the second and third generations without problem (**20B**,C). Compounds **22** and **20A**–C show ^1H, ^{13}C, and ^{29}Si NMR spectra consistent with the expected structures and have the retention volumes that correspond to their respective molecular weights on size-exclusion chromatography.[4,10] These values are corroborated with mass spectral data (FD) of **22**, **20A**, and **20B** that exhibit their M^+ and $(M - 15)^+$ peaks but the molecular weight of **20C** is apparently too large to be determined with this spectrometry. From the retention volume of **20C** in the chromatography, its molecular weight is estimated to be 14790, in excellent agreement with the calculated value of 15073 (with ^{28}Si).[4] Note that the "surfaces" of these silicone dendrimers are "coated" with SiH groups that are readily amenable to functional group transformation to modify physical properties of the polymers.[11]

Synthesis of $^HMD_4H^H$. To a mixture of 500 g (1.70 mmol) of D_4, 304 g (16.9 mol) of water, and 50.1 g of silica gel was added dropwise 480 g (5.07 mol) of Me_2SiHCl over 2 h. After the mixture was stirred for 4 h, the silica gel was filtered off and low-boiling side products were removed on a rotary evaporator. The residue was diluted with 500 mL of benzene. The water layer was separated and the organic layer washed with 500 mL of water, 500 mL of 1% $NaHCO_3$ solution twice, and finally 500 mL of water twice. Distillation provided 341 g (47% yield and 78% based on the consumed D_4) of $^HMD_4M^H$, bp 81 °C (0.1 Torr), as a colorless oil and 199 g of recovered D_4.

Supplementary Material Available: Representative experimental procedures, size-exclusion chromatographic results, and physical properties of oligosiloxanes with pertinent references (16 pages). Ordering information is given on any current masthead page.

(10) *Steric Exclusion Liquid Chromatography of Polymers*; Janca, J., Ed.; Chromatography Series; Marcel Dekker: New York, 1984; Vol. 25.

(11) The work at M.I.T. was supported by a grant from the National Science Foundation (CHE-8706760-03). The mass spectra were provided by the facilities supported by the National Institutes of Health (Grant RR 00317, Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Pimaricin. Stereochemistry and Synthesis of Its Aglycon (Pimarolide) Methyl Ester†

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Pimaricin (**1**) is a representative antifungal polyenemacrolide of significant physiological activity and practical utility.[1] Its correct gross structure was documented in 1977,[2] but the entire stereochemistry of its aglycon, pimarolide, remained unknown until the completion of this work mainly because **1** and its derivatives fail to crystallize in a form suitable for X-ray analysis. We degraded the antibiotic to the major fragment **7** (of unknown stereochemistry) through a pimarolide derivative (**4**) (Scheme I). Reagent-controlled syntheses[3] of a set of diastereomers possible for the structure of **7** unambiguously established its stereochemistry,[4] and subsequently **7** was converted into the pimarolide methyl ester **4b**. These accomplishments summarized below represent the first synthesis of a polyenemacrolide aglycon without prior knowledge of its stereochemistry and also provide synthetic proof for the correctness of the stereostructure disclosed for **1** by Lancelin and Beau[5] during the preparation of this manuscript. The set of NMR techniques employed in their study is indeed powerful.

Degradation of 1 to 7. The degradation pathway from **1** to **7** via **2**–**6** outlined in Scheme I[6] is patterned after that developed in our laboratory in conjunction with the synthesis of amphoterolide B.[7,8] Two comments are appropriate. (1) The normally problematic step of cleaving the mycosamyl moiety (step b) proceeded well through oxidative deglycosidation of **2** with DDQ[7a] to provide tetraenone **3**, and this method appears generally applicable to many other polyenemacrolides. (2) Reduction of **3** with $NaBH_4$ (step c)[8a] led to the exclusive formation of a single tetraenol (**4**). The 15*R* configuration was assigned to **4** through the observation of a negative Cotton effect in the CD spectrum of the *p*-nitrobenzoate derivative **4a**.[9,10] That both the MOM ether of **4** ($J_{14,15}$ 2.8, $J_{14',15}$ 8.0, $J_{15,16}$ 7.0 Hz) and **2** ($J_{14,15}$ 2.5, $J_{14',15}$ 8.0, $J_{15,16}$ 7.5 Hz) show very similar coupling patterns for H_{14}, $H_{14'}$, H_{15}, and H_{16} confirms the 15*R* assignment of **1**.[10]

