3.22 ppm) for the OCH_3 at the 6-position suggests that the 1 molecule is preferentially bound to DMe-β-CDx from the upper side of the cavity. Since the lower side of the DMe-β-CDx cavity is wider than that of the TMe-β-CDx cavity, the 1 molecule may be bound to the upper side of the DMe-β-CDx cavity to optimize a van der Waals contact.

Although NMR measurements of the 1–TMe-β-CDx system in acidic medium should be essential to know the reason for the inversion of the bisignate CD signals, precipitation of 1 in acidic solution made it impossible to measure NMR spectrum of this complex.

Conclusion

The present paper reports a new conformational enantiomerism in the γ-CDx cavity. We regard the 1–γ-CDx complex as a model for studying the mechanism of chiral recognition by CDxs in aqueous solutions.

The relative enantioselectivities were conveniently evaluated from the intensities of the bisignate CD signals of the inclusion complexes. γ-CDx is the most effective host molecule, where a carboxylate anion of a naphthalene moiety of 1 included in the γ-CDx cavity interacts with a secondary hydroxyl group of γ-CDx through hydrogen bonding and another naphthalene moiety of 1 is located at the rim of the primary hydroxyl group side of γ-CDx. The hydrogen-bonding interaction seems to be achieved when the size of the guest molecule fits well with that of the host to optimize the van der Waals contact. Such cooperative hydrogen bonding and van der Waals interactions give rise to the large stability of the 1-γ-CDx inclusion complex. According to the three-point attachment model,[5] a guest molecule should interact with CDx at, at least, three points in order for chiral recognition to occur. For the 1–γ-CDx system, two points are clarified: namely, (1) hydrogen bonding between the host and guest molecules and (2) tight inclusion of the guest in the host cavity. An additional point seems to be a steric factor. An X-ray crystallographic study indicates that γ-CDx has an almost round shape but is somewhat distorted from the regular octagonal structure.[23]

The present study also reveals that the hydrogen-bonding interaction is not essential for chiral recognition by CDx. Few examples of chiral recognition by CDxs without the aid of hydrogen bonding have been reported.[10,13,14] In the case where hydrogen bonding does not participate, steric factors should dominate the enantioselectivity.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research on Priority Areas, "Multiplex Organic Systems" (No. 01649006), and by a Grant-in-Aid for Science Research (No. 01550657) from the Ministry of Education, Science and Culture, Japan. We are indebted Y. Kojima for her experimental assistance.

Registry No. 1, 6640-22-8; 2, 1096-84-0; 3, 607-50-1; 4, 92-70-6; β-CDx, 7585-39-9; γ-CDx, 17465-86-0; DMe-β-CDx, 51166-71-3; TMe-β-CDx, 55216-11-0.

Supplementary Material Available: Analytical data of 1–3, disodium salt of 1, DMe-β-CDx, and TMe-β-CDx and the NOE difference spectrum of the equimolar solution of 1 and γ-CDx in D_2O (3 pages). Ordering information is given on any current masthead page.

(23) Harata, K. *Chem. Lett.* **1984**, 641–644.

Base-Induced and -Directed Elimination and Rearrangement of Perhydronaphthalene-1,4-diol Monosulfonate Esters. Total Synthesis of (±)-Alloaromadendrane-4β,10α-diol and (±)-Alloaromadendrane-4α,10α-diol

Louis H. D. Jenniskens, Joannes B. P. A. Wijnberg,* and Aede de Groot*

Laboratory of Organic Chemistry, Agricultural University, Dreijenplein 8, 6703 HB Wageningen, The Netherlands

