The conversion of *syn*-(methyl,hydro)bimane (1) to products was between 50% and 100%, based on the recovery of 1. The yields of 2 were between 25% and 30%, of 3 between a trace and 5%, and of 4 from 50% to 60%.

Kinetic Measurements. *syn*-(CH_3,F)B (2) was dissolved in CH_3CN. An aliquot (100 μL) was added rapidly to aqueous buffer, pH 10.2, maintained at 50.0 °C in a thermostated quartz cell located in the cell compartment of a Cary 17 spectrophotometer. The decrease of absorption at 360 nm was followed with time for more than 10 half-lives. The second-order rate constant for the reaction of the bimane with hydroxide ion was obtained from the experimental curve from the slope of the plot of log ($D_t - D_{inf}$) vs. time and dividing by the temperature corrected hydroxide ion concentration.

Regeneration of 2 from the Pyrazolinoylacrylic Acid. A mixture of the acid (obtained from base-catalyzed ring opening of *syn*-(CH_3,F)B and acidification) (1 mg) and thionyl chloride (10 μL) was stirred for 24 h. After removal of thionyl chloride under vacuum, the residue was shown to be identical with authentic *syn*-(CH_3,F)B (2) in absorption maximum (340 nm; dioxane), emission maximum (433 nm; dioxane), and thin-layer chromatographic behavior.

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A Convenient Method for Obtaining *trans*-2-Aminocyclohexanol and *trans*-2-Aminocyclopentanol in Enantiomerically Pure Form

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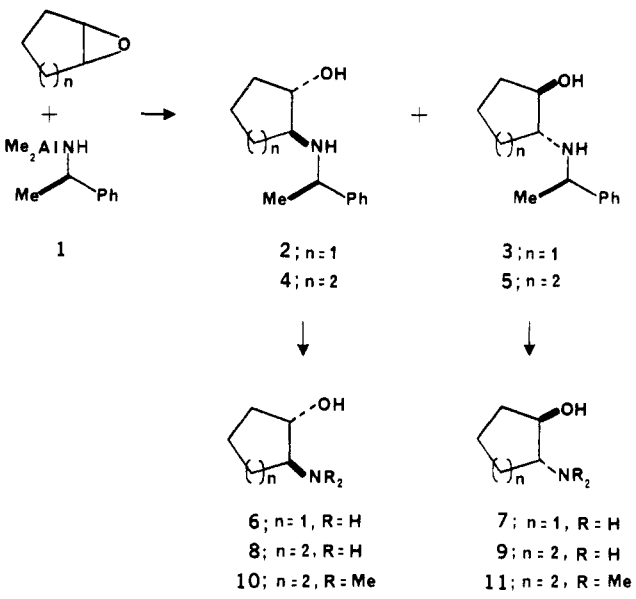
We recently reported[2] that Amaryllidaceae alkaloids could be prepared in good yield from 2-aminocyclopentanones by a sequence whose key step was a cationic aza-Cope rearrangement. In order to extend this approach to the preparation of these alkaloids in enantiomerically pure form,[3] we required a method for preparing (1*R*,2*R*)-*trans*-2-aminocyclopentanol on a large scale. This intermediate had previously been obtained by classical resolutions, which proceeded, however, in low overall efficiency.[4,5] In this paper, we report that both enantiomers of *trans*-2-aminocyclopentanol and *trans*-2-aminocyclohexanol can be conveniently obtained by the chromatographic separation of the diastereomeric *trans*-amino alcohols resulting from the reaction of cyclopentene oxide or cyclohexene oxide with the reagent[6] formed from (*R*)-α-methylbenzylamine and trimethylaluminum.

Scheme I



Aminolysis[6] of cyclopentene oxide or cyclohexene oxide with aluminum amide 1 proceeded in nearly quantitative yield at room temperature. Although this reaction occurred, not surprisingly, with virtually no diastereoselectivity, the amino alcohol products were easily separated in high yield (see Table I) by simple flash chromatography on silica gel. Hydrogenolysis[7] then provided highly enantiomerically pure samples of **6**–**9**[8] (Scheme I) in overall yields from the starting epoxide of 36–41%.

