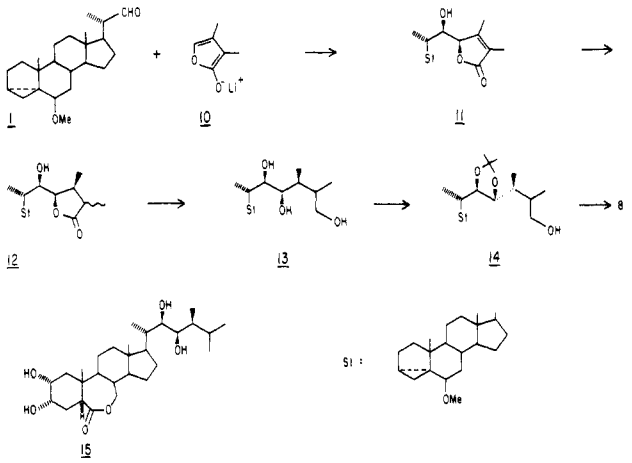

lactone with $LiAlH_4$ gave the triol **13** which was converted to the acetonide **14**. This compound was treated with methanesulfonyl chloride and pyridine, and the product was reduced with lithium aluminum hydride to give the same intermediate **8** (22*R*,23*R*,24*S*) obtained in the earlier sequence. The overall yield for the four steps from the saturated lactone **12** was 70%.

It should be noted that catalytic hydrogenation of **3** and of **11** gave products which had mainly the 24*S* stereochemistry. Initially, we had reasoned that if hydrogenation occurred at the face of the butenolide ring nearest the C-22 hydroxyl, then **3** would yield the 24*S* product while **11** would yield the 24*R* isomer. The fact that hydrogenation of **11** gave mainly the 24*S* isomer suggests that the hydroxyl does not have a directive influence on the course of the hydrogenation.

Conversion of intermediate **9** to brassinolide **15** was achieved in 15% yield by utilizing procedures similar to those described by other workers. Our synthetic brassinolide, mp 273–276 °C (lit.[1a] mp 273–274 °C), had the same biological activity as natural brassinolide in the bean second internode bioassay at all concentrations tested. It was also found to possess identical activity to authentic brassinolide in the rice lamina inclination test. The synthetic route reported here makes available 28-homobrassinolide and also new analogues of brassinolide and 28-homobrassinolide which may be of interest for structure–activity studies of this group of steroids.

Acknowledgment. We are indebted to Dr. N. Bhushan Mandava, United States Environmental Protection Agency, and Professor Shingo Marumo, Nagoya University, Japan, for the biological assays. The interest of Professor David Toft, Mayo Foundation, is gratefully acknowledged. This investigation was supported in part by a Grant NIH AM 25625 (to the Mayo Foundation).

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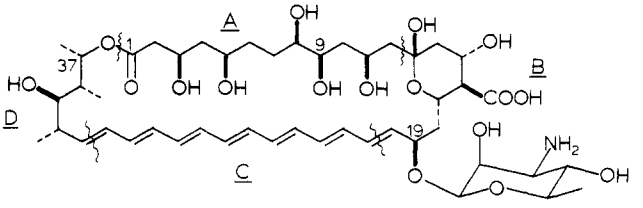
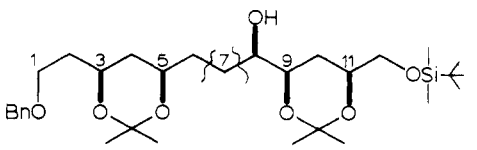
Synthesis of Amphotericin B. 1. Fragment A of the Aglycon

Summary: The C(1)–C(12) unit (fragment A) of the aglycon of amphotericin B has been synthesized with excellent regio- and stereoselection.

Sir: A variety of highly diastereoface-selective chiral reagents and catalysts have been developed for several major organic reactions.[1] The availability of these reagents and catalysts combined with an enriched chiral pool[2] now allows us to design a practical plan for the synthesis of stereochemical complex molecules such as macrolide antibiotics.[3] We have chosen the polyene macrolide amphotericin B (**1**)[4] as our target and record herein the synthesis of its C(1)–C(12) unit, fragment A (**2**). The syntheses of the other fragments B, C, and D shown in **1** and also the assembly of A and these fragments will follow this report shortly.



