Table IV. MMP Results for Dicyano Diene 5 and Pentadienyl Radical 32 Conformers

conformer	steric energy, kcal/mol	dihedral C1,C2,C3,C4, deg	dihedral C2,C3,C4,C5, deg
	Dicyano Diene **5**		
"half-U" **5′**	48.43	32.3	151.6
"half-U" **5″**	48.39	148.6	32.9
"W"	49.77	157.1	138.0
"U"	51.12	44.6	47.4
	Pentadienyl Radical **32**		
"half-U" **32′**	108.48	0.0	180.0
"half-U" **32″**	106.64	180.0	0.0

Table V. MMP Steric Energies of 1,3-Heptadiene 26 Conformers

conformer	steric energy, kcal/mol	dihedral C3,C4,C5,Ci,[a] deg	dihedral C1,C2,C3,C4, deg
26′[b]	38.20	−58.9	117.5
26′[c]	40.71	−90.0	102.7
26′[c,d]	51.13	−90.0	180.0
26″[b]	38.99	57.6	103.1
26″[c]	42.20	33.5	119.3
26″[c,d]	56.23	36.2	180.0

[a] Ci = ipso carbon of migrating phenyl. [b] Fully optimized. [c] p orbitals at C4 and ipso carbon of migrating phenyl fixed coplanar. [d] Butadienyl group (C1–C4) fixed planar.

SHELXS86[37] or, in the case of dicyanovinylcyclopropane **14**, MULTAN80.[38] Hydrogen atoms were located by difference Fourier synthesis, and full-matrix least-squares refinement was carried out using anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The results of the structure determinations are summarized in Table III, and final parameters are available as supplementary material.

Molecular Mechanics Calculations. All molecular mechanics calculations employed Gajewski's MMP program.[18b] For the reactant 1,1-dicyano-5,5-diphenyl-3,3-diisopropyl-1,4-pentadiene (**5**), minima were found which correspond to the "W", "U", and the two "half-U" conformations of the pentadiene skeleton. The MMP steric energy for each of these is given in Table IV with the C1,C2,C3,C4 and C5,C4,C3,C2 dihedral angles for each to indicate the orientations of the two vinyl groups. Also listed in Table IV are the steric energies and corresponding dihedral angles for the conformers **32′** and **32″** of the 1,1-dicyano-5,5-diphenyl-3-isopropylpentadienyl radical. In these latter two calculations, all atoms of the π-system were constrained to be coplanar. In calculations on radicals and diradicals where torsional or bending constants were not available, constants approximating them were used.

The MMP calculations on *cis*-1,1-dicyano-5,5-diphenyl-3-isopropyl-6-methyl-1,3-heptadiene **26** showed minima at C3,C4,C5,C6 dihedral angles of 58 and 177°, with the latter preferred by 0.8 kcal/mol. When the p orbitals involved in phenyl–vinyl bridging (ipso on the migrating phenyl and at C4) were made coplanar, this energy difference increased to 1.5 kcal/mol. A still larger energy difference (5.1 kcal/mol) resulted when the butadienyl moiety (C1–C4) was constrained to be in a planar s-trans conformation. In each case, the conformer corresponding to **26′** was favored over that corresponding to **26″**. These results are summarized in Table V.

Calculations on the cyclopropyldicarbinyl diradicals corresponding to structures **46a** and **46b** treated these species as cyclopropanes with the odd-electron centers (the para carbon of the bridging phenyl and the dicyanovinyl-substituted carbinyl carbon) represented by sp^2 carbons. The migrating phenyl was constrained to be planar, and the rotational orientation used for the bond between the three-ring and this carbinyl carbon was that which allows maximum overlap of the carbinyl p orbital with the two adjacent "cyclopropane" bonds (note eq 10). The MMP steric energies calculated for diradicals **46a** and **46b** were 63.43 and 70.24 kcal/mol, respectively.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Supplementary Material Available: Tables of direct quantum yield results for **5**, **19a**, and **26** in acetonitrile and sensitized quantum yield results of **5** in acetonitrile and benzene; experimental data for the photomixtures obtained from direct and sensitized photolyses of **7**; ORTEP drawings of **14**, **16**, **17**, and **26**; tables of positional parameters, interatomic distances, bond angles, anisotropic temperature factors, and isotropic temperature factors for **14**, **16**, **17**, and **26** (22 pages). Ordering information is given on any current masthead page.

(37) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189.
(38) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect A* **1971**, *27*, 368–376.