Synthesis of 7. ^1H NMR spectral comparison between the pimarolide derivative **4** and the amphoterolide B methyl ester as well as between a pair of their respective degradation products strongly suggests that the pyran moieties [C(9)–C(13) in **1**] of both antibiotics possess the same stereochemistry. Thus, a synthetic intermediate (**8**) representing the C(9)–C(15) fragment and used in our amphoterolide B synthesis[7b,11] served as starting material and was converted into aldehyde **12** via **9**–**11** as shown in Scheme II.[12–14] Two different reagent-controlled reactions were used to prepare the two possible configurations at C(7) in **7**. (1) The asymmetric aldol reaction of aldehyde **12** with the enolate derived from 3-ethylpentyl ethanethioate and chiral (*R*,*R*)-dimethylborolanyl triflate[15] provided a 1:8 mixture of **13a** and **13b**, while the use of (*S*,*S*)-dimethylborolanyl triflate reversed the product ratio (10:1 of **13a** and **13b**). Silylation of **13a** and **13b** followed by $NaBH_4$ reduction[16] and oxidation afforded the aldehydes **14a** and **14b**, respectively. (2) Asymmetric allylboration[17] of **12** with chiral (*S*)-*B*-allyl-2-(trimethylsilyl)borolane led to the predominant formation of diastereomer **15** (9.5:1), which was then transformed to **14a**. The stereochemical outcome of the aldol reaction and allylboration are governed by the rule of double

†This work was initiated at M.I.T. and completed at I.F.R., Kao. A.J.D. participated in an exchange program between the two institutions.

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(4) Notable examples of establishing stereochemistry through this methodology include Kishi's palytoxin quoted in ref 3 and Schreiber's mycoticin A and B (Schreiber, S. L.; Goulet, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 8120).

(5) Lancelin, J.-M.; Beau, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 4060. Also see: Lancelin, J.-M.; Paquet, F.; Beau, J.-M. *Tetrahedron. Lett.* **1988**, *29*, 2827.

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(10) We thank Prof. N. Harada, Tohoku University, for the CD spectrum of **4a** and Dr. K. Furihata, Tokyo University, for the 500-MHz ^1H NMR spectra of several compounds prepared in this work.