1



2

At the outset of this project we designed two schemes for the synthesis of **2**. Scheme I involves the coupling of the C(1)–C(6) fragment **3** and the C(7)–C(12) fragment **4**, both of which have a common four-carbon unit, readily derivable from (*S*)-malic acid. This coupling, although expected to be only partially successful (see below), offers the advantage that it will provide after desulfurization only one product which must have the stereostructure shown in **2**. No new chiral center is created in this final process. Alternatively, **2** can be retrosynthetically dissected at the C(7)–C(8) bond, giving the two fragments **5** and **6** (Scheme II). The coupling of these fragments will definitely proceed, but it is not without an anticipated problem. The unpredictable stereochemical outcome[5] of the reaction [which creates the C(8) chiral center] can only be evaluated in comparison with **2** hopefully to be secured in the first approach. A brief outline of the experimental results follows.

(1) For a fundamental strategy for the construction of acyclic systems and also for the principle of multiple asymmetric synthesis, see: (a) Masamune, S. *Heterocycles* **1984**, *21*, 107. Also see: (b) Masamune, S.; Choy, W. *Aldrichimica Acta* **1982**, *15*, 47.

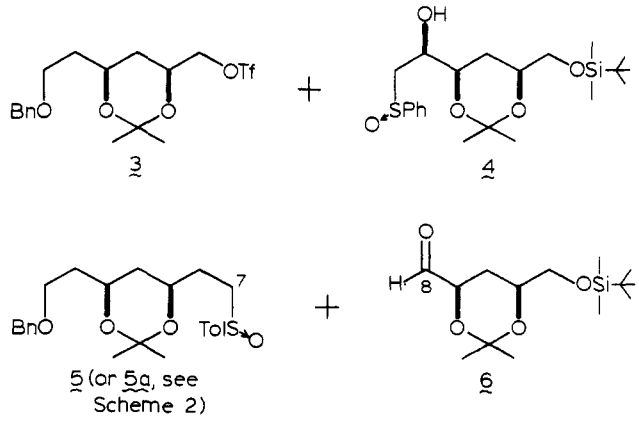
(2) (a) Seebach, D.; Hungerbühler, E. "Modern Synthetic Methods 1980"; Scheffold, R., Ed.; Salle and Sauerländer-Verlag: Frankfurt and Aarau, 1980. (b) Hanessian, S. "Total Synthesis of Natural Products: The 'Chiron' Approach"; Pergamon Press: New York, 1983.

(3) Masamune, S.; McCarthy, P. A. In "Macrolide Antibiotics"; Omura, S., Ed.; Academic Press: New York, 1984.

(4) (a) Isolation from *Streptomycetes nodosus*: Vandeputte, J.; Wachtel, J. L.; Stiller, E. T. *Antibiot. Annu.* **1956**, 587. (b) Chemical degradation: Borowski, E.; Mechlinski, W.; Falkowski, L.; Ziminski, T.; Dutcher, J. D. *Tetrahedron Lett.* **1965**, 473. Cope, A. C.; Axen, U.; Burrows, E. P.; Weinlich, J. *J. Am. Chem. Soc.* **1966**, *88*, 4228. Dutcher, J. D.; Walters, D. R.; Wintersteiner, O. *J. Org. Chem.* **1963**, *28*, 995. Dutcher, J. D.; Young, M. B.; Sherman, J. H.; Hibbits, W. E.; Walters, D. R. *Antibiot. Annu.* **1957**, 866. von Saltza, M.; Dutcher, J. D.; Reid, J.; Wintersteiner, O. *J. Org. Chem.* **1963**, *28*, 999. (c) X-ray analysis: Ganis, P.; Avitabile, G.; Mechlinski, W.; Schaffner, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 4560. Mechlinski, W.; Schaffner, C. P.; Ganis, P.; Avitabile, G. *Tetrahedron Lett.* **1970**, 3873.

(5) In this coupling reaction, Li^+ may coordinate with oxygen atoms in a number of possible modes. See: (a) Masamune, S.; Ellingboe, J. W.; Choy, W. *J. Am. Chem. Soc.* **1982**, *104*, 5526 and references quoted therein. Also see: (b) Stork, G.; Paterson, I.; Lee, F. K. C. *Ibid.* **1982**, *104*, 4686.