Microbial Products. 9. Roxaticin, a New Oxo Pentaene Antibiotic

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Roxaticin, produced by an unidentified streptomycete, has been identified as [(13*S*,14*R*,16*R*,18*R*,20*R*,22*S*,24*R*,26*R*,29*S*,30*S*)-(*all-E*)]-14,16,18,20,22,24,26-heptahydroxy-13,29-dimethyl-30-(1-methylethyl)oxacyclotriaconta-3,5,7,9,11,27-hexaen-2-one (**1**). It is the first example of an oxo polyene whose structure was solved by Roentgen diffraction analysis of a crystalline derivative. Roxaticin and the mycotins are now the only oxo polyenes with known configurations. Based on the available results, the topography of most stereogenic centers of roflamycoin and the dermostatins can be proposed.

Known representatives of the oxo polyene macrolide antibiotics[1] include oxo pentaenes and oxo hexaenes. Mycoticins A (**2a**) and B (**2b**)[2] (flavofungins)[3] and roflamycoin (flavomycoin, **3**)[4,5] are those oxo pentaenes that

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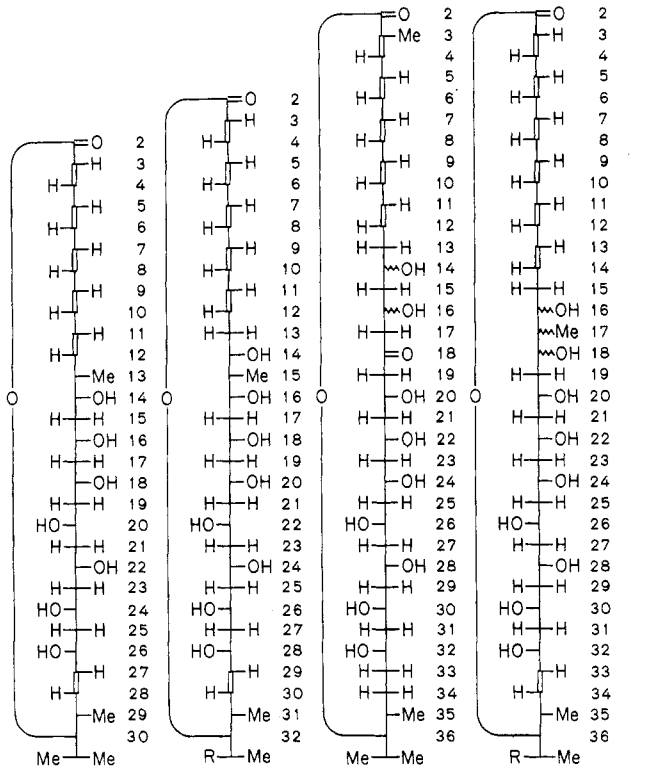
have been studied chemically. The dermostatins A (**4a**) and B (**4b**)[6] are the sole examples of oxo hexaenes and the two mycoticins are the only oxo polyenes with established configuration.

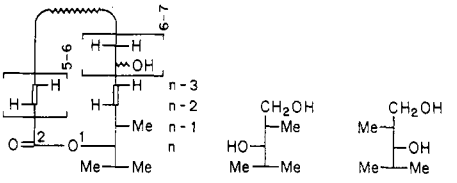


1 Roxaticin; **2a**: R=H (Mycoticin A); **2b**: R=Me (Mycoticin A); **3** Roflamycoin; **4a**: R=H (Dermostatin A); **4b**: R=Me (Dermostatin A)

We have now discovered oxo pentaenes' newest member, termed roxaticin (1). The elucidation of its complete stereochemistry is significant as it confirms mycoticin's stereochemical assignments based on spectroscopic and intricate synthetic model studies[7] and permits extrapolation of the topographic assignments to other oxo polyenes as shown in **3** and **4**.

Roxaticin is produced by an unidentified streptomycete, strain X-14994,[8] isolated from a soil sample collected in Escalante, UT. The compound was obtained in crystalline form as a member of several closely related, coproduced antibiotics.[9] Similar to other oxo polyenes, roxaticin is toxic and its antimicrobial activity is limited to fungi.

