using Wittig reaction.

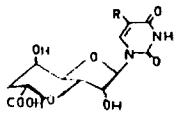
Introduction

The ezomycin complex[1,2] and octosyl acids[3] were recently isolated from the fermentation broth of two different strains of *Streptomyces*. Eight components, namely ezomycins A_1(1), A_2(2), B_1, B_2, C_1, C_2, D_1, and D_2 have been isolated from the ezomycin complex, and three octosyl acids, namely octosyl acids A(3), B(4), and C have been identified.



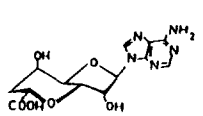
1 R = NHCHCH$_2$CH$_2$SCH$_2$CHNH$_2$ (COOH, COOH)

2 R = OH



3 R = COOH

4 R = CH_2OH



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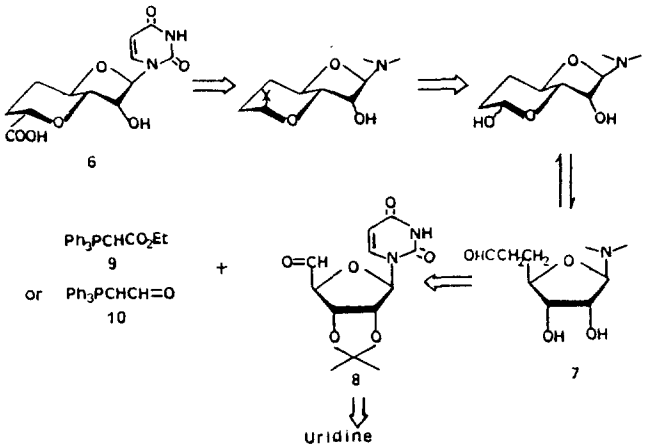
The degradative and spectroscopic studies of ezomycins[4] and octosyl acids[3] revealed that an unusual higher-carbon sugar, namely a 3,7-anhydroocturonic acid, was a common structural backbone of these two series of compounds. The 3,7-anhydroocturonic acid is the first octose derivative containing a rigid bicyclic system in which a furanoid ring is *trans*-fused to a pyranoid ring. In spite of their structural similarities, the ezomycins and octosyl acids show marked differences in biological activities. Thus, whereas the ezomycins are antifungal antibiotics,[2] the octosyl acids are devoid of any such activity. However, the adenine analog (**5**) of the octosyl acids, readily obtained from *3* by transglycosylation,[5,6] was found to be an inhibitor of cyclic-AMP phosphodiesterases from various animal tissues.[6] In fact, octosyl acids 3 and 4 may be regarded as carboanalogs of 3′, 5′-cyclic nucleotides. The unique structures and the biological activities of the ezomycins and the octosyl acids have inspired various studies related to these compounds during the past several years. For example, a biosynthesis of octosyl acid A has been accomplished by Sato *et al.*,[7] and a ^{13}C NMR spectroscopic study of the ezomycins has been also reported.[8]

Although total synthesis of ezomycins and octosyl acids has not been accomplished yet, a few methods of approach toward their synthesis have been explored by synthesizing model compounds.[9-12] Among them, the methods devised by Hanessian *et al.*[11] and by Kim *et al.*[12] are promising ones for the eventual

total synthesis of ezomycins and octosyl acids, yet have shortcomings. Thus, introduction of a hydroxy group at C-2′ position of the bicyclic octose nucleoside would be difficult in Hanessian's method[11] and the Wittig reagent used in Kim's method[12] is not readily available.

Scheme 1 shows a new retrosynthetic plan for a model compound of ezomycins and octosyl acids. This plan is different from approaches reported before.[9-12] We expected that heptofuranose nucleoside **7** in Scheme 1 would be readily obtained from nucleoside aldehyde **8** and ylide **9** or **10**. Suprisingly, however, Howgate and co-workers[13] have reported that no reaction occurred between **8** and **9**.

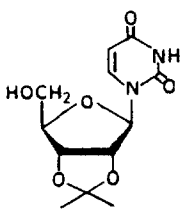


Scheme 1.

