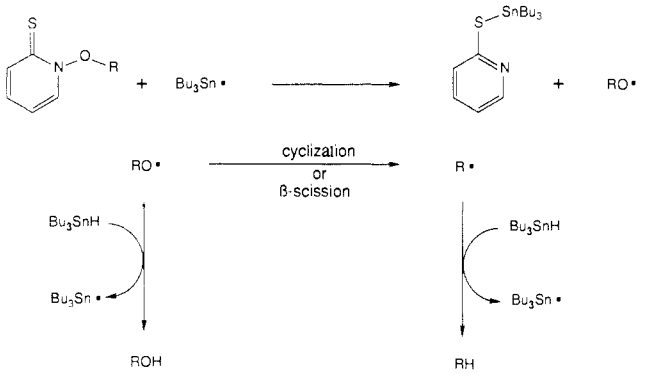
Scheme I



constant for cyclization and k_H that for hydrogen atom transfer from tributylstannane. As the value of k_H for 4-pentenyloxy radicals should be very similar to that for *tert*-butoxy radicals (estimated to be 4×10^8 M^{-1} s^{-1} at 80 °C)[19,20] it follows that $k_C \geq 6 \times 10^8$ s^{-1} at 80 °C.

The propensity of the ring-opened radicals to undergo ring closure and other rearrangements[22] complicates the estimation of the rate constants for β-fission of the cycloalkoxy radicals generated from **4** and **5**. Nevertheless, it is clear that the relative ease of β-fission is in the order cyclopentyloxy ≫ cyclohexyloxy ≫ *tert*-butoxy.

N-Alkoxypyridine-2-thiones should also be useful precursors of alkoxy radicals for synthetic work. Details of such applications and of kinetic studies now in progress will be reported shortly.

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(20) On the basis of the reasonable assumption that H• abstraction from tributylstannane by alkoxy radicals has a pre-exponential factor of log $A \simeq 10$,[21] it follows from the value of the rate constant for *tert*-butoxy radical at 25° ($k_H = 2 \times 10^8$ M^{-1} s^{-1})[9] that $E_a \simeq 2.3$ kcal/mol. These Arrhenius parameters allow the estimation of $k_H = 4 \times 10^8$ M^{-1} s^{-1} at 80 °C.

(21) Other reactive radicals abstract H• from tributylstannane with similar pre-exponential factors, e.g., benzoyloxy (log $A = 10.0 \pm 0.2$) and $(CH_3)_2C{=}CH^{\bullet}$ (log $A = 9.7 \pm 0.3$): Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickrema, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594 (Due to the slow rate of decarboxylation, the data reported in this reference for the phenyl radical actually pertain to the benzoyloxy radical.)

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The Structure of Liposidomycin B, an Inhibitor of Bacterial Peptidoglycan Synthesis

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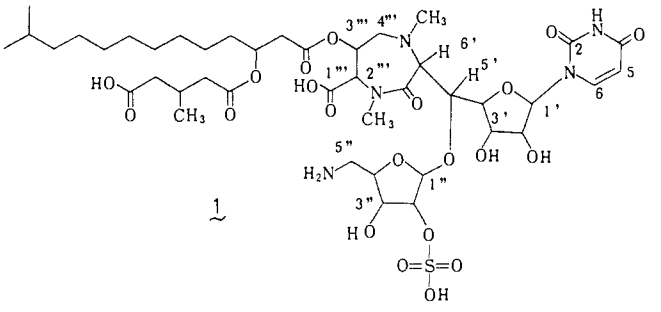
The liposidomycins are a family of nucleoside antibiotics, recently isolated from *Streptomyces griseosporeus*,[1] which strongly inhibit bacterial peptidoglycan synthesis. Liposidomycins inhibit formation of the lipid intermediate in peptidoglycan synthesis (unpublished data), as does tunicamycin,[2] but with three orders of magnitude greater activity (ID_{50} 0.03 μg/mL) and extremely high specificity. For liposidomycin B, one of the principal constituents, we propose structure **1**, a novel lipid-containing nucleoside of unusual complexity. Compound **1** resembles the reaction intermediate between UDP-*N*-acetylmuramylpentapeptide and undecaprenyl phosphate in the lipid cycle of peptidoglycan synthesis.[3]



1

Liposidomycin B (mol wt 1009, $C_{42}H_{67}N_5O_{21}S$)[4] contains nine active hydrogen atoms,[5] is amphoteric, and gives a positive ninhydrin test. Uracil, 3-methylglutaric acid, and 3-hydroxy-12-methyltridecanoic acid were identified in an acid hydrolyzate of **1** (e.g., 3 M HCl, 100 °C, 3 h) by NMR spectroscopy and by GC/MS[8] of the trimethylsilylated hydrolyzate, including comparison with authentic uracil and 3-methylglutaric acid.[9,10] The methyl ester derivative of isolated 3-hydroxy-12-methyltridecanoic acid (M^+, *m/z* 258) showed ions characteristic of β-hydroxylation [$(M-C_3H_5O_2)^+$, *m/z* 185; $C_4H_7O_3^+$, *m/z* 103].[11]