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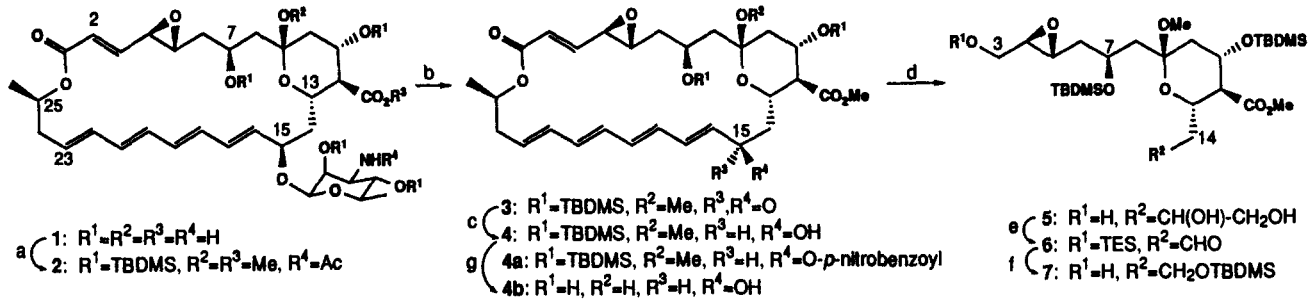
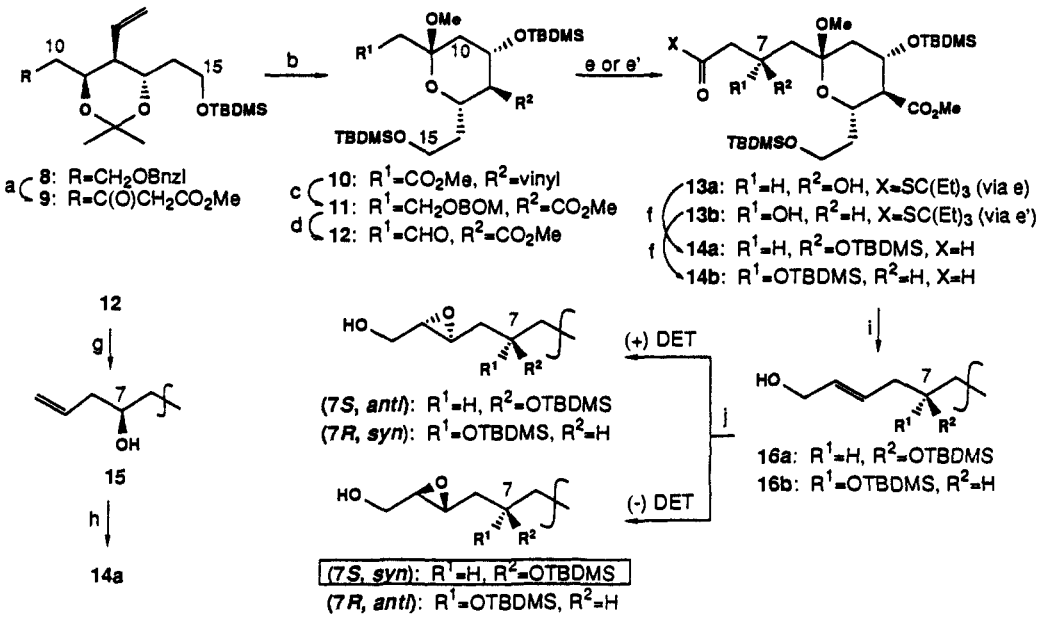
Scheme I[a]



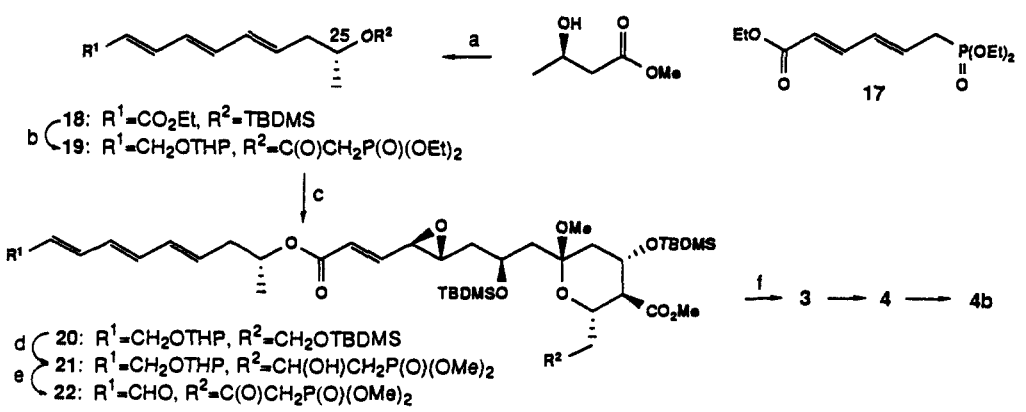
[a] Reagents and conditions: (a) (1) Ac_2O, MeOH–$CHCl_3$ (1:1); CH_2N_2, 86%; (2) catalytic PPTS, $CH_3C(OCH_3)_3$–MeOH–CH_2Cl_2 (1:4:6), 82%; (3) TBDMSOTf, 2,6-lutidine, 55%; (b) DDQ, THF, 50%; (c) $NaBH_4$, MeOH, 0 °C, 99%; (d) (1) O_3, CH_2Cl_2–MeOH (9:1); Ph_3P; (2) $NaBH_4$, MeOH, 0–25 °C, 62% overall; (e) (1) $NaIO_4$, 96%; (2) (TES)Cl, NEt_3, DMF, 80%; (f) (1) $NaBH_4$, 97%; (2) TBDMSOTf, 2,6-lutidine; (3) HF–pyr, pyr, −10 °C, 82% (two steps); (g) (1) HF–pyr, MeOH, 35 °C, 48 h, 35%; (2) catalytic CSA, MeOH–H_2O (5:1), 81%.