Received May 13, 1991

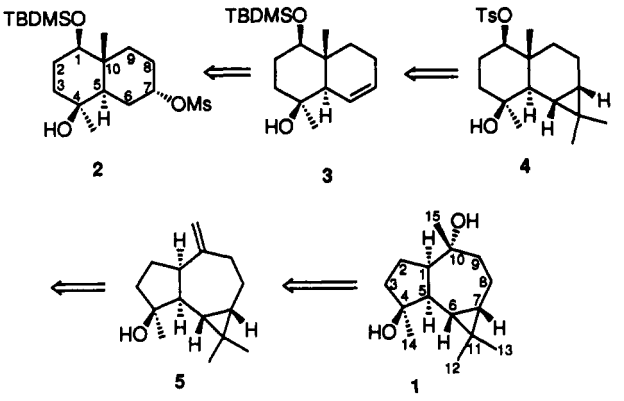
The total synthesis of (±)-alloaromadendrane-4β,10α-diol (1), supposedly isolated from *Ambrosia peruviana* Willd., is described. The strategically positioned axial hydroxyl group at C(4) played a crucial role in the two key steps of this synthesis (2 and 11 → 3; 4 → 5). Upon treatment with sodium *tert*-amylate in refluxing toluene, both the mesylates 2 and 11 predominantly gave the olefin 3. A mechanism for this regioselective elimination is proposed. The double bond of 3 at C(6)–C(7) was used to introduce a dimethylcyclopropane ring at this position. The intramolecular base-induced rearrangement of 4 proceeded with high selectivity, again guided by the alkoxide at C(4). The resulting exo olefin 5 was converted into diol 1, but its spectral data did not agree with those reported for the natural diol. The epimeric (±)-alloaromadendrane-4α,10α-diol (23) was prepared from 5 via a dehydratation, epoxidation, reduction sequence. Now the spectral data of the natural and the synthetic diol agreed very well and a revision of the structure of the natural product is postulated.

Previous publications[1] from this laboratory demonstrated the base-induced and -directed rearrangement of substituted *trans*-perhydronaphthalene-1,4-diol monosulfonate esters as an effective route to *cis*-perhydroazulene systems with an exocyclic methylene unit. The highly developed understanding of the stereochemistry and conformational analysis of the substituted perhydronaphthalenes makes this rearrangement a very useful one for the synthesis of cis-fused guaianes and other natural products bearing a cis 5,7 fused-ring framework.

(1) (a) Wijnberg, J. B. P. A.; de Groot, Ae. *Tetrahedron Lett.* **1987**, *28*, 3007. (b) Wijnberg, J. B. P. A.; Jenniskens, L. H. D.; Brunekreef, G. A.; de Groot, Ae. *J. Org. Chem.* **1990**, *55*, 941.

0022-3263/91/1956-6585$02.50/0

Scheme I

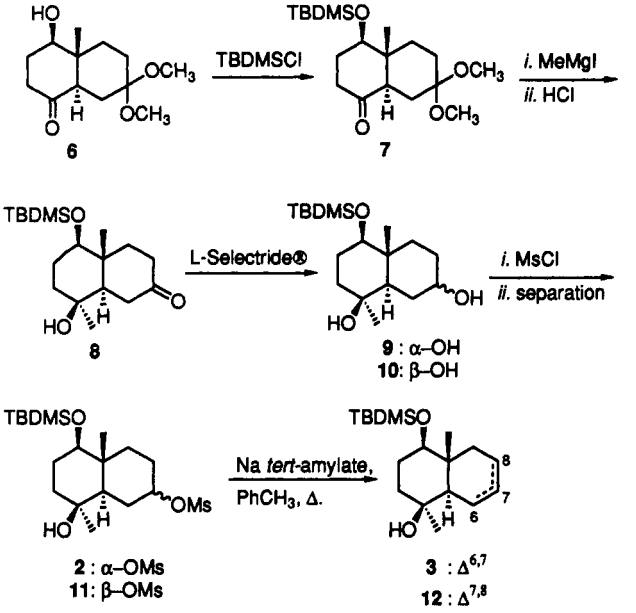


Recently the isolation of an (+)-alloaromadendrane-4,10-diol from *Ambrosia peruviana* Willd. has been reported.[2] This compound is an effective inhibitor to the growth of the fungus *Cladosporium herbarium* and stimulates root and shoot growth in lettuce seedlings at low concentrations. The aromadendrane skeleton and the cis 5,7 fused-ring junction of this compound have been identified by chemical and spectroscopic means. The stereochemistry of the hydroxyl groups at C(4) and C(10) has been assigned by correlating features of molecular models with data from its NMR spectra and the NMR spectra of four isomeric trans-fused aromadendrane-4,10-diols obtained from natural spathulenol.[3,4] Based on these informations, it has been proposed that the natural product isolated from *A. peruviana* possesses the stereochemistry as shown in structure **1**. In this paper the total synthesis of (±)-alloaromadendrane-4β,10α-diol (**1**) and of (±)-alloaromadendrane-4α,10α-diol (**23**) is described and a revision of the structure of the natural product is proposed.

