media and the observation of high-resolution ^{19}F NMR spectra of a chemisorbed compound.

We reasoned that if the oxide surface could be subdivided sufficiently, the resulting particles, when dispersed in a suitable fluid, would exhibit correlation times short enough to allow observation of NMR spectra of surface phase(s). This describes, in a limiting case, a colloid, and we have used as the oxide adsorbent colloidal 350 Å mean diameter silica particles in 2-ethoxyethanol (EEO).[5] The silica has a surface area of 150 M^2 gm^{-1} and is amorphous to electrons. The iron content, determined by emission spectrography, is 3 ppm. The adsorbate studied is palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$. This fluorinated organometallic compound is a strong Lewis acid and readily forms complexes with a wide variety of molecular and condensed phase donors.[6,7] For the purpose of preparation and study of surface compounds, it offers several advantages: (1) there is high Lewis acidity; (2) the molecule contains 12 fluorines per acidic metal site; (3) the ^{19}F chemical shifts are sensitive to chemical environment; (4) spin rotation and dipole–dipole relaxation in the CF_3 groups are expected to be efficient even when the molecule is bound to the surface of a particle.

The 94.1-MHz Fourier transform ^{19}F spectrum of a 1.3×10^{-2} M solution of $Pd(F_6acac)_2$ in the silica colloid exhibits a sharp peak at 73.32 ppm (w/2 1.8 Hz, relative area 1) whose position and width are the same as that of $Pd(F_6acac)_2$ in EEO. In addition, a broad peak at 75.4 ppm (w/2 21 ± 2 Hz, relative area 0.6) is observed in the colloid–EEO but not in pure solvent. Such an upfield shift is typical of Lewis base adducts of $Pd(F_6acac)_2$,[6] and we attribute this new resonance to a complex between $Pd(F_6acac)_2$ and basic site(s) on the surface of the colloidal particles. The observation of separate peaks for free and bound $Pd(F_6acac)_2$ indicates that the exchange between these two forms is not rapid on the NMR time scale. In this system, which has a kinematic viscosity of 5.50 cSt,[8] the ^{19}F spin–lattice relaxation time, T_1, of the fluorines in free $Pd(F_6acac)_2$ is 1.01 s and that of the surface-phase fluorine is 0.26 s. When the viscosity is reduced to 3.55 cSt by dilution with pure EEO, T_1 for the free and bound forms are 0.87 and 0.24 s, respectively.

If the T_1/T_2 ratio as described by Navon and Lanie[9] is used and it is assumed that an intramolecular dipole–dipole relaxation mechanism is dominant, τ_C for the fluorines in the $Pd(F_6acac)_2$ surface compound was calculated to be 4×10^{-9} s. This is much shorter than the 3×10^{-5} s overall correlation time for tumbling of a particle of 175-Å radius[11] and is indicative of fast reorientation of the axially symmetrical CF_3 groups. This provides a relaxation mechanism which is not dependent on motion of the small particles bearing the surface compound. The observed magnitude of T_1 is reasonable for a trifluoromethyl group in a surface phase bound for times longer than $(2\pi\Delta\nu)^{-1}$ but in which internal rotation is almost free, and so we defer consideration of more complex models of anisotropic rotation. Minimal importance of particle motion as a determinant of T_1 is also indicated by the absence of a dependence of T_1 on the viscosity of the medium.

T_2 and intrinsic line width are related by $T_2 = \pi\nu_{1/2}$ where $\nu_{1/2}$ is the full width (in Hz) at half-height of a peak.[10] The line width of the bound $Pd(F_6acac)_2$ peak in the spectra obtained at 188.2 MHz is 58 Hz. Direct measurement of T_2 (Carr–Purcell Meiboom–Gill pulse sequence) gave T_2 for this peak as 0.026 ms; so the intrinsic line width is 12 Hz. Therefore, the linewideth of the bound $Pd(F_6acac)_2$ may reflect chemical heterogeneity of the silica surface and residual intramolecular broadening. Adsorption of $Pd(F_6acac)_2$ to a colloidal particle is analogous to the absorption of a fluorine-labeled amino acid on a protein. Thus, T_1 and T_2 of the surface phase are comparable to T_1 and T_2 of the CF_3 group in *N*-trifluoroacetyltryptophan-*d* bound to α-chymotrypsin.[11a-c]