The general resolution method reported here should be useful for the preparation of other optically active β-amino alcohols.[10]

Experimental Section[11]

(1*S*,2*S*)-*trans*-2-[(*R*)-(α-Methylbenzyl)amino]cyclohexanol (4) and (1*R*,2*R*)-*trans*-2-[(*R*)-(α-Methylbenzyl)amino]cyclohexanol (5). A solution of Me_3Al (6.2 mL of a 2.0 M solution in toluene, 12.4 mmol) was added dropwise at 0 °C to a rapidly stirred solution of (+)-(*R*)-α-methylbenzylamine (1.50 g, 12.4 mmol)[11] and CH_2Cl_2 (10 mL). The resulting solution was maintained for 1 h at 0 °C and then a solution of cyclohexene oxide (1.28 g, 13.1 mmol) and CH_2Cl_2 (10 mL) was added dropwise. The resulting solution was maintained for an additional 3 h at 0 °C and then left overnight at 25 °C. The aluminate salt was decomposed[12] at 0 °C by adding 2.2 g (52 mmol) of NaF followed

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(4) See, inter alia: (a) *trans*-2-Aminocyclopentanol: Godchot, M.; Mousseron, M *Bull. Soc. Chim. Fr.* **1932**, *51*, 1270. (b) *trans*-2-(Benzylamino)cyclopentanol: Barr, A. A.; Frencel, I.; Robinson, J. B. *Can. J. Chem.* **1977**, *55*, 4180.

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(6) (a) Overman, L. E.; Flippin, L. A. *Tetrahedron Lett.* **1981**, *22*, 195. (b) This aminolysis can be accomplished with the reagent prepared from (*R*)-α-methylbenzylamine and triethylaluminum; however, the reaction is considerably slower.

(7) Anwer, M. K.; Spatola, A. F. *Synthesis* **1980**, 929.

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(10) A similar resolution procedure was recently employed in the synthesis of a fortimycin aglycone: Schubert, J.; Schwesinger, R.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 167.

(11) For general experimental details, see: Overman, L. E.; Jacobsen, E. J.; Doedens, R. J. *J. Org. Chem.* **1983**, *48*, 3393. (+)-(*R*)-α-Methylbenzylamine ($[\alpha]^{25}_D$ +39.4°, neat) was purchased from *Norse Laboratories*, Newbury Park, CA. Flash chromatography was carried out with E. Merck silica gel, 230–400 mesh.

(12) Yamamoto, H.; Muruoka, K. *J. Am. Chem. Soc.* **1981**, *103*, 4186.

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Table I. Physical Properties and Yields of Amino Alcohol Products

				HCl salt			
compd	$[\alpha]^{25}_D$, deg	c, solvent	mp, °C	$[\alpha]^{25}_D$, deg	c, solvent	mp, °C	yield, %[a]
2	+76.8	0.96, MeOH	oil			239–240	41
3	+22.1	1.2, MeOH	74–75			244–247	45
4	+86.7	1.3, MeOH	45–47			275–277	48
5	−15.5	1.0, MeOH	oil			201–203	51
6	+29.7[b,g]	1.5, EtOH	oil	+35.7[c]	0.86, H_2O	164–165	88
7	−32.9[g]	1.1, EtOH	oil	−34.1[d]	1.1, H_2O	163–164	82
8	+48.2[g]	1.0, MeOH	88–89				85
9	−48.5[g]	1.0, MeOH	85–86				71
10	+37.5[e]	5.0, H_2O	bp 96–98 (15 mm)				65
11	−37.9[f]	4.1, H_2O	bp 90–95 (12 mm)				74