Our synthetic plan for diol **1**, shown in Scheme I, was inspired by the possibility of a base-induced and -directed rearrangement of the tosylate **4** to the cis-fused perhydroazulene compound **5** with an exocyclic double bond. This double bond will permit easy introduction of the α-hydroxyl group at C(10). The synthesis of compound **4** requires annelation of a cyclopropane ring at C(6)–C(7), which should be possible starting from a double bond at this position as shown in compound **3**. The β-hydroxyl group at C(4) of the mesylate **2** was estimated to be able to guide the elimination of the mesylate group in the proper direction.[5,6] Therefore, the main feature of this strategy is the central role of the axial tertiary hydroxyl group at C(4) in the two key steps of this total synthesis: (i) the selective formation of **3** and (ii) the skeletal rearrangement.

The readily available monoacetalized hydroxy dione **6**, previously used in the total syntheses of eudesmane[7] and guaiane[1b] sesquiterpenes, was the starting material for the synthesis of the α-mesylate **2** (Scheme II). The secondary hydroxyl group of **6** was first protected as its TBDMS ether, and the resulting product **7** was treated with an excess of MeMgI in dry ether at rt.[8] Hydrolysis of the dimethyl acetal function with a catalytic amount of HCl in aqueous acetone afforded the monoprotected keto diol **8**. For the synthesis of the α-mesylate **2**, it was necessary to reduce the ketone **8** to the corresponding α-alcohol **9**. For that purpose L-Selectride (Aldrich) seemed the most suitable reagent.[9] Unexpectedly, however, treatment of **8** with this reagent in dry THF at −78 °C produced a 1:1.1 mixture of **9** and the β-alcohol **10**, respectively. Other reducing reagents were tried but invariably gave more of the β-alcohol **10**; $NaBH_4$ reduction of **8** for instance produced a 1:6.6 mixtures of **9** and **10**, respectively, in quantitative yield.

Scheme II

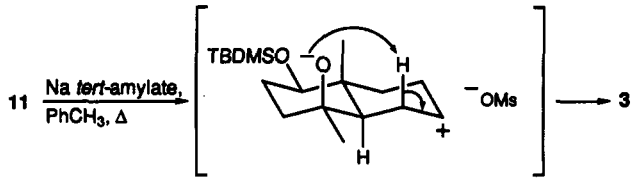


Confronted with this problem, we decided to investigate not only the usefulness of the α-mesylate **2** but also that of the β-mesylate **11** for the synthesis of the olefin **3**. Therefore, the 1:1.1 mixture of **9** and **10**, obtained from the L-Selectride reduction of **8**, was mesylated and separated by column chromatography to give pure **2** and **11** in a total yield of 96% overall from **8**.

In the elimination reactions (**2** and **11** → **3**) we decided to employ the same reaction conditions as we had planned for the base-induced skeletal rearrangement of **4** (vide infra), i.e., sodium *tert*-amylate in refluxing toluene. When the α-mesylate **2** was treated in this way with 10 equiv of sodium *tert*-amylate, the reaction was completed within 2 min and an inseparable mixture of the double-bond isomers **3** and **12** was obtained in high yield. According to GC analysis, this mixture consisted of more than 90% of one olefin, which was expected to be the desired olefin **3**. This was confirmed by the ^{13}C NMR spectrum of this mixture. The signals due to the olefinic carbon atoms of the major olefin **3** appear at δ 124.11 and 129.35 and the corresponding signals of the isomeric minor olefin **12** resonance at δ 125.30 and 125.47. Furthermore, the bridgehead carbon C(5) in **3** has a chemical shift of 49.95 ppm, while in the minor olefin **12** C(5) gives rise to a signal at 46.10 ppm. Similar differences in the chemical shifts