It seemed plausible that if NMR spectra can easily be obtained from a surface compound on a colloidal support, it ought to be possible to obtain the spectrum of the colloid itself. The ^{29}Si NMR spectrum (39.7 MHz, 10K transients) of the silica colloid consists of a broad (w/2 650 Hz) resonance 105 ppm upfield of external $(CH_3)_4Si$. In this experiment, we are observing silicon at or near the surface because T_1 for ^{29}Si buried in the colloidal particles should be very long. For example, T_1 is at least 12 h for dipole–dipole relaxation in a 175-Å particle, assuming only rotational motion.[12] The only ^{29}Si nuclei observable in the NMR are probably those on the outside of the sphere which can be relaxed by protons from the solvent, or which participate in chemical reactions, such as exchange of silanol protons or equilibrium solvolysis of siloxane linkages.

We believe that, in suitable cases, colloids will constitute useful models for bulk oxides and that nuclear magnetic resonance will be a useful tool for the study of surfaces of colloidal materials and chemical compounds formed on them.

Acknowledgment. We are grateful to S. Shiffman and P. F. Cullen for the electron miscroscopy and viscosity measurements, A. Cirillo for helpful discussion, and W. C. Jankowski of Varian Associates for the 188-MHz spin–spin relaxation time measurements.

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Structures of BBM-928 A, B, and C. Novel Antitumor Antibiotics from *Actinomadura luzonensis*

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In the course of our antibiotic screening program, a complex of potent antitumor agents designated BBM-928 was isolated from the culture broth of *Actinomadura luzonensis* nov. sp.[1,2] BBM-928 resembles the quinoxaline group of antibiotics, which include actinoleukin,[3] echinomycin,[4] and quinomycins,[5] in that they are all cyclic depsipeptides having two chromophoric units in the structure. However, BBM-928 differs from the latter group in the chromophore structure and by virtue of the lack of a sulfur-containing cross-linkage. In the present communication we report the structures of BBM-928 A (**1a**), B (**1b**), and C (**1c**) (Figure 1).

BBM-928 A (**1a**) ($C_{64}H_{78}N_{14}O_{24}$, mp 246–248 °C, $[\alpha]^{25}_D$ −27°)[6] and BBM-928 C (**1c**) ($C_{60}H_{74}N_{14}O_{22}$, mp 244–248 °C, $[\alpha]^{25}_D$ −91°) were isolated as major components, while BBM-928

(1) The fermentation, isolation, characterization, and antitumor activity of BBM-928 have been studied by Ohkuma et al. [H. Ohkuma, F. Sakai, Y. Nishiyama, M. Ohbayashi, H. Imanishi, M. Konishi, T. Miyaki, H. Koshiyama, and H. Kawaguchi, *J. Antibiot.*, in press].
(2) The taxonomy of the BBM-928 producing organism *Actinomadura luzonensis* ATCC 31491 has been studied by Tomita et al. (K. Tomita, Y. Hoshino, T. Sasahira, and H. Kawaguchi, *J. Antibiot.*, in press).
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(6) The formula indicated in text was in accord with microanalyses and mass spectrum. Field-desorption mass spectrum of **1a**: *m/e* 1427 ($M^+ + 1$). Melting points are not corrected and $[\alpha]_D$'s were determined in 1% $CHCl_3$ solutions unless otherwise stated.