Scheme II[a]



[a] Reagents and conditions: (a) (1) Na, NH_3 (l), 97%; (2) Swern, 100%; (3) $NaClO_2$, 96%; (4) CDI; $Mg(OC(O)CH_2CO_2Me)_2$, 98%; (b) (1) catalytic TsOH, MeOH, 85%; (2) TBDMSOTf, 2,6-di-^{t}Bu-pyr, 98%; (c) (1) LAH, THF, 96%; (2) (BOM)Cl, 89%; (3) O_3, CH_2Cl_2–MeOH (5:1); Ph_3P, 90%; (4) $KMnO_4$(aq); (5) CH_2N_2, 81% (two steps); (d) (1) Raney Ni, MeOH, 90%; (2) Swern, 99%; (e) ref 15, using (*S*,*S*)-dimethylborolanyl triflate, 88–93%; (e') ref 15, using (*R*,*R*)-dimethylborolanyl triflate; (f) (1) TBDMSOTf, 2,6-di-^{t}Bu-pyr; (2) $NaBH_4$, EtOH, 86% (50% conv); (3) Swern, 100%; (g) ref 17, 95%; (h) (1) TBDMSOTf, 2,6-di-^{t}Bu-pyr, 72%; (2) O_3, CH_2Cl_2–MeOH; Ph_3P, 94%; (i) (1) $Ph_3PCHCHO$, C_6H_6, 45 °C, 67%; (2) $NaBH_4$, 99%; (j) $Ti(O^iPr)_4$, TBHP, 60–70%.

Scheme III[a]



[a] Reagents and conditions: (a) (1) TBDMSOTf, 2,6-lutidine, 81%; (2) DIBAL, −78 °C, 1 h, 71% aldehyde and 28% alcohol; (3) Li(TMP), **17**, THF, −78 °C, 15 min; addition of aldehyde, 66%; (b) (1) DIBAL, 95%; (2) DHP, catalytic PPTS, 94%; (3) HF–pyr, pyr, 92%; (4) triethyl phosphonoacetate, catalytic 4-DMAP, 75%; (c) LDA, THF, −78 °C, 15 min; addition of aldehyde, 64%; (d) (1) HF–pyr, pyr, 65%; (2) Swern, 84%; (3) $LiCH_2P(O)(OMe)_2$, THF, −95 °C, 73% (62% conv); (e) excess CrO_3, pyr, 35 °C, 3 h, 68%; (f) K_2CO_3, 18-crown-6, C_6H_6, reflux, 58%.

asymmetric synthesis,[3] and therefore the assignments of stereochemistry are secure.

The allylic alcohols **16a** and **16b** prepared from **14a** and **14b**, respectively (step i), were subjected to asymmetric epoxidations,[18] each with (+)-DET and (−)-DET (another set of double asymmetric syntheses) to provide four diastereomers, one of which was expected to be **7**. Comparison of the $[\alpha]_D$ and ^1H NMR spectra of each isomer with the degradation product **7** revealed that the configuration of **1** at C(7) was *S* and that the epoxide was syn with respect to the C(7) hydroxyl group.

Synthesis of 4b from 7. The only stereochemistry of **1** yet to be established concerned the C(25) stereogenic center, and this task was readily achieved by isolating the C(23)–C(26) fragment of **1** as 1,3-butanediol and comparing it to authentic material as summarized in the supplementary material. With the assignment of the 25*R* configuration the synthesis of the C(17)–C(2) fragment **19** (see **1** for numbering) started with (*R*)-methyl 3-hydroxybutyrate and involved a Horner–Wadsworth reaction with **17**[19] (step a, reaction 3) and a DMAP-mediated transesterification of triethyl phosphonoacetate[20] with the 25-hydroxyl compound derived from **18** (step b, reaction 4) (Scheme III).