(2) Goldsby, G.; Burke, B. A. *Phytochemistry* **1987**, *26*, 1059.
(3) Beechan, C. M.; Djerassi, C.; Eggert, H. *Tetrahedron* **1978**, *34*, 2503.
(4) Jizba, J.; Laudová, V.; Samek, Z.; Ubik, K.; Novotny, C. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1048.
(5) In the absence of a directing group, elimination reactions in trans-fused steroid systems lead mainly toward the formation of $\Delta^{2,3}$ double-bond isomers. For example, see: (a) Hanessian, S.; Kagotani, M.; Komaglou, K. *Heterocycles* **1989**, *28*, 1115. (b) Loibner, H.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100.
(6) Similar elimination reactions have been reported: (a) Menger, F. M.; Chow, J. F.; Kaiserman, H.; Vasquez, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4996. (b) Lansbury, P. T.; Mojica, C. A. *Tetrahedron Lett.* **1986**, *27*, 3967.
(7) Wijnberg, J. B. P. A.; Vader, J.; de Groot, Ae. *J. Org. Chem.* **1983**, *48*, 4380.
(8) MacKenzie, B. D.; Angelo, M. M.; Wolinsky, J. *J. Org. Chem.* **1979**, *44*, 4042.
(9) Brown, E.; Lebreton, J. *Tetrahedron* **1987**, *43*, 5827.

Scheme III



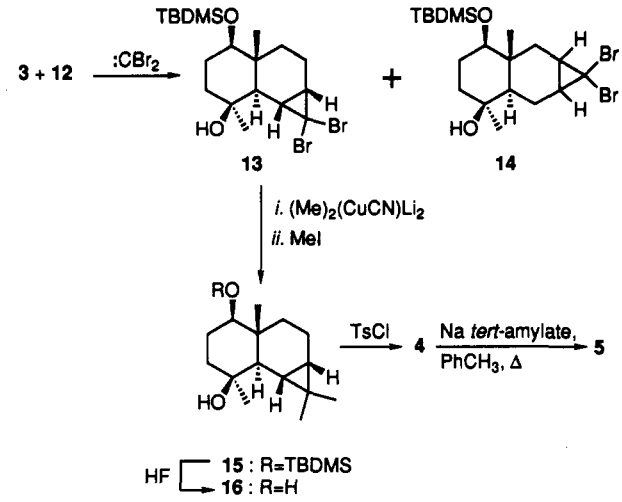
A

of the olefinic carbon atoms and the bridgehead carbons of Δ^2- and Δ^3-steroids have been reported.[10] For the equatorial β-mesylate **11**, a very slow elimination process was expected. To our surprise, it was found that the reaction was completed within 2 min when the β-mesylate **11** was treated with 10 equiv of sodium *tert*-amylate in refluxing toluene. After workup and purification, a 6.5:1 mixture of **3** and **12**, respectively, was isolated in 57% yield. In a similar way, a 8.4:1 mixture of **3** and **12** was prepared in 66% yield from the 1:1.1 mixture of **2** and **11**. So, both the epimeric mesylates **2** and **11** gave the olefin **3** as the major product.

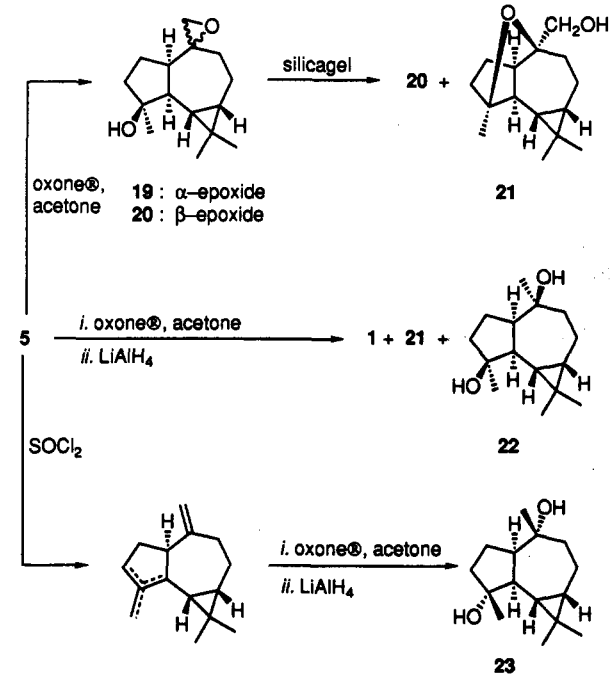
These results may lead to the conclusion that the elimination reaction of the β-mesylate **11** proceeds via a dipolar intermediate, just as in our earlier proposed mechanism for the rearrangement process.[1b] Thus, deprotonation of the hydroxyl group of **11** by the strong base induces a heterolysis of the sulfonate ester bond via a "through-bond" inductive mechanism over four σ bond leading to the dipolar intermediate **A** (Scheme III). Additional support for this idea was obtained from an experiment in which the O^- group was omitted. When (2α,4aα,8aβ)-decahydro-4a-methyl-2-naphthol methanesulfonate was treated with sodium *tert*-amylate in benzene at reflux temperature, no elimination or fragmentation products were found and most of the starting material could be recovered. Formation of **A** may additionally be facilitated by an indirect "through-space" inductive effect because the back lobe of the C(4)–C(5) bond can give overlap with the incipient p orbital of the cationic center in **A**.[11] In **A** the alkoxide substituent and the β-H on C(6) are 1,3-diaxially positioned, and this makes the formation of **3** via an intramolecular deprotonation the most favorable process. A similar dipolar intermediate formed during the elimination reaction of the α-mesylate **2** is also possible and cannot be excluded. Further studies probing the mechanism of this intramolecular alkoxide-induced elimination reaction are in progress.