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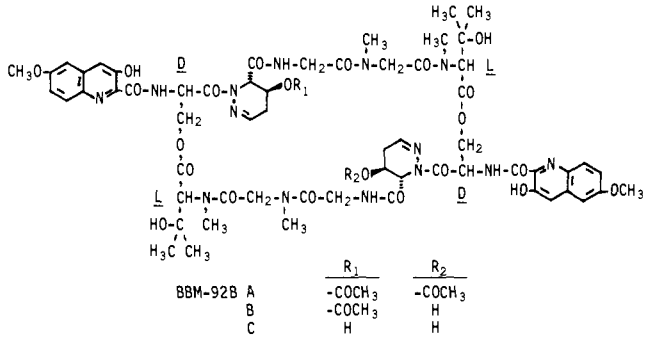
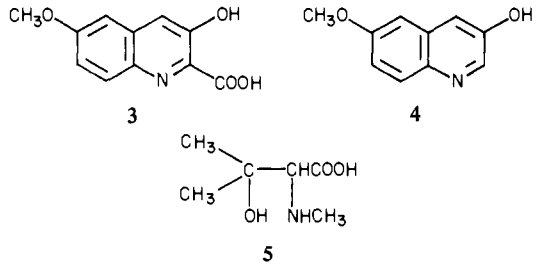


	R_1	R_2
BBM-928 A	$-COCH_3$	$-COCH_3$
B	$-COCH_3$	H
C	H	H

Figure 1. Structures of BBM-928 A, B, and C.

B (**1b**) ($C_{62}H_{76}N_{14}O_{23}$, mp 214–217 °C, $[\alpha]^{25}_D$ −74°) was produced in smaller amount. The UV [λ_{max} (EtOH) 235, 264, and 345 nm; (EtOH–0.05 N NaOH) 230, 256, 330, and 383 nm] and IR [(KBr) 3500–3300, 1745, 1650, and 1230 cm^{-1}] spectra of **1a** are similar to those of **1b** and **1c**. The ^{13}C NMR of **1a** demonstrated a total of 32 well-defined signals, and its ^1H NMR indicated the presence of a multiple of nearly 40 protons, suggesting that **1a** consisted of two equivalent halves assuming a sterically symmetric conformation. The ^{13}C and ^1H NMR spectra of **1c** also indicated a symmetric structure, whereas those of **1b** (46 carbon signals) suggested its asymmetric conformation. Acetylation (Ac_2O–pyridine, 25 °C) of **1a**, **1b**, and **1c** afforded an identical product, **2** ($C_{68}H_{82}N_{14}O_{26}$), which, together with the analytical and spectroscopic data, indicated that **1a** and **1b** were diacetyl and monoacetyl congeners of **1c**, respectively.[7]

Complete hydrolysis (6 N HCl, 100 °C, 18 h) of **1c** afforded a UV-absorbing, lipophilic compound (**3**) ($C_{11}H_9NO_4$, mp 223–225 °C, positive $FeCl_3$ test) along with four amino acids. The



3 **4**

5

UV spectrum of **3** (λ_{max} (MeOH) 225, 256, and 350 nm) was similar to that of **1c**. The ^{13}C NMR (D_2O–NaOD) δ of **3** exhibited one OCH_3 [δ 56.3 (q)], one COOH [δ 177.6 (s)], and nine aromatic carbons [δ 104.7 (d), 116.2 (d), 118.7 (d), 129.0 (d), 133.2 (s), 134.5 (s), 155.4 (s), 157.5 (s), and 158.3 (s)], and its ^1H NMR (D_2O–NaOD, J in Hz) included one OCH_3 [δ 3.80 (s)] and four aromatic protons [δ 6.89 (d–d, J = 10.5 and 1.9), 6.91 (d, J = 1.9), 7.11 (s), and 7.66 (d, J = 10.5)], revealing that **3** has a quinoline or isoquinoline structure substituted with OH, OCH_3, and COOH groups. The chemical shift of the aromatic protons indicated that they are not located vicinal to nitrogen. Irradiation at 3.80 ppm (OCH_3) produced a nuclear Overhauser enhancement of two protons at 6.89 (18%) and 6.91 (22%) ppm, showing that the methoxy group is located at the 6 position and the 5, 7 and 8 positions are unsubstituted. At 240 °C **3** was decarboxylated to afford **4** ($C_{10}H_9NO_2$, mp 215–216 °C) whose ^1H NMR showed a newly generated low-field proton resonating in meta coupling [δ 8.36 (J = 2.5 Hz)]. Thus **3** is 3-hydroxy-6-methoxyquinaldic acid and **4** is 6-methoxy-3-quinolinol.