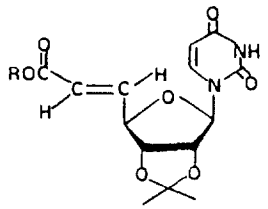
In this article we report the results of the reinvestigation of the reaction of **8** with **9** and the synthesis of various heptofuranose nucleosides. The nucleosides synthesized in this work are potential precursors for the synthesis of ezomycins and octosyl acids. Also, the present work might promote biological studies related to these heptofuranose nucleosides since nucleosides substituted at C-5′ by methylphosphonate group or other moieties may penetrate cell membranes and inhibit critical enzyme by virtue of their similarity to nucleotides.[14]

Results and Discussion

On the basis of the retrosynthetic plan shown in Scheme 1, 2′, 3′-*O*-isopropylidene uridine (**11**) was prepared from uridine by protection of its vicinal hydroxy groups with acetone using a slightly modified procedure of a known method.[15] Oxidation of **11** with dimethyl sulfoxide and dicyclohexylcarbodiimide afforded 1-(2,3-*O*-isopropylidene-ß-*D*-*ribo*-pentodialdo-1,4-furanosyl) uracil (**8**). The aldehyde **8**, obtained without isolation from the reaction mixture, was allowed to react with carbetoxymethylenetriphenylphosphorane (**9**). Chromatographic purification gave pure 1-[ethyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-hept-5-enofuranosyluronate] uracil (**12**) in 73% yield from **11**. On a preparative scale, it was not necessary to purify **12** because the product obtained in the next step could be easily purified by recrystallization. This result is in sharp contrast with Howgate's report[13] that compound **12** could not be obtained in the reaction of **8** and **9** and that when the phosphorane **9** was generated *in situ* by means of sodium ethoxide, a mixture of five products was obtained of which four were established to be undesired unsaturated derivatives. The



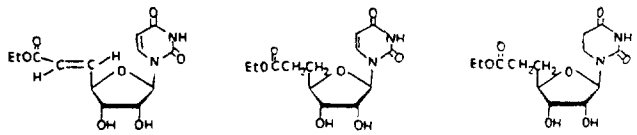
11



12 R = Et
16 R = Me

reason for Howgate's failure to obtain **12** is not clear but we speculate that Howgate and co-workers might not detect and, therefore, could not isolate the desired product actually generated in the reaction mixture because we found the R_f values of the starting aldehyde **8** and the product **12** were same on the TLC plates using various eluents. Evidence for the structural assignment of **12** came from many sources. Its UV spectrum, having λmax (EtOH) 256 nm, indicated that compound **12** had the intact uracil moiety. The ^{1}H NMR spectrum of α, ß-(*E*)-unsaturated ester **12** clearly exhibited all the expected resonances. Thus, it showed a large *trans*-ethylenic coupling constant ($J_{5'}$, $_{6'}$ = 15.8Hz) and a small, long-range coupling constant ($J_{4'}$, $_{6'}$ = 1.2Hz).

The transformation of **12** into 1-[ethyl (*E*)-5,6-dideoxy-ß-*D*-*ribo*-hept-5-enofuranosyluronate] uracil (**13**) provided further evidence for the formation of the adduct **12**. Deisopropylidenation of **12** with 90% formic acid at room temperature afforded crystalline **13**, and repeated crystallization provided analytically pure **13** in 78% yield.

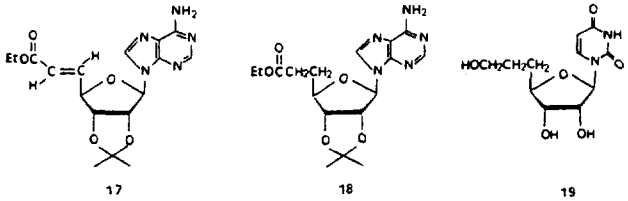


13 14 15

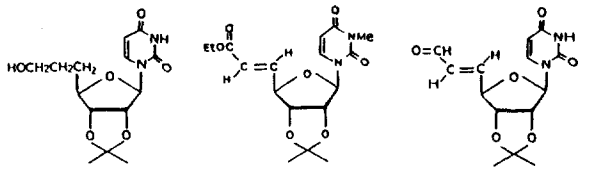
Catalytic hydrogenation of **13** in ethanol over 10% palladium-on-charcoal under a hydrogen pressure of 1 atm for 10 min reduced selectively the C-5′—C-6′ double bond to give 1-(ethyl 5,6-dideoxy-ß-*D*-*ribo*-heptofuranosyluronate) uracil (**14**) in almost quantitative yield. Carefully controlled hydrogenation of **13** was required in order to prevent hydrogenation of C-5—C-6 double bond in the nucleoside base of **13**. Hydrogenation of **13** under forementioned condition for 15 min generated substantial amount of syrupy 1-(ethyl 5,6-dideoxy-ß-*D*-*ribo*-heptofuranosyluronate)-5,6-dihydrouracil (**15**) which interfered crystallization of **14**.