0022-3263/84/1949-2834$01.50/0



Scheme I. Triol 7[2] prepared from (*S*)-malic acid was converted almost exclusively to its 1,2-diol 3-pentylidene derivative **8** with 3,3-dimethoxypentane,[6] the ratio of **8** to its corresponding 2,4 derivative being 45:1. The use of this protecting group eliminates the earlier problem of regioselection encountered in the preparation of the acetonide corresponding to **8**.[7] The application of a standard two-carbon extension sequence [(PCC oxidation, Horner–Emmons reaction using triethyl phosphonoacetate (*E*/*Z* stereoselectivity, 45:1), Dibal reduction] provided allylic alcohol **9**, which was subjected to Sharpless epoxidation[8] with diethyl (−)-tartrate to afford exclusively epoxy alcohol **10**, a common intermediate leading to both **3** and **4**.

A route to **3** involves reductive opening of the epoxide in **10** and then a series of protecting group manipulations. Thus, Redal reduction of **10** provided 1,3-diol **11** exclusively,[9] the primary hydroxyl group of which was selectively benzhydrylated to afford **11a**.[10a] A sequence of reactions including (1) removal of the 3-pentylidene group with acid from **11a**, (2) selective silylation of the resulting primary hydroxyl group with *t*-BuMe$_2$SiCl, and (3) acetonide formation provided **12** which was further subjected to the following transformations: (1) replacement of the benzhydryl group with benzyl by using Na/liquid NH$_3$ followed by benzyl bromide,[10b] (2) deprotection of the primary hydroxyl group, and (3) trifluoromethanesulfonylation. The final product is **3**.

Conversion of **10** to **4** also uses now well-established methods for the transformation of oxygen functionalities. Thus, **10a**, the benzyloxycarbonate of **10** underwent AlCl$_3$-catalyzed epoxide opening,[9b,11] and the resulting cyclic carbonates[12] were converted with acid to a single pentaol monocarbonate (**13**). Succesive treatment of **13** with *t*-BuMe$_2$SiCl, Me$_2$C(OMe)$_2$, and K$_2$CO$_3$ provided **14** which, after monobenzoylation with PhCOCN, was further transformed to **4** through the following set of reagents: (1) MsCl, (2) *n*-Bu$_4$NOH with a trace of MeOH (to form a terminal epoxide functionality (see **15**) with inversion of the stereochemistry at the C(8) position), (3) PhS$^-$, and (4) NaIO$_4$ (to oxidize the sulfide to the corresponding sulfoxide).

Compound **13** was also obtained from L-glucose via five steps:[13a–c] (1) conversion to the diacetonide **16**, (2) reductive removal of the C(3)-OH group, (3) selective removal of the 5,6-acetonide group, (4) carbonate formation with carbonyldiimidazole, (5) removal of the remaining acetonide, and finally (6) NaBH$_4$ reduction. This conversion corroborates the stereochemical assignments shown in Scheme I.