Oxo polyenes, whose general structural features are illustrated in **5**, are *n*-membered macrocyclic lactones containing a polyene segment in conjugation with the lactone carbonyl group, followed by a skipped polyol moiety whose last oxygenated position, identical with locant *n*-4, is further substituted by a (3*S*,4*S*)-4-hydroxy-3,5-dimethyl-1-hexenyl portion or a derivative thereof.[10] This moiety augments the lactone sequence from *n*-3 to *n* and its 4-hydroxy group provides the ring oxygen of the lactone. The isopropyl group at position *n* of the oxo polyenes may be replaced by isobutyl as in **2b** and **4b** and the double bond at *n*-3 may be reduced as in **3**. Roflamycoin is further distinguished as the polyol sector is interrupted by a carbonyl group. This functionality, usually masked as a hemiacetal, is common to many polyene antibiotics.



5 **6a** **6b**

Spectroscopic analysis of roxaticin revealed all characteristic oxo polyene features, including the oxo pentaene chromophore. The ^{1}H NMR spectrum showed 10 olefinic protons due to the *all-E* oxo pentaene moiety, as well as the two protons of the isolated alkene. The signals of two different allylic protons were shown to be coupled to a methyl doublet each and were thus consistent with H13 and H29 as formulated in **1**. Further, the spectrum supported the presence of an isopropyl moiety with diastereotopically differentiated methyl groups and revealed

(1) Omura, S.; Tanaka, H. In *Macrolide Antibiotics. Chemistry, Biology and Practice*; Omura, S., Ed.; Academic Press: New York, 1984; pp 351–404.

(2) (a) Burke, R. C.; Swartz, J. H.; Chapman, S. S.; Huang, W.-Y. *J. Invest. Dermatol.* **1954**, *23*, 163. (b) Wasserman, H. H.; Van Verth, J. E.; McCaustland, D. J.; Borowitz, I. J.; Kamber, B. *J. Am. Chem. Soc.* **1967**, *89*, 1535. (c) Schreiber, S. L.; Goulet, M. T. *Tetrahedron Lett.* **1987**, *28*, 6001. (d) Schreiber, S. L.; Goulet, M. T.; Sammakia, T. *Tetrahedron Lett.* **1987**, *28*, 6005. (e) Schreiber, S. L.; Goulet, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 8120.

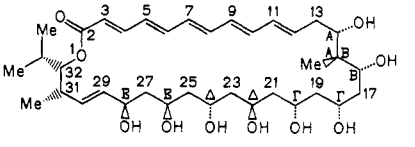
(3) Bognar, R.; Markleit, S.; Zsupan, K.; Brown, B. O.; Lockley, W. J. S.; Weedon, B. C. L. *J. Chem. Soc.* **1972**, 1848.

(4) (a) Schlegel, R.; Thrum, H.; Zielinski, J.; Borowski, E. *J. Antibiot.* **1981**, *34*, 122. (b) Lipshutz, B. H.; Barton, J. C. *J. Org. Chem.* **1987**, *53*, 4495. (c) Lipshutz, B. H.; Moretti, R.; Crow, R. *Tetrahedron Lett.* **1989**, *30*, 15–18.

(5) To permit the display of alkene geometry in the Fischer convention we are using an extended notation, yet to be published in detail, whereby the alkene double bond is placed into the Fischer plane so that the substituents are situated above and below the Fischer plane. The Fischer-chain member preceding the alkene is positioned below the plane. Consequently, the "substituent" on the first sp^2 carbon will be located above the Fischer plane. Any substituent above the plane is then denoted on the right in the Fischer projection, those below on the left. According to this convention, substituents of *cis*-alkenes will appear consistently on the right in the projection, those of *trans*-alkenes on opposite sides where the first substituent will always be written on the right and the second one on the left.

(6) Pandey, R. C.; Rinehart, K. L., Jr.; Millington, D. S. *Hind. Antibiot. Bull.* **1980**, *22*, 47.

(7) Diol **6a** established the topography of stereogenic centers 31 and 32 and five independent relative configurations within the polyol sector involving two stereogenic centers each, A-anti, B-anti, Γ-syn, Δ-anti and E-syn, were established spectroscopically as shown below where coherent stereogenic centers comprising an independent relative configuration are designated by identical greek capital letters. For details of this convention, see: Maehr, H. *J. Chem. Ed.* **1985**, *62*, 114. The determination of the overall geometry of the polyol sector C13–C29 required the determination of three unknown relative configurations, B-Γ, Γ-Δ, and Δ-E. Of the resulting eight diastereomeric possibilities, one was selected by comparisons with synthetic models. The topographic commitment was based on CD spectral comparisons of the "natural" and synthetic *O*-acetyl polyol sectors.[2c-e]



(8) A preliminary comparison indicates that this culture is similar to, or identical with the mycoticin producing *Streptomyces ruber*, which we gratefully obtained from Prof. S. L. Schreiber.