We further examined the feasibility of two—carbon chain extension of pentofuranose nucleosides by means of Wittig reactions. Unlike Howgate's report, the reaction of compound **8** with carbomethoxymethylenetriphenylphosphorane smoothly proceeded to give 1-[methyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-hept-5-enofuranosyluronate] uracil (**16**). Wittig reaction of 9-(2,3-*O*-isopropylidene-ß-*D*-*ribo*-pentodialdo-1,4-furanosyl) adenine and **9** also afforded 9-[ethyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-hept-5-enofuranosyluronate] adenine (**17**) and the subsquent hydrogenation of **17** gave 9-[ethyl 5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-heptofuranosyluronate) adenine (**18**) in high yield.

The next step should be the reduction of ester group of **14** directly to the aldehyde group which might form a intramolecular hemiacetal with the hydroxy group at C-3′. Another way to generate an aldehyde function is the reduction of **14** to triol **19** followed by the subsquent selective oxidation of the primary hydroxy group of **19** to an aldehyde.[16] So we carried out the reduction of **14** with several hydride reducing agents.



17 **18** **19**



20 **21** **22**

The reduction of **14** by diisobutylaluminum hydride was performed with various molar ratios of the substrate and the reducing agent in tetrahydrofuran at −60°C to −70°C. Unexpectedly, at least five major products were detected on TLC with several minor products, and the yield of the mixture was also very low. This mixture did not reduce Fehling's solution and ^{1}H NMR spectrum of the mixture did not show the expected resonances attributable to the desired product. Because of the solubility problem, the reduction of **14** with lithium aluminum hydride in ether was not desirable. Instead, we performed the reduction of a protected nucleoside **12**. Reduction of **12** by lithium aluminum hydride under various condition unexpectedly, gave a complex mixture. On the other hand, however, lithium borohydride in ether converted compound **12** into 1-(5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-heptofuranosyl) uracil (**20**). Even sodium borohydride in 1,2-dimethoxyethane reduced **12** to **20** in 23% yield. The results of the reduction of **12** and **14** are a little unusual. The reasons are not clear but the nucleoside base of **12** and **14** might be attributable to these results. The base part of **12** was then modified. Thus, the reaction of **12** with *N,N*-dimethylformamide dimethyl acetal afforded 1-[ethyl (*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-hept-5-enofuranosyluronate]-3-methyluracil (**21**).

If the selective oxidation of the primary hydroxy group of *19* is not successful in the next step, the aldehyde function at C-7′ should be generated before the cleavage of the protective group of two hydroxy groups at C-2′and C-3′. For this reason, we also synthesized 1-[(*E*)-5,6-dideoxy-2,3-*O*-isopropylidene-ß-*D*-*ribo*-hept-5-enodialdo-1,4-furanosyl] uracil (**22**) by the reaction of **8** with formylmethylenetriphenylphosphorane(**10**).[17]

The results of the present work, unlike the earlier report,[13] indicate that Wittig reaction employing stabilized ylides is generally applicable to synthesis of the heptofuranose nucleosides by two-carbon chain extension of pentofuranose nucleosides.

Experimental

Evaporations were performed under reduced pressure at or below 40°C (bath temperature). Melting points are uncorrected. Infrared spectra were run on Shimadzu Model IR-435 or on a Perkin-Elmer IR 710B spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM-360L spectrophotometer with tetramethylsilane as the internal standard. Ultraviolet spectra were measured with a Shimadz UV-240 spectrophotometer. Optical rotations were measured with a Perkin-Elmer Model 141 automatic polarimeter at 23 ± 3°C. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario or in Korea Research Institute of Chemical Technology, Daejon. Thin-layer chromatography (TLC) was performed on precoated glass plates (silica gel 60 F-254, 0.25 mm thickness) from EM Laboratories.

