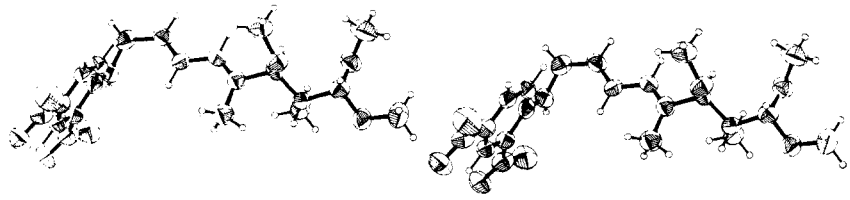
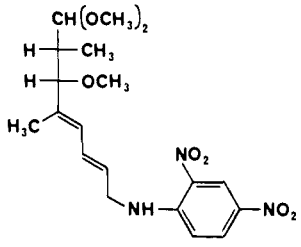


Figure 1. Stereodrawing of conformation of **4** in the crystal.



4

Crystals of **4** are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 7.945$ (5), $b = 9.026$ (8), $c = 29.22$ (2) Å, and $d_{calcd} = 1.297$ g cm^{-3} for $Z = 4$. The structure was elucidated by a multiple solution procedure.[2] Hydrogen atoms were located from a difference Fourier calculated after preliminary refinement of the structure. The final refinement was carried out by full-matrix least squares with anisotropic thermal parameters for all atoms except hydrogen atoms; the hydrogen atoms were held fixed at their calculated positions. The final discrepancy index, R, was 5.9%. A stereodrawing of the conformation of **4** in the crystal is shown in Figure 1.

Although the absolute stereochemistry of **4** could not be deduced from Roentgen data, gross structure, threo configuration and all-trans isomerism, was established.

The partial structure of **1** derived by degradation reactions is shown in Scheme I. In addition to fragments **2** and **3**, periodate oxidation of **1** liberated 2 mol of formic acid from the central $C_4H_6O_3$ moiety identified as a 2,5-disubstituted 3,4-dihyroxyfuran ring based on the following evidence.

N-Protected derivatives of **1** and **1d** readily formed di-*O*-acetyl and *O*-isopropylidene compounds and benzeneboronic acid esters; two of the unassigned oxygen atoms in **1** (Scheme I) are thus most likely vicinal, nontertiary hydroxyl groups. The 100-MHz nmr spectra of **1b** show, in addition to peaks due to the isopropylidene group and peaks indicative of the **2** and **3** moieties, signals for four hydrogen atoms bonded to carbon as follows: $\delta_{TMS}^{CDCl_3}$ 3.56 (m, H-5′, partly hidden by NCH_3), 3.98 (dd, H-2′, $J = 7$ and 4 Hz), 4.68 (m, H-3′ and H-4′). The corresponding signals were also found in spectra of **1a**: $\delta_{TMS}^{CDCl_3}$ 3.53 (dd, H-5′, $J_{1,5'} = 7$ and $J_{4',5'} = 4$ Hz), 4.17 (H-2′, masked by NCH_2), and 4.36 (m, H-3′ and H-4′). These spectral assignments were based on comparisons with those of the di-*O*-acetyl compound **1c**: $\delta_{TMS}^{CDCl_3}$ 2.19 (ddq, H-1, $J_{1,2} = 10$ and $J_{1,5'} = J_{1,Me} = 7$ Hz; irradiation at this field collapsed the H-2 doublet at δ 3.21 to a singlet, and the H-5′ dd at δ 3.92 to a doublet with $J_{4,'5'} = 4$ Hz), 4.59 (t, H-2′, $J_{2',3'} = J_{2'7''} = 7$ Hz; irradiation at this field collapsed the H-3′ dd at δ 5.42 to a doublet with $J_{3',4'} = 5$ Hz and the H-7′′ dd at δ 5.85 to a doublet with $J_{6'',7''} = 15$ Hz), 5.52 (dd, H-4′, $J_{3',4'} = 5$ and $J_{4'5'} = 4$ Hz).

The periodate oxidation products of **1** (Scheme I) are explained by inferring glycol cleavage of the 2,5-disubstituted 3,4-dihydroxytetrahydrofuran ring to afford a dialdehyde with subsequent enolization and oxidative cleavage of the 2′,3′ bond analogous to the periodate oxidation of 3-hydroxy-2-methoxy-2-cyclopentenone.[3] This would produce formic acid and an ester which, upon hydrolysis, yields the corresponding trienoic acid **2** and an α-hydroxyaldehyde, further degradable to formic acid and octadienal **3**. In analogy to 2,3-dihydroxy-2-cyclopentenone and related compounds,[3] oxidation of **1** proceeded with the transient appearance of free iodine.

Therefore, goldinamine (**1e**) is identified as 4-hydroxy-3-{2-methyl-1-oxo-7-[3,4-dihydroxy-5-(*threo*-7-amino-2-methoxy-1,3-dimethyl-3(*trans*),5(*trans*)-heptadienyl)-tetrahydro-2-furyl]-2(*trans*),4(*trans*),6(*trans*)-heptatrienyl}-1-methyl-2(1*H*)-pyridone.