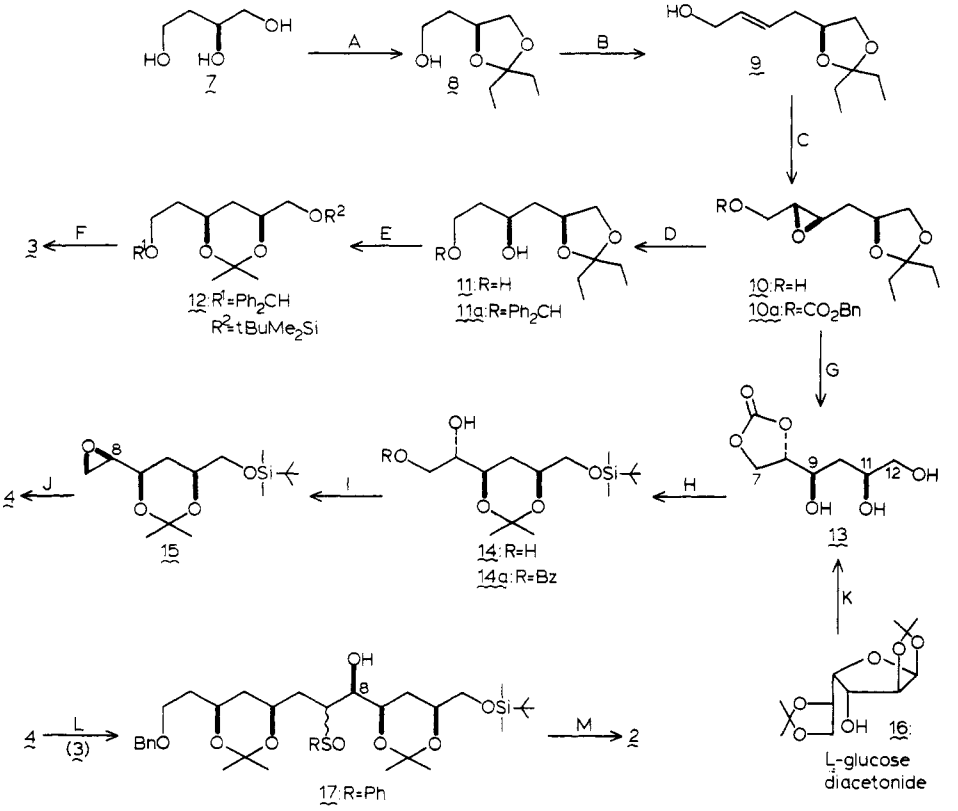
The coupling reaction of **3** with the dianion generated from **4** with *n*-BuLi did proceed to afford the C-alkylated products **17** isomeric at the C(7) position, but in a maximum yield of only 30%, the major side reaction being a base-catalyzed elimination of TfOH from **3**. This low yield in the coupling step compelled us to modify Scheme I. However, Raney nickel desulfurization of **17** proceeded smoothly to provide the target molecule **2** which would serve as a reference compound for the second approach.

Scheme II. The reaction of **3** with the anion derived from (*R*)- and (*S*)-tolyl methyl sulfoxide (**18** and **18a**)[14] provided **5** and **5a**, respectively, while diol **14** was converted to **6** with NaIO$_4$. Thus, the fragments required for this scheme were readily available. Compound **6** was also prepared from D-glucose via **19** through a lengthy but straightforward process including three known steps (**19** → **6**); (1) benzoylation, (2) acid hydrolysis, (3) thioacetal formation (EtSH),[13d] (4) acetonation, (5) base hydrolysis, (6) silylation (*t*-BuMe$_2$SiCl), and finally (7) liberation of the aldehyde.

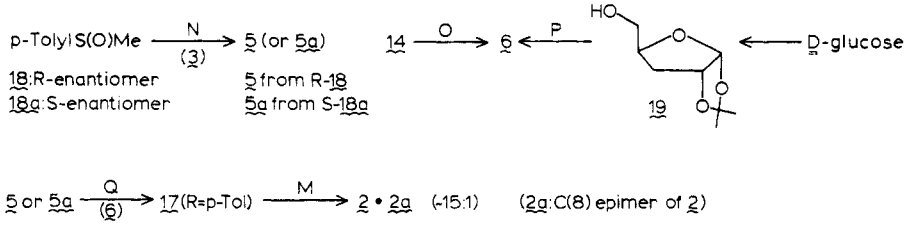
The reaction of aldehyde **6** with the anion generated from **5** gave rise, in excellent yield (90%), to a mixture of coupled products which upon desulfurization brought about two chromatographically separable (HPLC)[15] isomers in a ratio of ~15:1, the major isomer being indistinguishable from **2** obtained earlier (HPLC and ^{1}H and ^{13}C NMR). The minor product **2a** was the C(8) epimer of **2**: PCC oxidation of the major isomer followed by NaBH$_4$ reduction provided a ca. 1:1 mixture of **2** and **2a**. When **5a** (note the absolute configuration of the sulfoxide is reversed to *S*) was subjected to the above sequence of coupling (90%) and desulfurization (86%), the ratio of **2** and **2a** remained unchanged (~15:1). These results obtained from **5** and **5a** show that (1) the stereochemistry of the sulfoxide exerts virtually no noticeable influence on