2′,3′-O-Isopropylideneuridine (**11**). A suspension of finely powdered uridine (5.13g, 21 mmol) and anhydrous copper (II) sulfate (10g) in acetone containing C·H_2SO_4 (0.13 m*l*) was vigorously stirred with a mechanical stirrer at room temperature for 60 hr. The mixture was filtered with suction and the residue was washed with acetone. The combined filtrate and washing was transfered to a flask containing anhydrous calcium hydroxide (5g) and the mixture was stirred with a mechanical stirrer at room temperature for 1 hr. The mixture was filtered and the evaporation of the filtrate afforded white crystalline **11**. The crude crystals were dissolved in boiling acetone and then a small amount of acetone was added to the solution. After overnight, pure **11** was obtained from the solution as fine needles (5.43g, 91%), R_f 0.69 (methanol-ether, v/v 2:8), mp 161-163°C (lit.[15] 159-160°C); ^{1}H NMR (DMSO-d_6) δ 1.33 and 1.52 (*s*, 3H, CMe_2), 3.37 (*bs*, 1H, OH), 3.64 (*d*, J = 4.0Hz, 2H, H-5′), 4.14 (*q*, 1H) 4.71-5.04 (*m*, 2H), 5.71 (*d*, J = 8.0Hz, 1H, H-5), 7.87 (*d*, 1H, H-6).

1-(2,3-O-Isopropylidene-ß-D-ribo-*pentodialdo-1,4-furanosyl) uracil* (**8**) and 1-[*ethyl* (*E*)-5,6-*dideoxy*-2,3-O-*isopropylidene-ß-D*-ribo-*hept-5-enofuranosyluronate*] *uracil* (**12**). To a solution of **11** (0.70g, 2.5 mmol) in dimethyl sulfoxide (12 ml), stirred at room temperature under nitrogen, pyridine (0.20 m*l*), trifluoroacetic acid (0.09 m*l*), and *N,N′*-dicyclohexylcarbodiimide (1.53g, 7.4 mmol) were added. After 12 hr, without isolation of **8**, carbetoxymethylenetriphenylphosphorane (**9**, 1.23g, 3.5 mmol) was added and stirring was continued for further 24 hr at room temperature. Oxalic acid dihydrate (9g) and ethyl acetate (60 m*l*) were then added and the mixture was stirred for 10 min. This mixture was poured into saturated, aqueous sodium chloride solution (30 m*l*), stirred for a few min, and filtered. The separated aqueous layer was extracted once more with ethyl acetate (25 m*l*). The combined ethyl acetate solution was washed successively with dilute aqueous sodium hydrogen carbonate solution, saturated aqueous sodium chloride solution, and cold water, dried ($MgSO_4$), and evaporated to give a dark red syrup. This thick syrup was dissolved again in ethyl acetate and insoluble *N,N′*-dicyclohexylurea was removed by filtration. This procedure was repeated a few more times in order to remove *N,N′*-dicyclohexylurea. The resulting

red syrup was chromatographed on a column of silica gel by elution with ethyl acetate-hexane, 1:1 (v/v), to afford **12** as white needles (0.57g, 73%), R_f 0.56 (ethyl acetate), mp 68-70°C, $[\alpha]_D$ +48° (*c* 0.3 in chloroform); IR (film) 1710, 1670, 1620 cm^{-1}; UV λmax (EtOH) 212 (ε 15500), 256 (1280) nm; ^1H NMR ($CDCl_3$) δ 1.27 (*t*, J = 6.7Hz, 3H, OCH_2-*Me*), 1.36 and 1.58 (*s*, 3H, CMe_2), 4.16 (*q*, 2H, *OCH_2*-Me), 4.52-4.90 (2H, H-4′, H-3′), 5.09 (*dd*, J = 6.0Hz and 1.5Hz, 1H, H-2′) 5.64 (*d*, 1H, H-1′), 5.74 (*d*, J = 8.0Hz, 1H, H-5), 5.99 (*dd*, J = 15.8Hz and 1.2Hz, 1H, H-6′), 7.01 (*dd*, J = 5.5Hz and 15.8Hz, 1H, H-5′), 7.24 (*d*, J = 8.0Hz, 1H, H-6).