Acid hydrolysis of **1** also gave nucleoside **2** (mol wt 426, $C_{17}H_{22}N_4O_9$)[4] and a small amount of **3** (mol wt 444). The complete structure of **3** is undetermined but was shown by EI mass spectrometry to differ from **2** by 18 mass units in the seven-membered heterocycle, from which it was concluded that **2** is a dehydrated form of **3**. The structure of **2** was determined by ^1H NMR and in comparison with the anhydrodeacylliposidomycin **4** (see below). High voltage paper electrophoresis of **2** showed presence of acidic (–COOH) and basic (–N<) groups. Presence of a sulfate group in **1** was established from IR spectroscopy (KBr,

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(4) High resolution and FAB mass spectra, VG 70-SEQ and MAT 731 instruments; **1**, MH^+, *m/z* 1010; $(M-H)^-$, *m/z* 1008.403 (calcd 1008.397); **2**, as tetratrimethylsilyl (TMS) derivative, M^+, *m/z* 714.2961 (calcd 714.2968); **3**, $(TMS)_5$, M^+, *m/z* 804; **4**, MH^+, *m/z* 558.2053 (calcd 558.2048); **5**, MH^+, *m/z* 638; **6**, MH^+, *m/z* 656. NMR spectra were measured by using JEOL GX 400, GSX 400, GSX 270 instruments; **1**, ^1H NMR CD_3OD(TMS): uracil moiety, δ 7.82 (1 H, d, $J = 8$ Hz), 5.76 (1 H, d, $J = 8$ Hz); 3-methylglutaryl moiety, 1.0 (3 H, d, $J = 6.4$ Hz), 2.37 (1 H, m), 2–2.4 (4 H, m); 3-hydroxy-12-methyltridecanoyl moiety, 0.88 (6 H, d, $J = 6.8$ Hz), 1.51 (1 H, m), 1.3 (12 H, m), 1.6 (1 H, m), 5.2 (1 H, m), 2.61 (1 H, dd, $J = 8.5$ Hz, $J = 15.7$ Hz), 2.69 (1 H, dd, $J = 4.4$ Hz, $J = 15.7$ Hz), 1′, 5.64 (1 H, d, $J = 1.5$ Hz), 2′, 4.14 (1 H, overlapping), 5′, 4.42 (1 H, brd, $J = 10.7$ Hz), 6′, 3.79 (1 H, d, $J = 10.7$ Hz), 1″, 5.45 (1 H, s), 2″, 4.67 (1 H, d, $J = 4.8$ Hz), 3″, 4.30, (1 H, overlapping), 4″, 4.16 (1 H, overlapping), 5″, 3.43 (1 H, dd, $J = 2.7$ Hz, $J = 12$ Hz), 3.24 (1 H, dd, $J = 3.7$ Hz, $J = 12$ Hz), 3‴, 5.45 (1 H, m). **1**, ^{13}C NMR CD_3OD(TMS): COOR, CON (176.7, 173.8, 172.9, 172.6, 171.1 each s), 4 (166.5, s), 2 (152, s), 6 (142.5, d), 1″ (110.2, s), 5 (102.4, d), 1′ (92, d), 4′ (83.6, d), 2″ (81.6, d), 6′ (64.6, d).

(5) Determined by FAB mass spectrometry with a ^2H exchange method.[6,7]

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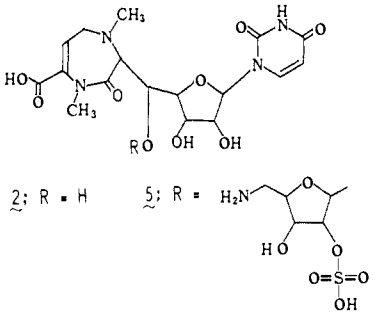
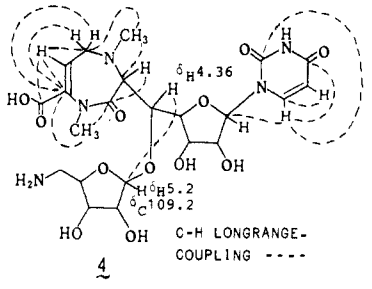