(6) Huggins, M. J.; Kubler, D. G. *J. Org. Chem.* **1975**, *40*, 2813.
(7) Meyers, A. I.; Lawson, J. P. *Tetrahedron Lett.* **1982**, *23*, 4883. Use of 1,1-dimethoxycyclopentane leads to the formation of a 2:1 mixture favoring the six-membered ketal (Ito, Y.; Masamune, S., unpublished results).
(8) (a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. For an improved workup procedure, see: (b) Reed, L. A., III; Ito, Y.; Masamune, S.; Sharpless, K. B. *Ibid.* **1982**, *104*, 6468.
(9) (a) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *J. Org. Chem.* **1982**, *47*, 1378. (b) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109.
(10) (a) Benzylation of **11** proceeded nonregioselectively, even under carefully controlled conditions. (b) The benzhydryl group of **11a** was replaced by benzyl in this stage of the scheme, because the benzhydryl group has an acidic proton which is readily removed by the dianion of **4** generated for the coupling reaction of **3** and **4**.
(11) (a) Corey, E. J.; Hopkins, P. B.; Munroe, J. E.; Marfat, A.; Hashimoto, S. *J. Am. Chem. Soc.* **1980**, *102*, 7986. (b) Roush, W. R.; Brown, R. J. *J. Org. Chem.* **1982**, *47*, 1371. (c) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *Ibid.* **1982**, *47*, 1373.
(12) The acetonide present in **10** underwent partial migration from the C(11,12) position to the C(9,11) position.
(13) Most of these reactions are well-known in sugar chemistry and have been applied to D-glucose and its derivatives. See: (a) Schmidt, O. T. *Methods Carbohydr. Chem.* **1963**, *2*, 318. (b) Barton, D. H. R.; Motherwell, W. B. *Pure Appl. Chem.* **1981**, *53*, 15. (c) Robins, M. J.; Wilson, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 932. (d) Wong, M. Y. H.; Gray, G. R. *Ibid.* **1978**, *100*, 3548.
(14) Obtained through the resolution of the corresponding menthyl esters. $[\alpha]^{25}_D$ of **18** +187.1° (*c* 1.19, CHCl$_3$); $[\alpha]^{25}_D$ of **18a** −189.1° (*c* 1.11, CHCl$_3$). Reported for **18**: $[\alpha]^{25}_D$ +168° (*c* 1.8, acetone) (Solladie, G. *Synthesis* **1981**, 185); $[\alpha]^{20}_D$ +145.5° (acetone) (Mislow, K.; Green, M. M.; Laur, P.; Melillo, J. T.; Simmons, T.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1958); $[\alpha]_D$ +189.1° (*c* 1.11, CHCl$_3$) (Tsuchihashi, G.; Iriuchijima, S.; Ishibashi, M. *Tetrahedron Lett.* **1972**, 4605). Asymmetric oxidation of sulfides to the corresponding sulfoxide was recently reported: Pitchen, P.; Kagan, H. *Ibid.* **1984**, *25*, 1049.
(15) The retention times for **2** and **2a** in HPLC (μ-Porasil SI Radialpak B liquid chromatography cartridge, 1 mL/min, hexane containing 1% isopropyl alcohol) were 5.1 and 3.5 min, respectively.

Scheme I[a]



Scheme II[a]