*1-[Ethyl (E)-5,6-dideoxy-ß-D-*ribo*-hept-5-enofuranosyluronate] uracil* (**13**). Compound **12** (0.51g, 1.6 mmol) was dissolved in cold 90% formic acid (5 m*l*) and the solution was stirred at room temperature for 3 hr. Cold water (1.5 m*l*) was added to the reaction mixture which was then evaporated below 30°C. Addition of more water and evaporation were repeated to afford a pale yellow solid residue. From the chloroform solution of this solid, crude crystalline **13** was obtained by addition of hexane. Crude **13** was purified by recrystallization from toluene-methanol (trace)-chloroform to give pure **13** (0.39g, 78%), R_f 0.18 (toluene-acetone, v/v 1:1), mp 161-162°C, $[\alpha]_D$ +73° (*c* 0.5 in methanol); IR (KBr) 3440, 3420, 1710, 1620 cm^{-1}; UV λmax (EtOH) 211 (ε 6800), 258 (9700) nm; ^1H NMR (DMSO-d_6) δ 1.25 (*t*, J = 6.7Hz, 3H, OCH_2-*Me*), 3.87-4.58 (5H, *OCH_2*-Me, H-2′, H-3′, H-4′), 5.53 (*d*, J = 8.0Hz, 1H, H-5), 5.76 (*d*, J = 4.0Hz, 1H, H-1′), 6.01 (*dd*, J = 15.8Hz and 1.2Hz, 1H, H-6′), 7.01 (*dd*, J = 15.8Hz and 6.0Hz, 1H, H-5′), 7.66 (*d*, J = 8.0Hz, 1H, H-6). *Anal.* Calcd. for $C_{13}H_{16}N_2O_7$: C, 50.00; H, 5.17; N, 8.97. Found: C, 50.09; H, 5.03; N, 8.89.

*1-(Ethyl 5,6-dideoxy-ß-D-*ribo*-heptofuranosyluronate) uracil* (**14**) *and 1-(ethyl 5,6-dideoxy-ß-D-*ribo*-heptofuranosyluronate)-5,6-dihydrouracil* (**15**). A solution of **13** (0.10g, 0.32 mmol) in ethanol (30 m*l*) was shaken in a standard Paar bottle along with 10% palladium-on-charcoal catalyst (15 mg) under a hydrogen pressure of 1 atm at room temperature. As soon as shaking was started, hydrogen was consumed very rapidly. After 10 min, the hydrogen uptake almost ceased. TLC showed that the R_f value of the product was exactly same as that of the starting material. The reaction mixture was filtered through Celite twice and concentration of the filtrate afforded a white solid which was recrystallized from toluene-hexane to give **14** (0.098g, 97%), R_f 0.18 (toluene-acetone, v/v 1:1), mp 120-121°C, $[\alpha]_D$ +84° (*c* 0.4 in methanol); IR (KBr) 3435, 3420, 1710, 1620 cm^{-1}; UV λmax (EtOH) 211 (ε 7200), 258 (11000) nm; ^1H NMR (methanol-d_4) δ 1.24 (*t*, J = 6.7Hz, 3H, OCH_2-*Me*), 2.08 (m, 2H, H-5′), 2.50 (*t*, J = 7.0Hz, 2H, H-6′), 4.07 (*q*, 2H, *OCH_2*-Me), 3.81-4.28 (m, 3H, H-2′, H-4′), 5.72 (*d*, J = 8.0Hz, 1H, H-5), 5.76 (*d*, J = 4.2Hz, 1H, H-1′), 7.59 (*d*, J = 8.0Hz, 1H, H-6). *Anal.* Calcd. for $C_{13}H_{18}N_2O_7$: C, 49.68; H, 5.77; N, 8.92. Found: C, 49.32; H, 5.77; N, 8.93.

*1-[Methyl (E)-5,6-dideoxy-2,3-O-isopropylidene-ß-D-*ribo*-5-enofuranosyluronate] uracil* (**16**). Wittig reaction of **8** generated *in situ* from **11** (0.70g, 2.5 mmol) with carbomethoxymethylenetriphenylphosphorane (1.17g, 3.5mmol) was performed as described above for **12** and afforded, after column chromatography (ethyl acetate-hexane, v/v 1:1), **16** as a syrup (0.63g, 75%), R_f 0.54 (ethyl acetate); IR (neat) 1715, 1660 cm^{-1}; UV λmax (EtOH) 212, 256 nm; ^1H NMR ($CDCl_3$) δ 1.37 and 1.59 (*s*, 3H, CHe_2), 3.69 (*s*, 1H OCH_3), 3.75-4.55 (2H, H-2′, H-3′, H-4′), 5.58 (*d*, J = 8.0Hz, 1H, H-5), 5.77 (*d*, J = 4.0Hz, 1H, H-1′), 6.02 (*dd*, J = 16.0Hz and 1.4Hz, 1H, H-6′), 7.03 (*dd*, J = 16.0Hz and 6.0Hz, 1H, H-5′), 7.71 (*d*, J = 8.0Hz, 1H, H-6).