(9) HPLC analyses of broth extracts derived from *S. ruber* and strain X-14994 suggest roxaticin to be coproduced with the mycoticins by both cultures, albeit in different ratios (RP-HPLC, Microbondapack, 3.8 × 150 mm, 3:7 methanol–water, 1 mL/min).

(10) It should be pointed out that stereoisomers of **6a** appear to be present in the 5-alkyl-4-(hydroxymethyl)-1-hexenyl portion of certain non oxo polyene macrolides. Representatives of the virginiamycin or streptogramin family, e.g. virginiamycin M_1 and M_2, antibiotic A2315A, pristinamycin IIB, and madumycin I, members of the milbemycin–avermectin family, e.g. avermectin A_{1a} and bafilomycin-type macrolides, represent examples.

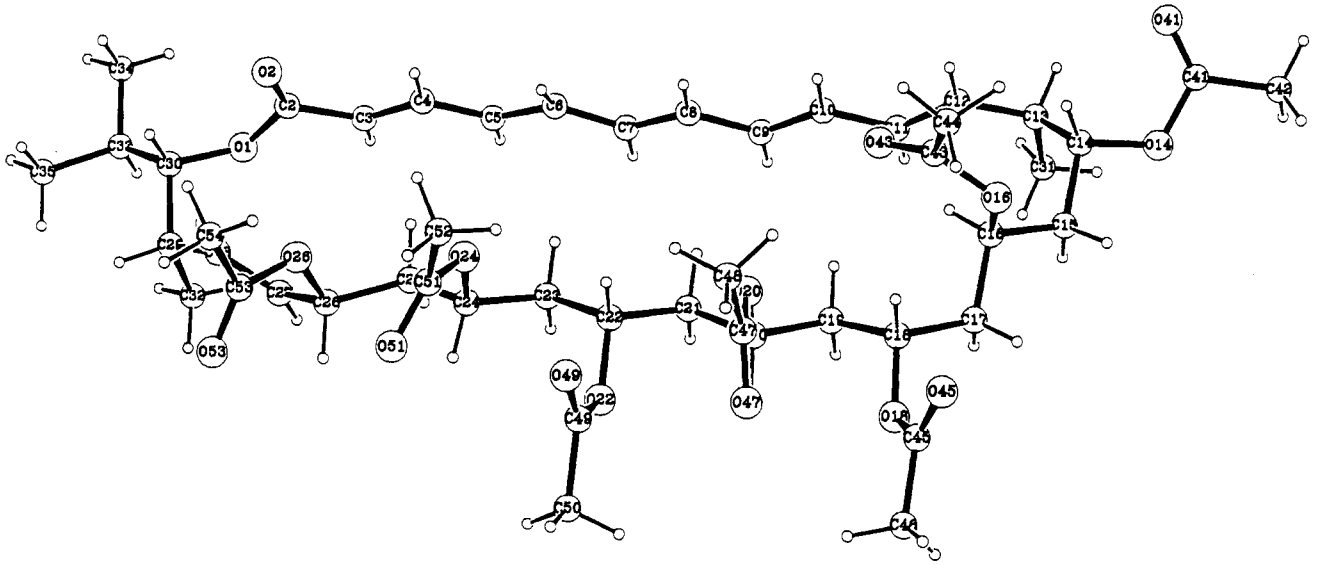


Figure 1. ORTEP drawing of hepta-*O*-acetylroxaticin (**7**).

seven hydroxyl groups, six methylene moieties, and seven methine protons of the type C*H*OH. A molecular weight of 606 and a composition of $C_{34}H_{54}O_9$ were supported by FAB mass spectrometry and elemental analysis. These findings are compatible with the constitution of structure **1**.

Peracetylation of roxaticin led to a hepta-*O*-acetyl derivative (**7**) that confirmed the gross structure and furnished crystals suitable for Roentgen diffraction analysis. As a result, the all-trans geometry of the seven alkenes was confirmed and the relative configuration comprising the 10 stereogenic centers was established (Figure 1).

Whereas the mycoticins are derivatives of oxacyclodotriacontan-2-one (n = 32), roflamycoin and the dermostatins are oxacyclohexatriacontan-2-ones (n = 36). Roxaticin, however, is the first example of an oxo polyene macrolide exhibiting a 30-membered lactone skeleton.