The next step in our synthetic route toward the 4β,10α-diol **1** was the introduction of the *gem*-dimethylcyclopropane ring, which is most commonly prepared by dimethylation of *gem*-dihalocyclopropane derivatives.[12,13] The reaction of dibromocarbene, prepared from bromoform and sodium *tert*-amylate, with a 7:1 mixture of the double-bond isomers **3** and **12** afforded the corresponding dibromides **13** and **14** in 76 and 11% yield, respectively (Scheme IV). Since one would expect the dibromocarbene

Scheme IV



Scheme V



to approach the double bond in **3** from the less hindered α-face of the molecule, the product **13** was assigned the indicated structure. The reaction of the dibromide **13** with the higher order organocuprate, prepared from copper(I) cyanide and methyllithium, followed by addition of methyl iodide, readily afforded the *gem*-dimethylcyclopropane compound **15** in 60% yield. Cleavage of the TBDMS protecting group (**15** → **16**) followed by tosylation of the secondary alcohol (**16** → **4**) could be achieved in 93% overall yield. The base-induced skeletal rearrangement of this tosylated maaliane derivative **4** was performed as described,[1b] using toluene in place of benzene.[14] After workup and column chromatography the hydroxy alloaromadendrane derivative **5** was isolated in 70% yield. Two minor products were identified as the cyclic ether **17** (7%) and the germacrane-like compound **18** (7%). The formation of **17** can be explained by direct trapping of the positive charge by the proximate alkoxide.[1b] A fragmen-

(10) (a) Tori, K.; Komeno, T.; Sangaré, M.; Septe, B.; Delpech, B.; Ahond, A.; Lukacs, G. *Tetrahedron Lett.* **1974**, 1157. (b) Blunt, J. W.; Stothers, J. B. *Org. Magn. Reson.* **1977**, *9*, 439. (c) Eggert, H.; Djerassi, C. *J. Org. Chem.* **1981**, *46*, 5399.

(11) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.

(12) (a) Rigby, J. H.; Bellemin, A.-R. *Synthesis* **1989**, 188. (b) Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911. (c) Harayama, T.; Fukushi, H.; Aratani, T.; Ogawa, K.; Murata, T.; Taga, T.; Yoneda, F. *Chem. Pharm. Bull.* **1987**, *35*, 1777.

(13) (a) Seyfert, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4258. (b) Taylor, M. D.; Minaskanian, G.; Winzenberg, K. N.; Santone, P.; Smith, A. B., III. *J. Org. Chem.* **1982**, *47*, 3960.

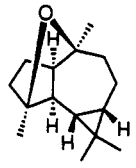
(14) Substantially shorter reaction times were found when the reaction was performed in the less hazardous toluene. Yields and product ratios were not affected by this change of solvent.