*9-[Ethyl (E)-5,6-dideoxy-2,3-O-isopropylidene-ß-D-*ribo*-hept-5-enofuranosyluronate] adenine* (**17**). 2′,3′-*O*-Isopropylidene adenosine (0.77g, 2.5 mmol) was oxidized to 9-(2,3-*O*-isopropylidene-ß-*D*-ribo-pentodialdo-1,4-furanosyl) adenine by dimethyl sulfoxide and dicyclohexylcarbodiimide as described above for **8**. Without isolation, Wittig reaction of the aldehyde and ylide **9** (1.23g, 3.5 mmol) was performed as described above for **12** and afforded, after column chromatography (ethyl acetate hexane, v/v 1:1), **17** as a white foam (0.66g, 70%); ^1H NMR ($CDCl_3$) δ 1.21 (*t*, J = 6.5Hz, 3H, OCH_2-*Me*), 1.30 and 1.53 (*s*, 3H, CMe_2), 3.99 (*q*, 2H, *OCH_2*-Me), 4.19 (*q*, 2H, *OCH_2*-Me), 4.70-4.84 (m, 1H), 5.02-5.20 (m, 1H), 5.45-5.63 (m, 1H), 5.77 (*d*, J = 16.0Hz, 1H, H-6′), 6.11 (*d*, J = 2.0Hz, 1H, H-1′), 6.95 (*dd*, J = 16.0Hz and 5.5Hz, 1H, H-5′), 7.86 (*s*, 1H, H-2), 8.31 (*s*, 1H, H-8).

*9-[Ethyl 5,6-dideoxy-2,3-O-isopropylidene-ß-D-*ribo*-heptofuranosyluronate] adenine* (**18**). Hydrogenation of **17** (0.38g, 1.0 mmol) in ethanol (40 ml) was performed as described above for **13** and afford **18** as a white foam (0.37g, 97%); ^1H NMR ($CDCl_3$) δ 1.19 (*t*, J = 7.0Hz, 3H, OCH_2-*Me*), 1.38 and 1.60 (*s*, 3H, CMe_2), 1.90-2.53 (*m*, 2H, H-5′, H-6′), 4.05 (*q*, J = 7.0Hz, 2H, *OCH_2*-Me), 4.10-4.33 (m, 1H, H-4′), 4.73-4.88 (m, 1H, H-3′), 5.44 (*dd*, J = 6.5Hz and 2.5Hz, 1H, H-2′), 5.99 (*d*, J = 2.5Hz, 1H, H-1′), 7.83 (*s*, 1H, H-2), 8.28 (*s*, 1H, H-8).

*1-(5,6-Dideoxy-2,3-O-isopropylidene-ß-D-*ribo*-heptofuranosyl) uracil* (**20**). To a stirred solution of **12** (0.20g, 0.56 mmol) in ether (15 m*l*) was added lithium borohydride (60 mg) at room temperature in the dark. After stirring at room temperature for 2 hr, ether (10 m*l*) and water (15 m*l*) were added to the reaction mixture. Water layer was extracted with ether (5 m*l*) once. The combined organic layer was dried ($MgSO_4$) and evaporated to afford **20** as a syrup (0.15g, 72%). An analytical sample was obtained by prepartive TLC, R_f 0.23 (ethyl acetate); ^1H NMR ($CDCl_3$) δ 1.29 and 1.50 (*s*, 3H, CMe_2), 1.55-2.15 (m, 4H, H-5′, H-6′), 3.75-4.20 (*m*, 1H), 4.48-4.67 (*m*, 1H), 4.92 (*dd*, J = 7.5Hz and 2.5Hz, 1H, H-2′), 5.58 (*d*, J = 2.5, 1H, H-1′), 5.70 (*d*, J = 8.0Hz, 1H, H-5), 7.23 (*d*, 1H, H-6).