Acknowledgment. We are grateful to Professor G. Büchi for helpful discussions.

(2) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).

(3) G. Hesse and K. Mix, *Chem. Ber.*, **92**, 2427 (1959).

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Antibiotic X-5108. V. Structures of Antibiotic X-5108 and Mocimycin[1,2]

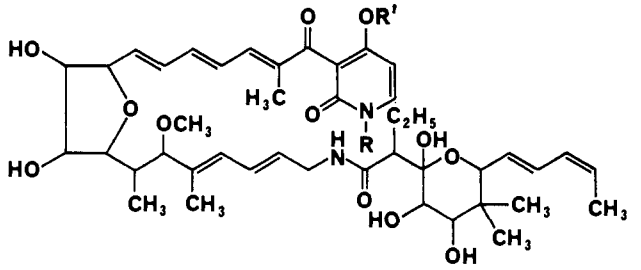
Sir:

In previous communications[1,3] we reported the degradation of **2b** yielding goldinono-1,4-lactone-3,7-hemiketal and goldinamine 4-bromobenzyl ether. These degradation products account for all atoms of the antibiotic molecule. The structure of antibiotic X-5108 is represented by **2**; the primary amino group of goldinamine and the carboxyl group of goldinonic acid 3,7-hemiketal[3] form an amide bond linking the two moieties. This assignment is based on the absence of amino, carboxyl, and γ-lactone groups in the intact antibiotic and the formation of two fragments with amine[1] and γ-lactone[3] functions upon mild acid treatment of **2a** and **2b**.

(1) Paper IV in this series: H. Maehr, M. Leach, T. H. Williams, W. Benz, J. F. Blount, and A. Stempel, *J. Amer. Chem. Soc.*, **95**, 8448 (1973).

(2) The structure determination of antibiotic X-5108 was presented at the Gordon Research Conference on Natural Products, New Hampton, N. H., July 30–Aug 3, 1973.

(3) H. Maehr, J. F. Blount, R. H. Evans, Jr., M. Leach, J. W. Westley, T. H. Williams, A. Stempel, and G. Büchi, *Helv. Chim. Acta*, **55**, 3051 (1972).



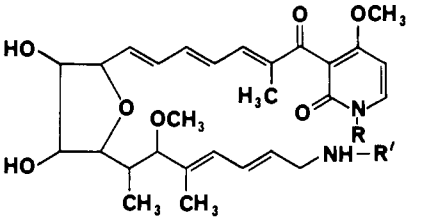
1, R = R′ = H (mocimycin)
1a, R = H; R′ = CH_3 (mocimycin methyl ether)
2, R = CH_3; R′ = H (antibiotic X-5108)
2a, R = R′ = CH_3 (antibiotic X-5108 methyl ether)
2b, R = CH_3; R′ = 4-BrBzl (antibiotic X-5108 4-bromobenzyl ether)

Recently, two new antibiotics, mocimycin (Delvomycin)[4-6] and kirromycin,[7,8] were described whose biological and physicochemical properties suggested similarity to antibiotic X-5108. Mocimycin and kirromycin could be clearly differentiated from antibiotic X-5108 by various tlc systems but not from each other. The nmr spectra of the three antibiotics were similar, but the spectrum of antibiotic X-5108 was distinguished by the presence of a signal for an *N*-methyl group which was absent in the spectra of both mocimycin[6] and kirromycin, suggesting close structural similarity or identity of mocimycin and kirromycin. Mocimycin was identified as des-*N*-methyl antibiotic X-5108 on the basis of the following observations.

Mocimycin sodium salt, $\delta_{TMS}^{CD_3OH}$ 3.17 (s, CH_3OCH), treated with methyl iodide, afforded a mixture of amorphous mono- and dimethylated products **1a** ([α]D −94° (*c* 0.9, ethanol), λ_{max} (ϵ) 207 (51,000), 231 (58,850), ~290 infl (16,050), and 334 nm (38,750) in 0.1 *N* HCl; 207 (51,200), 232 (60,100), ~290 infl (16,050) and 334–335 nm (39,200) at pH 7; 232 (62,900), ~290 infl (16,500), and 329 nm (40,500) in 0.1 *N* KOH; $\delta_{TMS}^{CD_3OD}$ 3.13 (s, CH_3OCH) and 3.83 (s, CH_3OC$\lessgtr$)) and **2a**, respectively ([α]D −93° (*c* 0.9, ethanol), λ_{max} (ϵ) 210–211 (53,200), 232–233 (58,500), ~297–298 infl (18,600), and 336 nm (40,000) in 0.1 *N* HCl; 210–211 (54,500), 232–233 (59,300), ~298–299 infl (18,600), and 336 nm (39,900) at pH 7; 232–233 (58,850), ~297–298 infl (18,600), and 336 nm (40,000) in 0.1 *N* KOH; $\delta_{TMS}^{CD_3OD}$ 3.13 (s, CH_3OCH), 3.49 (s, CH_3N), and 3.79 (s, CH_3OC$\lessgtr$)).