Table I. ^{13}C NMR Spectral Data of the Natural (+)-Alloaromadendrane-4,10-diol and the Synthetic Alloaromadendrane-4,10-diols 1, 22, and 23

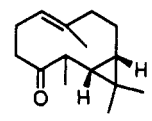
mult	natural product[a]	1	22	23
s	18.6	19.49	20.31	18.63
	74.3	74.72	74.79	74.32
	82.1	79.87	79.47	82.05
d	25.3	22.71	22.20	25.20
	28.8	26.25	25.38	28.73
	47.8	45.22	46.49	47.57
	54.0	50.37	46.76	53.80
t	18.7	20.71	22.20	18.67
	25.1	25.59	25.62	25.07
	37.4	39.16	39.72	37.34
	37.9	41.47	42.22	37.90
q	16.4	15.45	15.43	16.19
	25.6	27.39	23.74	25.53
	28.5	28.30	28.58	28.50
	32.2	28.86	29.29	32.09

[a] Taken from ref 2.

tation accompanied by a methyl shift accounts for the formation of 18.



17



18

A selective epoxidation of the olefin 5, followed by reduction of the resulting epoxide, was required for the synthesis of 1. When 5 was treated with in situ generated dimethyldioxirane,[15] a mixture of two products was formed in a ratio of 4.3:1, according to GC analysis. Attempts to separate this mixture on silica gel led to the isolation of the minor β-epoxide 20, while the major epoxidation product 19 was found to be completely converted into the cyclic hydroxy ether 21 (Scheme V). The acidic character of the silica gel facilitates the opening of the epoxide ring of 19 by an intramolecular nucleophilic attack of the tertiary hydroxyl group leading to 21. The formation of 21 corroborated the cis-fused ring junction of the 5,7-ring system and proved that the epoxidation step had occurred preferentially from the less hindered α-side of the olefin 5. In order to suppress the undesired formation of 21, we decided to reduce the crude epoxide mixture of 19 and 20 with $LiAlH_4$ without previous chromatographic purification. In this way a mixture of three products was obtained with the 4β,10α-diol 1 as the main product (46% yield overall from 5). The two other isolated products were identified as the 4β,10β-diol 22 (16%) and 21 (18%). Again, on the basis of these results, one can conclude with confidence that our synthetic product 1 possesses a cis-fused 5,7-ring junction and that the relative stereochemistry of the two hydroxyl groups at C(4) and C(10) is trans as shown in structure 1. However, the ^{13}C NMR spectral data of our synthetic product 1 are different from those of the natural alloaromadendrane-4,10-diol (Table I).

Even more noticeable differences were observed in the ^1H NMR spectra of both compounds. In the ^1H NMR spectrum of the natural product,[2] the two cyclopropane ring protons at C(6) and C(7) give rise to a t (J = 9.7 Hz) and a ddd (J = 5.8, 9.7, 11.6 Hz) at δ 0.00 and 0.62, respectively. Furthermore, the methyl groups give rise to s at δ 1.02, 1.03, 1.19, and 1.33. In the ^1H NMR spectrum of our synthetic product 1, the protons at C(6) and C(7) give rise to an overlapping m at δ 0.48–0.68. The signals due to the methyl groups appear at δ 0.95, 1.03, 1.24, and 1.32. Consequently, the natural product and the synthetic 1 must have differences in their stereochemistry. Comparison of the spectral data of the 4β,10β-diol 22 with those of the natural product also showed significant differences (Table I and Experimental Section).

As the natural product was easily silylated to its di-OTMS derivative,[2] we had reason to believe that in this structure the hydroxyl groups at C(4) and C(10) are positioned on the less hindered α-face of the molecule, so that in the natural product the hydroxyl group at C(4) probably has a different stereochemistry than proposed. The olefin 5 was converted to the 4α,10α-diol 23 in order to test this assumption (Scheme V). Treatment of 5 with thionyl chloride in pyridine at −15 °C afforded an uncharacterized, highly volatile mixture of double-bond isomers in a ratio of 6:3:1, according to GC analysis. Reaction of this mixture with dimethyldioxirane gave a complex mixture of epoxides. Again, as in the case of the epoxidation of 5, epoxidation was expected to occur preferentially from the less hindered α-face of the molecule. The mixture of epoxides was treated with $LiAlH_4$ and gave diol 23 in an overall yield of 23% from 5.

