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

---

[18] Gao, Y.; Hanson, R. M.; Klunder, R. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

[19] DeKoning, H.; Mallo, G. N.; Springer-Fidder, A.; Subramanian-Erhart, K. E. C.; Huisman, H. O. *Recl. Trav. Chim. Pays-Bas* **1973**, 683, and references quoted therein.

[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,