The four amino acids isolated were glycine, sarcosine, D-serine, and a new amino acid (**5**) [$C_6H_{13}NO_3$, mp 260–261 °C dec, $[\alpha]^{26}_D$ −3° (c 4.90, H_2O), pK_a' = 2.3 and 9.5]. It was determined that **5** was L-β-hydroxy-*N*-methylvaline by ^1H HMR [(D_2O) δ 1.21 (3 H, s), 1.44 (3 H, s), 2.66 (3 H, s), and 3.37 (1 H, s)], CD $[\theta]_{208}$ +3503 (peak)[(c 0.05, 0.5 N HCl)] and ORD $[[\Phi]_{226.5}$ +2420 (peak)(c 0.09, 0.5 N HCl)].

(7) Mild alkaline hydrolysis (0.02 N Na_2CO_3, 30 min) of **2** yielded **1a** which was converted to **1c** by treatment in stronger alkaline solution (0.1 N NaOH, 3 min).

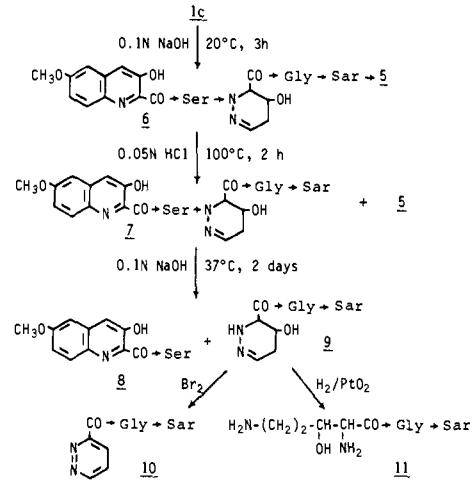
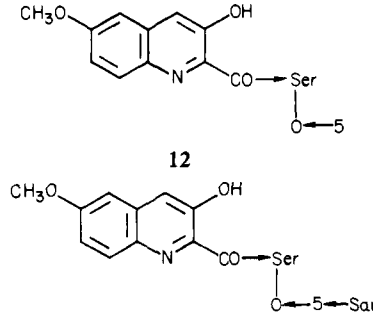


Figure 2. Hydrolysis of BBM-928 C (**1c**).

Upon mild alkaline hydrolysis (0.1 N NaOH, 25 °C, 3 h), **1c** afforded a linear peptide, **6** ($C_{30}H_{39}N_7O_{12}$),[8] having UV and IR spectra similar to those of **1c** except for the lack of ester carbonyl and the presence of carboxylate band in the IR spectra of **6**. Complete acid hydrolysis of **6** afforded the same degradation products (**3**, **5**, Gly, Sar, D-Ser) as those obtained from **1c**. These structural constituents accounted for 25 carbons of **6**, leaving a C_5-unit residue ($C_5H_6N_2O_2$, assigned by subtraction) as an unidentified moiety. Mild acid hydrolysis (0.05 N HCl, 100 °C, 2 h) of **6** cleaved its C-terminal amino acid **5** to give **7** which, upon mild alkaline treatment (0.1 N NaOH, 37 °C, 2 days), afforded **8** ($C_{14}H_{14}N_2O_6$, **3** → D-Ser) and **9** ($C_{10}H_{16}N_4O_5$). The ^{13}C NMR of **9** contained five signals [δ 173.4 (s), 140.7 (d), 61.5 (d), 61.2 (d), and 30.2 (t)] for the C_5-unit moiety in addition to five carbons assignable to Gly and Sar (C terminal). Bromine oxidation of **9** afforded an aromatized compound, **10** ($C_{10}H_{12}N_4O_4$, UV $\lambda_{max}^{H_2O}$ 240 and 300 nm), which yielded Gly, Sar, and pyridazine-3-carboxylic acid[9] by acid hydrolysis. Catalytic hydrogenation of **9** afforded a basic peptide **11**, which, upon acid hydrolysis, liberated L-*erythro*-β-hydroxyornithine.[10] Thus, the unidentified C_5 unit is determined to be *trans*-(3*S*,4*S*)-4-hydroxy-2,3,4,5-tetrahydropyridazine-3-carboxylic acid (Figure 2). Under a controlled acid hydrolytic condition (6 N HCl, 100 °C, 3 h), **1c** yielded depsipeptide fragments **12** ($C_{20}H_{25}N_3O_8$) and **13** (C_{23}-