The determination of roxaticin's absolute configuration was guided by published information on 2,4-dimethyl-1,3-pentanediols. Diol **6a**, readily obtained from **7** by ozonolysis, reduction, and hydrolytic workup, was dextrorotatory ($[\alpha]_D$ +9.94°, c 0.25, chloroform)[11] and hence identical with Masamune's diol ($[\alpha]_D$ +10.29°, c 0.91, chloroform) prepared by stereoselective alkylation of either [*S*-(*Z*)]-[(2-cyclohexyl-1-ethylidenyl)-2-[[(1,1-dimethylethyl)dimethylsilyl]oxy]ethoxy]dicyclopentylborane or the corresponding (*Z*)-cycloocta-1,4-diylboron enolate with 2-methylpropanal followed by cleavage with periodate and reduction of the resulting carboxylic acid.[12a]

The levorotatory antipode **6b** ($[\alpha]_D$ −7.54°, c 0.83, chloroform) was also available for comparison and had been prepared by stereoselective alkylation of (*Z*)-crotyl-(*R*,*R*)-2,5-dimethylborolane with 2-methylpropanal, followed by solvolytic liberation of the homoallylic alcohol and ozonolysis with reductive workup.[12b]

It is noteworthy that dermostatin A also had been degraded to 2,4-dimethyl-1,3-pentanediol by ozonolysis and sodium borohydride reduction.[6] Although this diol was found to be dextrorotatory ($[\alpha]_D$ +5.61°, c 0.89, chloroform), and is now identified as **6a**, no ready stereochemical recognition was possible at that time.

Recently, **6a** was also isolated as a degradation product of mycoticin A by Schreiber et al.,[2c] who identified it as the diol that they obtained by Evans' stereoselective aldol condensation of (4*R*,5*S*)-4-methyl-2-oxo-5-phenyl-3-propionyl-1,3-oxazolidine with 2-methylpropanal followed by reductive cleavage.

The results of biosynthetic studies conducted with similar antibiotics[13-15] can most likely be extended to the oxo polyenes. Thus, we postulate that the amino acid derived starter unit (V = isobutyryl, derived from valine) condenses with a propionate (P) and then with 15 acetates (A), followed by another propionate to account for the $VPA_{15}P$ sequence in roflamycoin. Roxaticin (VPA_7PA_5), mycoticin A (VPA_7PA_6), and dermostatin A (VPA_8PA_7) contain the second propionate in the center of the carbon chain.

With the absolute configuration of the lactone ring's last two stereogenic centers now firmly established for roxaticin, dermostatin A, and mycoticin A, the close biogenetic relationship permits the corresponding proposal for roflamycoin as 35*S*,36*S* and the proposition that mycoticin's and roxaticin's established topographic features are also shared by the other oxo polyenes as shown in **3**, **4a**, and **4b**. Thus, roflamycoin can be regarded as [(14ξ,16ξ,20*R*,22*R*,24*R*,26*S*,28*R*,30*S*,32*S*,35*S*,36*S*)-(*all-E*)]-14,16,20,22,24,26,28,30,32-nonahydroxy-3,35-dimethyl-36-(1-methylethyl)oxacyclohexatriaconta-3,5,7,9,11-pentaene-2,18-dione and dermostatin A as [(16ξ,17ξ,18ξ,20*R*,22*R*,24*R*,26*R*,28*S*,30*R*,32*S*,35*S*,36*S*)-(*all-E*)]-16,18,20,22,24,26,28,30,32-nonahydroxy-17,35-dimethyl-36-(1-methylethyl)oxacyclohexatriaconta-3,5,7,9,11,13,33-heptaen-2-one.

Experimental Section

EI mass spectra were recorded at an ionizing voltage of 70 eV and an ion-source temperature at 250 °C. TLC was performed with E. Merck silica gel G60 F-254 plates and Silica Woelm 32-63

(11) The low optical rotation suggested the erythro configuration. The threo diols apparently exhibit much more pronounced rotations as exemplified by **6b** ($[\alpha]_D$ −164°, c 0.64, chloroform) presumably containing the threo impurity derived from some trans epoxide in the starting material: Wood, R. D.; Ganem, B. *Tetrahedron Lett.* **1982**, *23*, 707.

(12) (a) Garcia, J.; Kim, B.-M.; Masamune, S. *J. Org. Chem.* **1987**, *52*, 4831. (b) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566.