*1-[Ethyl (E)-5,6-dideoxy-2,3-O-isopropylidene-ß-D-*ribo*-hept-5-enofuranosyluronate]-3-methyluracil* (**21**). A solution of **12** (0.91g, 2.55 mmol) and *N,N*-dimethylformamide dimethyl acetal (1.4 ml, 10.4 mmol) in chloroform (13 ml) was stirred at room temperature for 18 hr. Evaporation of the solvent afforded **21** as a syrup (0.61g, 65%). An analytical sample was obtained by preparative TLC, R_f 0.32 (ethyl acetate-hexane, v/v 1:1); ^1H NMR δ 1.17 (*t*, J = 7.0Hz, 3H, OCH_2-*Me*), 1.25 and 1.47 (*s*, 3H, CMe_2), 3.23 (*s*, 3H, NMe), 4.14 (*q*, 2H, *OCH_2*-Me), 4.45-5.07 (*m*, 3H, H-2′, H-3′, H-4′), 5.58 (*d*, J = 1.5Hz, 1H, H-1′), 5.73 (*d*, J = 8.0Hz, 1H, H-5), 5.96 (*dd*,

J = 15.8Hz and 1.2Hz, 1H, H-6'), 7.01 (*dd*, J = 15.8Hz and 5.5Hz, 1H, H-5'), 7.15 (*d*, J = 8.0Hz, 1H, H-6).

*1-[(E)-5,6-didexoy-2,3-O-isopropylidene-β-D-*ribo*-hept-5-enodialdo-1,4-furanosyl] uracil* (**22**). To a solution of **11** (0.50g, 1.8 mmol) in dimethyl sulfoxide (10 ml), trifluoroacetic acid (0.065 ml) and *N,N'*-dicyclohexylcarbodiimide (1.09g, 5.3 mmol) were added. After 10 hr, **10** (0.52g, 1.8 mmol) was added and stirring was continued for a further 24 hr at room temperature. The product was isolated by the procedure which was used for **12** to afford, after chromatography on silica gel, **22** as a pale yellow foam (0.32g, 62%), R_f 0.65 (toluene-acetone, v/v 1:1); ^1H NMR ($CDCl_3$) δ 1.39 and 1.61 (*s*, 3H, CMe_2), 4.68-5.04 (m, 2H, H-3', H-4'), 5.18 (*dd*, J = 6.0Hz and 0.5Hz, 1H, H-2'), 5.57 (*d*, J = 0.5Hz, 1H, H-1'), 5.77 (*d*, J = 8.0Hz, 1H, H-5), 6.25 (*ddd*, J = 16.0Hz, 7.5Hz, and 1.0Hz, 1H, H-6'), 7.00 (*dd*, J = 16.0Hz and 5.0Hz, 1H, H-5'), 7.27 (*d*, J = 8.0Hz, 1H, H-6), 9.62 (*d*, J = 7.5Hz, 1H, H-7'). *Anal.* Calcd., for $C_{14}H_{16}N_2O_6$: C, 54.54; H, 5.23; N, 9.09. Found: C, 54.48; H, 5.13; N, 9.12.

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^{13}C NMR Study of Segmental Motions of n-Heptane in Neat Liquid

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Carbon-13 nuclear spin-lattice relaxation times have been measured over the range of temperature from 213K to 353K for carbons in n-heptane in neat liquid. The experimental data have been analyzed to obtain informations of segmental motions in the chain polymers by employing a model which describes jumps between several discrete states with different lifetimes. The overall reorientation of the molecule is assumed to be isotropic rotational diffusion. From the above analysis the activation energies of each C-C bond reorientation as well as the overall reorientation have been obtained through the Arrhenius-type temperature dependence.

Introduction

Study of segmental motions in chain polymers plays an important role in understanding their physical properties.[1,2] Particularly, since the membrane transport in living cells is closely related to segmental motions of acyl chains in the phospholipid bilayer which is a building block of cellular membranes, the investigation of segmental motions of chain molecules becomes an important task in the field of life science thesedays.[3-5]

In the past, studies on the dynamics of polymer chains were mainly based on the stochastic approach and the results were rather qualitative. This might be inevitable when one deals with long polymer chains. Explicit roles of segmental motions in the polymer chain dynamics should become clear once we understand first the dynamics of rather short chain molecules such as n-hexane, n-heptane, etc.

Reorientation of small molecules in liquid has been widely studied experimentally and theoretically.[6] Several models are commonly used to describe molecular reorientation including internal rotations of side groups. Of these, rotational diffu-