2; R = H 5; R = H_2N

1240 cm^{-1}, 820 cm^{-1}) and by the characteristic expulsion of SO_3 (loss of 79.9517 mass units) from the MH^+ ion.[12] Negative ion MS/MS measurements[13] on **1** demonstrated the sulfate to be bound to a C_5 unit identified as outlined below to be an amino pentose (m/z 228, amino sugar sulfate anion). The amino pentose structure is based on (i) loss of 131.0531 mass units ($C_5H_9NO_3$) from the MH^+–SO_3 ion from **1**; (ii) elemental composition of the structural unit $C_5H_{11}NO_7S$ calculated as the difference between **1** and the sum of isolated hydrolysis products, having a total of three rings or double bonds and four exchangeable hydrogen atoms;[5] (iii) ^1H NMR [CH_2-5″, δ 3.43 (1 H, dd, J = 1 Hz, J = 15 Hz), δ 3.24 (1 H, dd, J = 4.4 Hz, J = 15 Hz)] and ^{13}C NMR [C-1″, δ 110] which characterize the amino sugar as having a furanose ring;[14] (iv) detailed analysis of the NMR spectra of hydrolysis product **4** (below).

Alkaline hydrolysis (0.035 M NaOH, 37 °C, 4 h) of a mixture of liposidomycins gave anhydrodeacylliposidomycins **4** (mol wt 557) and **5** (mol wt 637).[4] Heteronuclear multiple bond cor-



4

relation spectroscopy (HMBC)[15] of **4** shows ^1H–^{13}C long range coupling patterns[16] as indicated. The data established a seven-membered ring heterocycle as a 1,4-perhydrodiazepine and the position of the amino sugar in **4**. Phase-sensitive double-quantum-filtered COSY[17] in conjunction with ^1H-detected ^1H–^{13}C correlation (HMQC)[18] from **4** permitted the complete assignments of ^1H and ^{13}C NMR signals.

Reductive cleavage ($LiBH_4$) of **1** gave **6** (mol wt 655),[4] a hydrated form of **5**. The linkage of 3-acyloxy-12-methyltridecanoate was deduced by an upfield shift of H-3‴ (δ 4.4) in **6** compared with **1** (δ 5.4). Ester linkage of 3-methylglutaric acid to β-hydroxyl of the fatty acid was indicated by a downfield shift (1 ppm) of the fatty acid β-proton as compared with the unsubstituted hydroxy acids.[18]

The sulfate ester was located at C-2″ by comparing amino sugar assignments in ^1H and ^{13}C NMR[19] of **4** with those of **1**, **5**, and **6**. For example, downfield shifts of H-2″ (δ 4.13) and C-2″ (δ 74.5)[20] were observed in **4** compared with δ 4.63 and δ 80 in **5**, respectively.

Difference NOE spectra of **4** [e.g., 20% NOE, H-5′ and H-1″; 6.1%, N–CH_3 (δ 2.42) and H-6′ (δ 3.92)] supported the 1,4-perhydrodiazepine structure, amino sugar substitution at C-5′, and the uracil-1′ linkage.

The overall arrangement of structural units in **1** was supported by tandem mass spectrometry.[13] For example, the decomposition pathway from MH^+ of **1**, $1010^+ \rightarrow 930^+ \rightarrow 799^+ \rightarrow 687^+ \rightarrow 555^+ \rightarrow 373^+ \rightarrow 245^+$ represents sequential losses of SO_3, amino sugar, uracil, ribose, 1,4-perhydrodiazepine moiety, and 3-methylglutaric acid. This order was established by determination of product ions following sequential mass selection and collision-induced dissociation of each of the foregoing ions, thus placing constraints on the interconnectivity of the subunits.

Acknowledgment. We are indebted to Dr. Muneki Ohuchi, JEOL Co., Ltd., for measurement of HMBC, HMQC, and DQF COSY spectra and to Machiko Noguchi for technical assistance. This work was supported by NIH Grant GM 29812, the Life Science Research Project of the Institute of Physical and Chemical Research (RIKEN), and a grant-in-aid from the Scientific Ministry of Education and Culture of Japan.

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Oxidative Addition of Halosilanes to Zero-Valent Platinum Complexes

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The oxidative addition reactions of C–X bonds in organic halides to transition-metal complexes have been widely developed and applied to various organic syntheses.[1] Ge–X or Sn–X bonds in halogermanes or halostannanes are also known to be able to oxidatively add to some transition-metal complexes.[2,3] Unlike these reactivities of group IV element–halogen bonds, Si–X bonds in halosilanes have never been observed to undergo similar oxidative addition reactions though some attempts have been made.[2,4,5] This is, however, peculiar, because bond dissociation energies of Si–X bonds in Me_3SiX (76 or 57 kcal/mol for X = Br or I, respectively)[6] are comparable with that of C–Br or C–I in halobenzenes (71 or 61 kcal/mol, respectively)[7] which are capable of the oxidative addition. In addition, silicon-transi-

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