(13) Biosynthetic investigations of virginiamycin M_1, antibiotic A2315A,[14] and avermectin[15] have shown that the terminal carbon sequence corresponding to locant n and its isopropyl or isobutyl substituent is derived from valine or isoleucine. It can be assumed, therefore, that oxo polyenes are generated in a similar fashion. Derived from the corresponding amino acid, the isobutyryl or 2-methylbutyryl synthetases serve as starter units and subsequent propionate and acetate condensations complete the assembly of the polyketide network.

(14) LeFevre, J. W.; Kingston, D. G. I. *J. Org. Chem.* **1983**, *49*, 2588.

(15) Cane, D. E.; Liang, T.-C. *J. Am. Chem. Soc.* **1983**, *105*, 4110.

served for column chromatograms. Solutions were dried with magnesium sulfate and were evaporated under reduced pressure. Melting points were determined on a hot stage and are reported without correction.

[(13*S*,14*R*,16*R*,18*R*,20*R*,22*S*,24*R*,26*R*,29*S*,30*S*)-(*all-E*)]-14,16,18,20,22,24,26-Heptahydroxy-13,29-dimethyl-30-(1-methylethyl)oxacyclotriaconta-3,5,7,9,11,27-hexaen-2-one (1, Roxaticin). A medium consisting of (g/L) meat peptone (5), debittered yeast (5), distiller's solubles (5), tomato paste (5), Eclipse N starch (20), cerelose (1.5), calcium carbonate (1), dipotassium hydrogen phosphate (1), and cobalt(II) chloride hexahydrate (0.000 24) was adjusted to pH 7 and autoclaved and served as incubation and production medium as described.[16] The whole broth (200 L) was extracted once with an equal volume of ethyl acetate at pH 4. The extract was concentrated to a 4-L volume and refrigerated. The resulting precipitate (1.2 g) was filtered off, washed with 1:1 methanol–ethyl acetate, and chromatographed on silica gel using a gradient from 1:1 acetone–ethyl acetate to 1:1:0.5 acetone–ethyl acetate–methanol. Fractions containing the yellow solute with R_f 0.16 (silica gel, 5:5:1 acetone–ethyl acetate–methanol) deposited crystalline **1** (0.4 g) on standing: UV max (ethanol) 260 nm (ϵ 5765), 367/8 (66 263); IR (KBr) 1702 (lactone C=O); 400-MHz NMR (DMSO-d_6) δ 0.84, 0.93 (2 d, 3 H each, J = 6.5 Hz each, Me_2CH), 0.99, 1.01 (2 d, 3 H each, J = 6.5 and 7.5 Hz, C13-Me and C29-Me), 0.95–1.34, 1.16–1.34, 1.49 (3 m, 6 H, 4 H, 2 H; H15,17,19,21,23,25), 1.87 (m, 1 H, Me_2CH), 2.55 (m, 2 H, H13,29), 3.42, 3.71–3.89 (2 m, 1 H, 5 H; H14,16,18,20,22,24), 3.88 (d, 1 H, CHO*H*, J = 6 Hz), 3.94 (d, 1 H, CHO*H*, J = 6 Hz), 4.13 (d, 1 H, CHO*H*, J = 6 Hz), 4.16 (m, 1 H, H26), 4.22 (d, 1 H, CHO*H*, J = 5 Hz), 4.38 (d, 1 H, CHO*H*, J = 4.5 Hz), 4.60 (d, 1 H, CHO*H*, J = 4 Hz), 4.66 (dd, 1 H, H30, J = 2.5 and 7 Hz), 5.00 (d, 1 H, CHO*H*, J = 2.5 Hz), 5.35 (dd, 1 H, H28, $J_{27,28}$ = 15.5 and $J_{28,29}$ = 3 Hz), 5.55 (dd, 1 H, H27, $J_{27,28}$ = 15.5 and $J_{26,27}$ = 4.5 Hz), 5.83 (d, 1 H, H3, $J_{3,4}$ = 15.5 Hz), 5.89 (dd, 1 H, H12, $J_{11,12}$ = 15.5 and $J_{12,13}$ = 7 Hz), 6.12 (dd, 1 H, H11, $J_{11,12}$ = 15 and $J_{10,11}$ = 10 Hz), 6.28 (dd, 1 H, H9, $J_{9,10}$ = 15 and $J_{8,9}$ = 10 Hz), 6.33 (dd, 1 H, H7, $J_{7,8}$ = 14.5 and $J_{6,7}$ = 10 Hz), 6.36 (dd, 1 H, H10, $J_{9,10}$ = 15 and $J_{10,11}$ = 10 Hz), 6.40 (dd, 1 H, H5, $J_{5,6}$ = 15 and $J_{4,5}$ = 11 Hz), 6.48 (dd, 1 H, H8, $J_{7,8}$ = 14.5 and $J_{8,9}$ = 10 Hz), 6.70 (dd, 1 H, H6, $J_{6,7}$ = 10 and $J_{5,6}$ = 15 Hz), 7.13 (dd, 1 H, H4, $J_{3,4}$ = 15.5 and $J_{4,5}$ = 11 Hz); MS (FAB) m/e 629 (M + Na), 607 (M + H), 689 (M + H − H_2O); $[\alpha]^{25}_D$ +8.63° (c 0.15, dioxane).