Continued methylation of **1a** with methyl iodide or dimethyl sulfate yielded **2a**, also obtained directly as a major product by reaction of mocimycin sodium salt with dimethyl sulfate, identical in all respects with **2a** derived from antibiotic X-5108. Further, mocimycin derivatives **1a** and **2a** were treated with acetic acid, each yielding goldinono-1,4-lactone-3,7-hemiketal,[3] as well as amorphous **3** acetate ([α]D −53.5° (*c* 0.6, 90% ethanol); λ_{max} (ϵ) 236–237 (35,300), ~290 infl (14,700) and 330–331 nm (40,000) in 0.1 *N* HCl and 237 (33,200), ~290 infl (15,200), and 334–336 nm (39,650) in 0.1 *N* KOH and at pH 7; $\delta_{TMS}^{CD_3OD}$ 3.17 (s, CH_3OCH) and 3.84 (s, CH_3OC$\lessgtr$)) and amorphous **4** acetate, respectively ([α]D −49° (*c* 1.0, ethanol), λ_{max} (ϵ) 210 (43,200), 237–238 (33,750), ~298 infl (19,200), and 335–336 nm (39,400) in 0.1 *N* HCl and 210 (43,200), 237–238 (33,000), ~298 infl (18,600), and 335–336 nm (38,660) at pH 7; 237–238 (34,000), ~298 infl (18,600), and 335–336 nm (38,900) in 0.1 *N* KOH; $\delta_{TMS}^{CDCl_3}$ 3.17 (s, CH_3OCH), 3.50 (s, CH_3N), and 3.77 (s, CH_3OC$\lessgtr$)).

Goldinamine methyl ether (**4**) was converted to **4a**, whose composition of $C_{31}H_{39}F_3N_2O_8$ was confirmed by mass spectrometry. Similarly, acylation of **3** gave **3a**, $C_{30}H_{37}F_3N_2O_8$, with nmr and mass spectra consistent with the proposed structure.



3, R = R′ = H (des-*N*-methyl goldinamine methyl ether)
4, R = CH_3; R′ = H (goldinamine methyl ether)
3a, R = H; R′ = $COCF_3$
4a, R = CH_3; R′ = $COCF_3$

Compounds **4** and **4a**, derived from mocimycin, proved to be identical in all respects, including a comparison of CD spectra, with goldinamine methyl ether (**4**) and its *N*-trifluoroacetyl derivative **4a** prepared from antibiotic X-5108. In addition, periodate oxidations of **4**, derived from both mocimycin and antibiotic X-5108, afforded two products each, *threo*-8-amino-3-methoxy-2,4-dimethyl-4(*trans*),6(*trans*)-octadienal[1] with undetermined but identical absolute stereochemistry in both preparations as suggested by identical CD spectra of the *N*-acetyl derivatives, and 8-[4-methoxy-1,-2-dihydro-1-methyl-2-oxo-3-pyridyl]-7-methyl-8-oxo-2(*trans*),4(*trans*),6(*trans*)-octatrienoic acid, mp 220–223° dec, exhibiting uv and nmr spectra similar to its 4-bromobenzyloxy analog.[9,10]

(4) R. Beukers, J. G. Oostendorp, and C. J. van Eeken, Abstracts, Second World Congress on Animal Feeding, Madrid, Oct 23–28, 1972, p 127.
(5) E. J. van Weerden, P. van der Wal, and J. B. Schutte, ref 4, p 133.
(6) C. Vos and P. E. J. Verwiel, *Tetrahedron Lett.*, 2823 (1973).
(7) H. Wolf and H. Zähner, *Arch. Mikrobiol.*, **83**, 147 (1972).
(8) We are indebted to Professor Zähner for a 50-mg sample of crude kirromycin. This sample was purified prior to analysis.
(9) H. Maehr, J. F. Blount, M. Leach, and A. Stempel, *Helv. Chim. Acta*, **55**, 3054 (1972).
(10) NOTE ADDED IN PROOF. The designation "goldinodox" is being proposed as a nonproprietary name for antibiotic X-5108.

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Fragmentation Reaction of Ylides. III. A New Synthetic Route for Exo Methylenes

Sir:

N-Alkylaziridines react with dihalocarbenes to give the corresponding olefins by breaking the two C–N bonds in the aziridine ring. The reaction is highly stereospecific and the relative configuration of substituent groups is retained completely in the olefins.[1] We have previously suggested[1a] that the reaction gives aziridinium ylide as the initial intermediate, which then decomposes to the olefin by a cheletropic reaction.[2]

(1) (a) Y. Hata and M. Watanabe, *Tetrahedron Lett.*, 3827 (1972); (b) Y. Hata and M. Watanabe, *ibid.*, 4659 (1972).
(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., and London, 1970, p 152.