[a] From the previous precursor. [b] This rotation may be slightly low due to the hygroscopic nature of this material. [c] Lit.[4b] +32.2 (c 0.9, H_2O). [d] Lit.[4b] −34.8 (c 1.6, H_2O). [e] Lit.[9] +38.2 (c, 5, H_2O). [f] Lit.[9] +39.8 (c 5, H_2O). [g] The enantiomeric excess of this sample was >96% as determined by 250-MHz ^1H NMR analysis of the amide formed from (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride.

by 1.4 mL (78 mmol) of H_2O. The resulting suspension was rapidly stirred for 1 h at 25 °C and filtered through a short column of Celite and the column was subsequently washed with 30 mL of CH_2Cl_2. The combined filtrates were dried (K_2CO_3), concentrated, and separated by flash chromatography (4.8 × 15 cm column, hexane/ethyl acetate/Et_3N 4:1:0.2) to give, in the first fractions, 1.4 g (51%) of pure **5** as a colorless oil and, in later fractions, 1.3 g (48%) of **4** as a crystalline solid. **4**: mp 45–47 °C, mp (HCl salt) 271–277 °C dec; R_f 0.34 (hexane/ethyl acetate/Et_3N 1:1:0:1); IR ($CHCl_3$) 3200–3700, 1605, 1452, 1120, 1065 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.15–7.40 (m, Ph), 3.99 (q, J = 6.6 Hz, C*H*Me), 3.15 (app dt, J = 4.4, 10 Hz, OCH), 1.34 (d, J = 6.6 Hz, Me), 0.8–2.2 (m, 11 H). MS (isobutane, CI), m/e 220 (MH), 204, 142, 116, 98; $[\alpha]^{24}_{546}$ +103° (c 1.26, MeOH). Anal. Calcd (HCl salt) for $C_{14}H_{22}ClNO$: C, 65.75; H, 8.61; Cl, 13.89; N, 5.48. Found: C, 65.83; H, 8.67; Cl, 13.93; N, 5.46. **5**: mp (HCl salt) 201–203 °C; R_f 0.49 (hexane/ethyl acetate/Et_3N 1:1:0.1); IR ($CHCl_3$) 3200–3700, 1602, 1450, 1277, 1060 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.2–7.4 (m, Ph), 3.91 (q, J = 6.6 Hz, C*H*Me), 3.09 (ddd, J = 4.5, 9.8, 10.1 Hz, OCH), 2.32 (ddd, J = 3.9, 10.1, 10.3 Hz, NCH), 1.33 (d, J = 6.6 Hz, Me), 0.8–2.2 (m, 10 H); MS (isobutane CI) m/e 220 (MH), 204, 142, 116, 98; $[\alpha]^{24}_{546}$ −18.3 (c 1.0, MeOH). Anal. Calcd (HCl salt) for $C_{14}H_{22}ClNO$: C, 65.75; H, 8.61; Cl, 13.89; N, 5.48. Found: C, 65.86; H, 8.71; Cl, 13.99; N, 5.45.

(1*S*,2*S*)-*trans*-2-[(*R*)-(α-Methylbenzyl)amino]cyclopentanol (2) and (1*R*,2*R*)-*trans*-2-[(*R*)-(α-Methylbenzyl)amino]cyclopentanol (3). An identical sequence starting with 14.2 g of cyclopentene oxide provided 14 g (45%) of crystalline **3** [mp 74–75 °C, mp (HCl salt) 244–247 °C; R_f 0.33 (hexane/ethyl) acetate/Et_3N 1:1:0.1] and 13 g (41%) of pure **2** [colorless oil, mp (HCl salt) 239–240 °C; R_f 0.25 (hexane/ethyl acetate Et_3N 1:1:0.1].[3]