Anal. Calcd for $C_{34}H_{54}O_9$: C, 67.30; H, 8.67. Found: C, 67.05; H, 9.11.

Additional quantities of **1** could be isolated from extracts of the mycelial material with 1-butanol.

[(13*S*,14*R*,16*R*,18*R*,20*R*,22*S*,24*R*,26*R*,29*S*,30*S*)-(*all-E*)]-14,16,18,20,22,24,26-Heptaacetoxy-13,29-dimethyl-30-(1-methylethyl)oxacyclotriaconta-3,5,7,9,11,27-hexaen-2-one (Hexa-*O*-acetylroxaticin, 7). A solution of **1** (108 mg) with acetic anhydride (1.3 mL) and pyridine (5 mL) was allowed to stand at room temperature for 3 days. Ice–water (40 mL) was added, and the solution was extracted with ethyl acetate (20 mL). The organic phase was washed with 1 N hydrochloric acid and repeatedly with brine, dried, and evaporated to give a yellow powder (119 mg). Treatment with ethyl acetate gave **7** (84 mg) as light yellow crystals: mp 158–160 °C, UV max (methanol) 205/6 nm (ϵ 8740), 221 (7390), 229 (7030), 250 (infl, 7480), 257/8 (8200), 359 (86 500), 370 (sh, 82 900); IR (KBr) 1740 (acetyl C=O), 1702 (lactone C=O); 400-MHz NMR δ 0.96, 0.99 (2 d, 3 H each, Me_2CH), 1.08 (d, 6 H, J = 6.5 Hz, C13-Me and C29-Me), 1.3–1.9 (m, 12 H, H15,17,19,21,23,25), 2.01 (s, 6 H, 2 OAc), 2.037, 2.048, 2.054, 2.097, 2.12 (5 s, 3 H each, 5 OAc), 2.62, 2.71 (2 m, 1 H each, H13,29), 4.60 (m, 1 H, H14), 4.79–5.02 (m, 5 H, H16,18,20,22,24), 5.19 (m, 1 H, H26), 5.41 (dd, 1 H, H28, $J_{27,28}$ = 15 and $J_{28,29}$ = 5 Hz), 5.58 (dd, 1 H, H27, $J_{27,28}$ = 15 and $J_{26,27}$ = 4.5 Hz), 5.89 (d, 1 H, H3, $J_{3,4}$ = 15.5 Hz), 5.96 (dd, 1 H, H12, $J_{11,12}$ = 15 and $J_{12,13}$ = 7.5 Hz), 6.27 (dd, 1 H, H11, $J_{11,12}$ = 15 and $J_{10,11}$ = 10.5 Hz), 6.3–6.54 (m, 5 H, H5,7,8,9,10), 6.64 (dd, 1 H, H6, $J_{6,7}$ = 10.5 and $J_{5,6}$ = 14.5 Hz), 7.27 (dd, 1 H, H4, $J_{3,4}$ = 15.5 and $J_{4,5}$ = 11.5 Hz); EIMS m/e (rel intensity) 840 (<1, M − AcOH, 780 (1, M − 2 AcOH, 720 (2, M − 3 AcOH), 660 (3, M − 4 AcOH), 600 (5, M − 5 AcOH), 540 (5, M − 6 AcOH), 480 (9, M − 7 AcOH), 43 (100); FAB MS m/e 923 (M + Na), 841 (M + 1 − AcOH), 781 (M + 1 − 2 AcOH), 721 (M + 1 − 3 AcOH), 661 (M + 1 − 4 AcOH), 601 (M + 1 − 5 AcOH), 541 (M + 1 − 6 AcOH), 481 (M + 1 − 7 AcOH); $[\alpha]^{25}_D$ −106.53° (c 0.14, dioxane).