The construction of the macrocycle was achieved through the double Horner–Wadsworth coupling of **19** with the aldehyde derived from **7**. All of the steps proceeded smoothly,[21] and it was noted that under the conditions of the Sarrett oxidation (step e) the expected oxidation of the 15-hydroxyl group was accompanied by THP-like cleavage and oxidation to provide the desired ketoaldehyde (**22**). The synthetic macrolactone **3** was identical with that obtained from the natural source and its conversion into the pimarolide methyl ester proceeded in the manner shown in Scheme I, steps c and g.[22,23]

Supplementary Material Available: ^1H NMR spectra of all new compounds and experimental procedures of selected reactions (21 pages). Ordering information is given on any current masthead page.

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(20) Hatakeyama, S.; Satoh, K.; Sakurai, K. and Takano, S. *Tetrahedron Lett.* **1987**, *28*, 2713.
(21) Cf.: refs 7b and 8b for steps d–f.
(22) All new compounds showed mass spectra consistent with the structures assigned as shown above.
(23) We are grateful to Gist-Brocades (The Netherlands) for a generous gift of pimaricin. The work at M.I.T. was supported through a grant from the National Institutes of Health (Grant GM 35879).

Additions and Corrections

Theoretical Study on the Electronic Structure of Si–Ge Copolymers [*J. Am. Chem. Soc.* **1990**, *112*, 5043–5052]. KYOZABURO TAKEDA,* KENJI SHIRAISHI, and NOBUO MATSUMOTO

Page 5044, Reference 27: The last three sentences in this reference should be replaced by the following.

Note that, in the present and our previous works, the *x* axis is set to the main axis of the polymer skeleton chain. This is different from the usual setting of the coordinates, in which the *z* axis is set to the main axis. Therefore, one should change our *x*, *y*, and *z* coordinates to *z*, *x*, and *y* when referring to the usual character table.

Book Reviews

Studies in Organic Chemistry 39. Carbon-13 NMR of Flavonoids. By P. K. Agrawal (Central Institute of Medicinal and Aromatic Plants). Elsevier: Amsterdam and New York. 1989. XVI + 564 pp. $184.25. ISBN 0-444-87449-6.

P. K. Agrawal and his coauthors have made a significant scientific contribution by assembling this large data base for the carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra of flavonoid compounds. This extensive collection is an essential reference for anyone studying the flavonoids. The book should also be useful to chemists outside this specialized field of natural products chemistry. Carbon-13 NMR methods have been especially important to advances in the chemistry of plant phenolic compounds. The phenomenal growth of ^{13}C NMR spectra of flavonoids, from the several hundred entries presented in Markham's 1982 review to the nearly 2000 compounds listed in this volume, attests to the power of ^{13}C NMR in clarifying the structure of these compounds.

When compiling a large data base such as this, it is understandable that errors might be found. A partial check on selected compounds revealed some errors but most are immediately obvious. To assist in evaluating solvent effects, the authors often present spectral data from more than one reference for a compound. To extract chemical shift data for a compound, the reader must expend considerable effort by working between drawn structures and the tabular data. The most interesting data are often those presented for the vast array of substituent structures. Unfortunately, presentation of this valuable information is in a footnoted format that can be disconcerting. However, the novelty of the data makes it worthwhile to work through this difficult presentation. The vast array of structures represented by these compounds makes this volume a valuable reference for all organic chemists faced with the problem of structure elucidation.

Perhaps there is no better way to present such a vast amount of data and still keep the book to a manageable size. But, now that all these spectra have been assembled, the development of a computer-searchable file should not be too difficult. While one hesitates to ask the editor to add further to the huge effort that went into producing this book, the development of such a file would add substantially to its usefulness.

Because modern high-field instruments have not been readily available to many chemists studying plant phenolics, the data presented in this book are concentrated on the proton-decoupled spectra. Therefore, some caution must be exercised when using these assignments which, in many instances, have not been proven by other experiments. The text, however,