[a] (A) $Et_2C(OMe)_2$, *p*-TsOH catalyst, DMF, rt (93%); (B) (i) PCC, CH_2Cl_2, rt; (ii) $(EtO)_2P(O)CH_2CO_2Et$, NaH, $PhCH_3$, THF, −20 °C (52% for two steps); (iii) Dibal, THF, −40 °C (100%); (C) (**9** → **10**) $Ti(O\text{-}i\text{-}Pr)_4$, (−)-DET, TBHP, CH_2Cl_2, −20 °C (77%); (**10** → **10a**) $ClCO_2CH_2Ph$, pyridine, THF, −20 °C → rt (90%); (D) (**10** → **11**) Redal, THF, −20 °C (76%); (**11** → **11a**) Ph_2CHBr, NaH, HMPA, DMF, rt (65%); (E) (i) 0.8% H_2SO_4, MeOH, rt (100%); (ii) *t*-$BuMe_2SiCl$, imidazole, THF, rt (85%); (iii) $Me_2C(OMe)_2$, CSA catalyst, acetone, rt (98%); (F) (i) Na, liquid NH_3, THF, −78 °C (98%); (ii) $PhCH_2Br$, NaH, 18-crown-6, THF, 0 °C → rt (88%); (iii) *n*-Bu_4NF, THF, 0 °C (97%); (iv) $(CF_3SO_2)_2O$, 2,6-di-*tert*-butylpyridine, CH_2Cl_2, −20 °C (91%); (G) (i) $AlCl_3$, Et_2O, −20 °C (64%); (ii) 1% H_2SO_4, MeOH, rt (100%); (H) (**13** → **14**) (i) *t*-$BuMe_2SiCl$, imidazole, THF, −20 °C (74%); (ii) $Me_2C(OMe)_2$, *p*-TsOH, acetone, rt (92%); (iii) K_2CO_3, MeOH, rt (100%); (**14** → **14a**) PhCOCN, Et_3N, CH_3CN, −10 °C (77%); (I) (i) MsCl, Et_3N, Et_2O, 0 °C; (ii) *n*-Bu_4NOH, Et_2O, MeOH (trace), rt (91% for two steps); (J) (i) PhSH, 0.5 N NaOH, THF, 0 °C → rt (91%); (ii) $NaIO_4$, MeOH, H_2O, 0 °C (87%); (K) (i) ClC(S)OPh, DMAP, CH_3CN 0 °C → rt (88%); (ii) *n*-Bu_3SnH, AIBN, PhH, 80 °C (95%); (iii) 0.8% H_2SO_4, MeOH, rt; (iv) $(imid)_2CO$, THF, rt (61% for two steps); (v) Dowex-50 acidic resin, H_2O, PhH, 50 °C; (vi) $NaBH_4$, MeOH, H_2O, 0 °C (71% for two steps); (L) (1) *n*-BuLi, THF, HMPA, −30 °C, 1 h, (2) **3**, −30 °C → −20 °C (30%); (M) Ra-Ni, acetone, rt (86%); (N) (1) *n*-BuLi, *i*-Pr_2NH, THF, −60 °C, (2) **3**, −78 °C (75%); (O) $NaIO_4$, MeOH, H_2O, rt (96%); (P) (i) PhCOCl, pyridine, rt (97%); (ii) Dowex-50 acidic resin, H_2O, 50 °C; (iii) EtSH, concentrated HCl catalyst, 0 °C; (iv) 2-methoxypropene, CF_3CO_2H, CH_2Cl_2, rt (64% for three steps); (v) 1 N NaOH, MeOH, rt; (vi) *t*-$BuMe_2SiCl$, imidazole, DMF, −25 °C (100% for two steps); (vii) MeI, Na_2CO_3, CH_3CN, H_2O, rt (99%); (Q) (1) *n*-BuLi, *i*-Pr_2NH, THF, −60 °C, (2) **6**, −78 °C (90%).

the **2**:**2a** ratio and (2) the Li^+ coordination with both the aldehyde and the C(9) oxygen of **6** (rather than the many other oxygen atoms present in both **5** and **6**) appears to be most important in controlling the stereochemistry of the coupling reaction.[5,16] Thus, racemic **18** which is more readily obtainable can be used and indeed provided equally satisfactory results. Fragment A is now available in multigram quantities—adequate for further work.[17,18]

(16) For a recent review of the nucleophilic addition reaction of sulfoxide anions, see: Solladie, G. In "Asymmetric Synthesis"; Morrison, J. D. Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 6. Also compare: Williams, D. R.; Phillips, J. G.; Huffman, J. C. *J. Org. Chem.* **1981**, *46*, 4101.

(17) The synthesis proceeds in 17 steps from triol **7** (via Scheme II) in an overall yield of 6.3%.

(18) All new compounds prepared in this work have been fully characterized by means of high-resolution mass spectra, 250- or 270-MHz ^1H NMR, and IR spectra. Data for the compounds in Schemes I and II are listed in the supplementary material.

Acknowledgment. We are grateful to the National Institutes of Health (AI15403) and Kao Corporation, Japan, for financial support. P.M. is a National Cancer Institute Trainee (NCI Grant 5-T32-CA-09112). High-resolution mass spectra were provided by the facility supported by the National Institutes of Health (Grant RR 00317; principal investigator, Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Supplementary Material Available: Listing of spectral data for compounds in Schemes I and II (3 pages). Ordering information is given on any current masthead page.