Anal. Calcd for $C_{48}H_{68}O_{16}$: C, 63.98; H, 7.61. Found: C, 63,50; H, 7.61.

Crystals of **7** contained disordered ethyl acetate whose loss as room temperature caused deterioration of the crystal within ca. 30 min. Thus, the crystal (ca. 0.20 × 0.38 × 0.76 mm) was coated with mineral oil and cooled to 110 K during data collection. Of the 6330 independent reflections for θ <75°, 3885 were above background [$I > 3.0\sigma(I)$]. The structure was solved as the monosolvate ($C_{48}H_{68}O_{16}\cdot C_4H_8O_2$, orthorhombic, space group $P2_12_12_1$, a = 8.382 (5) Å, b = 17.035 (7) Å, c = 38.458 (13) Å, Z = 4, d_{calcd} = 1.196 g/cm^3, μ(Cu Kα) = 7.1 cm^{-1}) by a multiple solution procedure[17] and refined by full-matrix least-squares methods. Ten reflections, which were strongly affected by extinction, were excluded from the final refinement and difference map. The disordered ethyl chain of the solvate was resolved into two moieties. In the final refinement, the four carbons of these ethyl moieties were refined isotropically with occupancies of 0.5 while the remaining non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are R = 0.108 and R_w = 0.124 for the 3875 observed reflections. The final difference map has no peaks greater than ±0.6 e Å^{-3}.

(2*S*,3*S*)-2,4-Dimethyl-1,3-pentanediol (6a). The polyacetate **7** (250 mg) was ozonized at −48 °C in 4:1 dichloromethane–methanol solution for 2.5 min. Excess ozone was expelled with a stream of argon as the temperature was allowed to rise to −20 °C. The solution was concentrated to a volume of ca. 1 mL, diluted with methanol (25 mL), and hydrogenated in the presence of 10% Pd–C at 1 atm at room temperature for 45 min to destroy the ozonides. The catalyst was removed by filtration through Celite, and the filtrate was evaporated to yield a mixture of aldehydes as a colorless oil (378 mg). This mixture was redissolved in methanol (25 mL), cooled to 0 °C, and treated with three portions of sodium borohydride (63, 32, 63 mg) over a period of 1 h. The solution was neutralized (1 N hydrochloric acid) and evaporated. The residue was triturated with 3:2 dichloromethane–methanol and filtered. The filtrate was evaporated and allowed to stand overnight in methanol (25 mL) containing powdered potassium carbonate to ensure complete ester solvolysis. The solution was evaporated and triturated with 1:1 dichloromethane–methanol. The filtrate was passed through a short bed of silica gel, evaporated, and chromatographed on silica gel with 9:1 dichloromethane–methanol yielding **6a** (7 mg). Sublimation at 35 °C and 0.1 Torr gave 4.5 mg of pure **6a**, mp 84–85 °C; 400-MHz NMR ($CDCl_3$) δ 0.86, 0.96, 1.02 (3 d, 3 H each, J = 7 Hz each, C2-Me, C4-Me, H5), 1.71 (m, 1 H, H2), 1.86 (m, 1 H, H4), 2.08 (s, br, 2 H, 2 OH), 3.42 (m, 1 H, H3), 3.75 (m, br, 2 H, H1); EIMS m/e (rel intensity) 131 (<1, M − 1), 114 (<1, M − H_2O), 99 (2, M − H_2O − Me), 89 (42, M − Me_2CH), 73 (82, M − $HOCH_2CHMe$), 71 (45, M − Me_2CH − H_2O), 59 (27, M − Me_2CH − CH_2O); HRMS (FAB) m/e 133.1239 (M + 1), calcd for $C_7H_{17}O_2$ 133.1229; 133.1229; $[\alpha]^{25}_D$ +9.94° (c 0.25, chloroform).

Registry No. **1**, 121073-98-1; **6a**, 98391-91-4; **7**, 121073-99-2.

Supplementary Material Available: Coordinates, anisotropic thermal parameters, bond distances, bond angles, and torsion angles for **7** (7 pages). Ordering information is given on any current masthead page.

(16) Previous paper in this series: Maehr, H.; Liu, C.-M.; Palleroni, N. J.; Smallheer, J.; Todaro, L.; Williams, T. H.; Blount, J. F. *J. Antibiot.* **1986**, *39*, 17.

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