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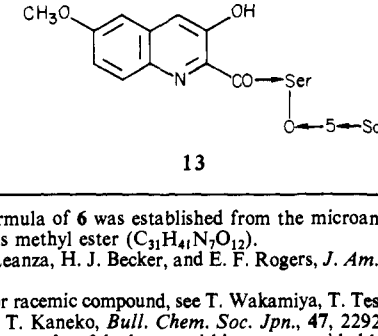

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(8) The formula of **6** was established from the microanalyses and mass spectrum of its methyl ester ($C_{31}H_{41}N_7O_{12}$).

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(11) A total of 37 (**1c**) and 39 (**1a**) well-defined proton signals indicated the symmetrical conformations of both compounds.

$H_{30}N_4O_9$), the IR of both compounds having an ester carbonyl band (1745 cm^{-1}). Upon mild alkaline hydrolysis, **12** yielded **8** and **5**, while **13** afforded **8**, **5**, and Sar.

In the 360-MHz ^1H NMR studies,[11] the OH-bearing methine proton of the tetrahydropyridazine moiety of **1c** appeared at 4.25 ppm while that of **1a** appeared at 5.52 ppm, indicating the location of the acetyl group on the hydroxy group of the tetrahydropyridazine moiety. Thus the structures shown are assigned to BBM-928 A, B, and C.

Acknowledgment. We are grateful to Professor T. Shiba of Osaka University, Osaka, for the sample of β-hydroxyornithine and related information, Professor M. Ohashi of the University of Electro-communication, Tokyo, for mass spectrometric analysis and valuable discussions, and Dr. T. W. Doyle and Dr. J. A. Matson of Bristol Laboratories, Syracuse, NY, for field desorption mass spectrum and 360-MHz ^1H NMR.

Supplementary Material Available: ^1H NMR, ^{13}C NMR, TLC, and amino acid analysis data of all the compounds (6 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of BBM-928 A, a Novel Antitumor Antibiotic from *Actinomadura luzonensis*

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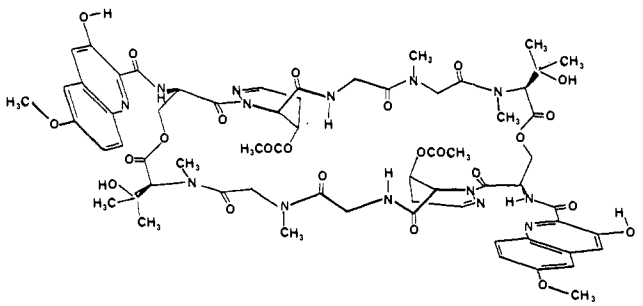
A series of potent antitumor antibiotics designated BBM-928 A, B, and C were recently isolated from *Actinomadura luzonensis*.[1,2] These compounds resembled the quinoxaline antibiotics in that they were cyclic depsipeptides containing two heteroaromatic chromophores[3-5] but differed in that they lacked the sulfur-containing bridge. Chemical[6] and crystallographic studies have now defined the structure of BBM-928 A to be that shown as **1**, and this note reports the crystallographic analysis. This is



the first crystal-structure determination of a naturally occurring[7] cyclic depsipeptide antibiotic which appears to be a bisintercalator.[8]