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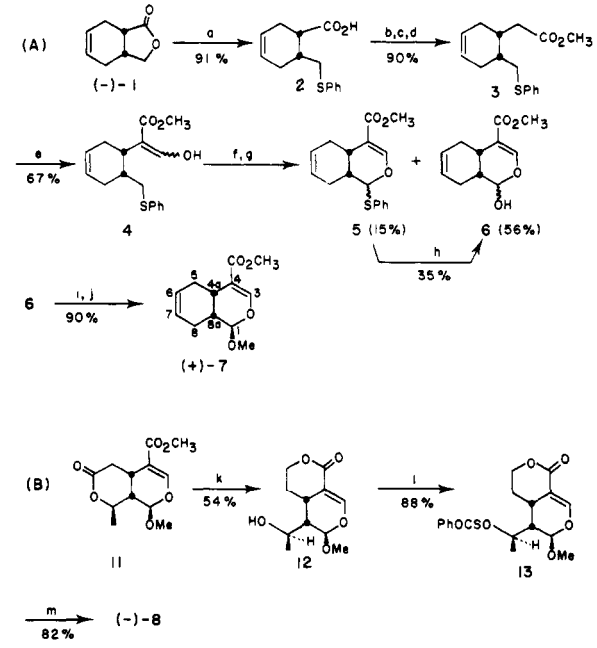
A General, Enantiospecific Synthesis of Cyclopentanoid Monoterpenes (Iridoids). The Total Synthesis of (−)-1-*O*-Methylsweroside Aglucon

Summary: A total synthesis of optically active cyclopentanoid monoterpenes (iridoids) can be achieved by using (−)-(1*S*,5*R*)-*cis*-3-oxabicyclo[4.3.0]non-7-en-2-one (1) to prepare a key bicyclic synthon, (+)-7. The generality and enantiospecificity of this approach is demonstrated by the preparation of (−)-1-*O*-methylsweroside aglucon (8).

Sir: The natural products known as cyclopentanoid monterpenes,[1] or iridoids,[2] are widely distributed in plants and are important for the biosynthesis of some types of indole alkaloids.[3] Because of this and the interest in those iridoids which have significant biological activity,[4] several research groups have pursued the synthesis of these natural products during the past 20 years.[1a,5] The inherent strategies have led to efficient and stereospecific total syntheses of many different iridoids[6] but cannot be adapted easily to the synthesis of structural analogues for use in biological studies and do not result in the correct absolute configuration in most cases. Four of the five previous syntheses of optically active iridoids involved resolution of racemic intermediates[6j] or lacked complete regio- and stereochemical control even when there was a high degree of asymmetric induction.[6h,cc,dd] We now report a general solution to the problem of synthetic versatility and enantiospecificity for the iridoids as exemplified by a synthesis of (−)-1-*O*-methylsweroside aglucon (8).[7]

The synthesis of (−)-8 employs (−)-(1*S*,5*R*)-*cis*-3-oxabicyclo[4.3.0]non-7-en-2-one (1), which can be produced on

Scheme I[a]



[a] (a) LiSPh, 1.05 equiv; DMF; reflux; 4 h. (b) $(COCl)_2$; C_6H_6; room temperature, 1.5 h. (c) CH_2N_2; Et_2O; room temperature, 4 h. (d) Ag_2O, catalyst; MeOH; reflux, 20 min. (e) LDA, 1.05 equiv; THF; −50 °C, 1 h; then HCO_2Et, 1.5 equiv; −50 °C, 1 h. (f) $NaIO_4$, 1 equiv; MeOH:THF:H_2O (6:3:4); room temperature, overnight. (g) 2,6-Lutidine, TFAA, 3 equiv; CH_3CN; −15 to 0 °C, 1 h. (h) $HgCl_2$, 3 equiv; CH_3CN:H_2O (3:1); reflux; 20 h. (i) BF_3; OEt_2; MeOH; 1 h, room temperature. (j) Allyl *O*-Me_3Si (excess); Tf-*O*-Me_3Si (catalyst); CH_2Cl_2, −20 to 0 °C, 3 h. (k) $NaBH_4$, 4 molar equiv; *i*-PrOH:H_2O (10:1); 0 to 15 °C, 6 h. (l) PhOC(S)Cl, DMAP, 2 equiv; CH_3CN:C_5H_5N (3:1); 80 °C, 3 h. (m) 170 °C, 20 min, N_2.

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(3) Cordell, G. A. "Introduction to Alkaloids. A Biogenetic Approach"; Wiley: New York, 1981; pp 810–830.

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