(1*R*,2*R*)-*trans*-2-Aminocyclopentanol (7). The general procedure of Anwer and Spatola was utilized.[7] A mixture of the HCl salt of **3** [prepared from 269 mg (1.31 mmol) of **3**], ammonium formate (420 mg, 6.6 mmol), 10% Pd/C (0.32 g), and dry *N*,*N*-dimethylformamide was heated at 110–120 °C for 4 h. After cooling to room temperature, the reaction mixture was filtered through Celite (~1 g), the filter cake was washed with MeOH (3 × 5 mL), and the combined filtrates were concentrated. The residue was partioned between $CHCl_2$ and saturated aqueous KOH and the organic layer was separated and dried (K_2CO_3). Concentration gave 109 mg (82%) of pure **7** as a colorless oil: mp (HCl salt) 163–164 °C, lit.[4b] mp 161–163 °C; optical rotations (HCl salt) $[\alpha]^{22}_D$ −34.1°, $[\alpha]^{22}_{546}$ −34.2°, $[\alpha]^{22}_{365}$ −76.0° (c 1.1, H_2O), lit.[4b] $[\alpha]^{20}_D$ −34.8° (c 1.6, H_2O); optical rotations (free base) $[\alpha]^{24}_D$ −32.9°, $[\alpha]^{24}_{546}$ −38.8° (c 1.1, EtOH), lit.[4b] $[\alpha]^{20}_D$ −33.3° (c 1.7, EtOH).

Amino alcohols **6**, **8**, and **9** were prepared in an identical fashion, and these results are summarized in Table I.

(1*S*,2*S*)-*trans*-2-(Dimethylamino)cyclohexanol (10). A solution of **8** (505 mg, 4.39 mmol), 37% HCHO (7 mL), and HCOOH (7 mL) was heated at reflux for 23 h and concentrated. The residue was partioned between Et_2O and 5 N NaOH, the organic layer was separated, the aqueous layer was washed with additional Et_2O, and the combined organic extracts were dried (K_2CO_3). Concentration and distillation of the residue [bulb to bulb; bp 96–98 °C, (15 mm)] gave 408 mg (65%) of pure **10**: $[\alpha]^{24}_D$ +37.5°, $[\alpha]^{24}_{546}$ +44.1°, $[\alpha]^{24}_{365}$ +186° (c 5.1, H_2O); lit.[9] $[\alpha]^{20}_D$ +38.2 (c 5, H_2O).

Amino alcohol **11** was prepared in an identical fashion (see Table I).

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An Unusual β,γ-Epoxy γ-Lactone from the Sponge *Dysidea etheria*[1,2]

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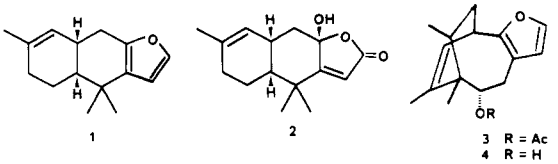
Our investigation of the secondary metabolites of the Bermudian sponge *Dysidea etheria* has resulted in the isolation and identification of a series of unusual ceramides[3] and a group of sesquiterpenes, including furodysinin (**1**), furodysinin lactone (**2**), and 5-acetoxy- and 5-hydroxynakafuran 8 (**3**, **4**).[4] In the course of reisolating quantities of 5-hydroxynakafuran 8 for stereochemical studies, we encountered a minor metabolite which exhibited some of the NMR spectral characteristics of furodysinin (**1**) but which was somewhat more polar.



This new sesquiterpene was readily purified by low-pressure adsorption and gel-permeation chromatography. Mass spectral analysis of the colorless oil revealed the molecular formula to be $C_{15}H_{20}O_3$. The presence of a γ-lactone (1783 cm^{-1}) and the absence of hydroxyl or additional carbonyl groups was evident from the IR spectrum; the remaining oxygen, then, had to constitute an ether linkage. A trisubstituted olefin was apparent from the ^{13}C NMR data, leaving the last three sites of unsaturation to be accommodated by two carbocyclic rings and a cyclic ether.

^1H NMR decoupling experiments (see Table I) provided part structure **5a**, which, together with the γ-lactone, 2

(1) Dedicated respectfully to Professor Paul J. Scheuer on the occasion of the seventieth anniversary of his birth.
(2) Contribution 1001 from the Bermuda Biological Station.
(3) Grode, S. H.; Cardellina, J. H. II. *Lipids* **1983**, *18*, 889.

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