Early experiments indicated that BBM-928 A crystallized from toluene-containing solutions with toluenes of crystallization. We hoped to exploit this finding by replacing toluene with bromobenzene and thus facilitate the X-ray analysis by use of the heavy-atom technique. Large single crystals of BBM-928 A containing bromobenzene could be grown from CH_2Cl_2–C_6H_5Br solvent mixtures. These crystals rapidly decomposed when removed from the mother liquor, and all manipulations and data collection had to be done with the crystal surrounded by the mother liquor. Preliminary X-ray photographs revealed monoclinic symmetry, and accurate cell constants of a = 19.881 (5), b = 12.303 (2), and c = 22.919 (3) Å and β = 100.52 (2)° were obtained from a least-squares fitting of diffractometer-measured 2θ values. The space group $P2_1$ was indicated by systematic extinctions, and rough density calculations indicated that the asymmetric unit was one molecule of BBM-928 A ($C_{64}H_{78}N_{14}O_{24}$) and three to five molecules of bromobenzene.[9] All unique diffraction maxima with $2\theta \leq 100°$, nominal resolution 1 Å, were collected by using a variable-speed ω scan and graphite-monochromated Cu Kα (1.54178 Å) radiation. Of the 5995 reflections recorded, 4583 (76%) were considered observed after correction for Lorentz, polarization, and background effects ($|F_o| \geq 3\sigma(F_o)$). No corrections were made for absorption, and no decomposition was noted.

The structure was solved by a combination of Patterson and tangent formula recycling techniques.[10-12] An initial phasing model of three independent bromines was obtained from deconvolution of a sharpened ($|E_h|^2 - 1$) Patterson synthesis. Tangent formula recycling led to a chemically sensible fragment of 22 connected atoms, including what appeared to be a quinaldamide system. Further tangent formula recycling and various Fourier syntheses based on these coordinates were attempted but led to no new information. After heavily damped refinement of the fragment positions in an unconstrained block-diagonal least-squares program and tangent formula recycling in which the initial phases were not allowed to vary lest they return to the purely heavy atom phases,[12] an E synthesis clearly showed both the input fragment and a chemically identical portion. These two fragments were related by a noncrystallographic twofold axis which was suggested by our earlier analysis of the Patterson. After inclusion of both fragments in the phasing model, the majority of the remaining nonhydrogen atoms were revealed in successive cycles of tangent formula phase extension with invariant input phases and refinement. On the last cycle of tangent formula recycling, which used all E's > 1.2 (1378), 101 of the 102 atoms in BBM-928 A were clearly visible. The BBM-928 A structure was completed by a Fourier synthesis following partial least-squares refinement. We still do not have a completely satisfactory picture of the partially disordered and complex array of solvent molecules. Our current model includes 4 relatively well-behaved bromobenzene molecules and 11 other solvent atoms in the asymmetric unit. The standard crystallographic residual has converged to 0.15 for this 141 nonhydrogen atom model with anisotropic bromines, and we are attempting to improve this. The absolute configuration il-

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(10) All crystallographic calculations were done on a PRIME 400 computer operated by the Materials Science Center and the Department of Chemistry, Cornell University. The principal programs used were REDUCE and UNIQUE, data reduction programs: Leonowicz, M. E., Cornell University, 1978; BLS78A, anisotropic block-diagonal least-squares refinement: Hirotsu, K. and Arnold, E., Cornell University, 1980; XRAY76, the X-ray system of crystallographic programs: Stewart, J. M., Ed., University of Maryland, Technical Report TR-445, March 1976; ORTEP crystallographic illustration program: Johnson, C. K., Oak Ridge, ORNL-3794; MULTAN-78 (locally modified): Main, P. et al. "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", University of York, England. For literature description of MULTAN see: Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. B* **1970**, *B26*, 274–285. Woolfson, M. M. *Acta Crystallogr., Sect. A* **1977**, *A33*, 219–225.
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