As this diol 23 differs clearly from the diols 1 and 22, 23 must have the opposite stereochemistry at C(4). The relative stereochemistry at C(10) was ascertained by ^1H NOE difference spectroscopy. By irradiation of the triplet for H(6) at δ −0.03, NOEs with the methyl groups at δ 1.30, 1.16, and 1.01/0.99 were observed. Since no NOE exists between H(6) and the α-methyl group of the *gem*-dimethylcyclopropane ring,[16] this observation led to the conclusions that one of the NOE signals arises from the methyl group at C(10) and that this methyl group is consequently positioned on the β-side of the molecule. To affirm this conclusion, we irradiated the H(1) at δ 2.45, which is on the α-face of the molecule. Now, no NOE with any of the methyl groups was observed, so the synthesized product is the 4α,10α-diol. The NMR spectral data of this 4α,10α-diol 23 agree very well with those reported for the natural product[2] (Table I and Experimental Section). Consequently, the natural product isolated from *A. peruviana* possesses the stereochemistry as shown in structure 23, and not the one proposed in structure 1.[17]

Experimental Section

Melting points are uncorrected. Chemical shifts are reported relative to TMS (δ 0.00), with $CHCl_3$ as internal standard (δ 7.23 (^1H) and δ 76.90 (^{13}C)). ^{13}C NMR multiplicities were determined by using a DEPT pulse sequence. ^1H NOE difference experiments were performed at 200 MHz, using a τ_m of 2 s. MS data were determined at 70 eV on either an AEI MS 902 spectrometer or a Hewlett Packard 5970B series Mass Selective Detector, coupled with a DB-17 fused silica capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm. GC analyses were carried out with FID and a DB-17 fused silica capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm. Peak areas were integrated electronically. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh).

Solvents were dried and freshly distilled by common practice. For all dry reactions, flasks were dried at 150 °C and flushed with

(15) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(16) Inagaki, F.; Abe, A. *J. Chem. Soc., Perkin Trans. II* **1985**, 1773.

(17) This conclusion is confirmed by other work going on at our laboratory in which (−)-apoaromadendrone[18] was converted into both (+)-23 and its C(10)-epimer, the 4α,10β-diol.[19]

(18) Gijsen, H. J. M.; Kanai, K.; Stork, G. A.; Wijnberg, J. B. P. A.; Orru, R. V. A.; Seelen, C. G. J. M.; van der Kerk, S. M.; de Groot, Ae. *Tetrahedron* **1990**, *46*, 7237.

(19) Details of this work are submitted for publication in *Tetrahedron* by H. J. M. Gijsen, J. B. P. A. Wijnberg, G. A. Stork, Ae. de Groot, M. A. de Waard, and J. G. M. van Nistelrooy.

dry N_2 just before use, and reactions were carried out under N_2, unless otherwise reported. Product solutions were dried over $MgSO_4$ prior to evaporation of the solvent under reduced pressure on a rotary evaporator. Bromoform was filtered over ICN alumina B-Super I (activity grade Super I) just before use. Sodium *tert*-amylate (3.5 M in toluene) was prepared as described elsewhere.[20]

(4α,4aα,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]octahydro-7,7-dimethoxy-4a-methyl-1(2*H*)-naphthalenone (7). To a solution of 16.56 g (68.4 mmol) of the alcohol **6**[7] in 90 mL of DMF were added 11.64 g (171 mmol) of imidazole and 12.87 g (85.5 mmol) of TBDMSCl. The reaction mixture was stirred at rt for 3 d and then poured into 300 mL of water. The two-phase mixture was separated, and the aqueous layer was extracted with five 100-mL portions of CH_2Cl_2. The combined organic layers were washed with 150 mL of brine, dried, and evaporated under reduced pressure. The resulting product was flash chromatographed on silica gel (10:1 to 1:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 21.28 g (87%) of silyl ether **7**: mp 69.5–70.5 °C (from absolute EtOH); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.05 (s, 6 H), 0.70 (s, 3 H), 0.80 (s, 9 H), 1.00–2.60 (m, 11 H), 3.04 (s, 3 H), 3.12 (s, 3 H), 3.73 (dd, J = 6, 10 Hz, 1 H); MS, m/e (rel intensity) 356 (M^+, 23), 341 (3), 325 (25), 299 (100), 267 (41), 193 (41), 175 (36), 101 (42); calcd for $C_{19}H_{36}O_4Si$ (M^+) m/e 356.2383, found m/e 356.2400. Anal. Calcd for $C_{19}H_{36}O_4Si$: C, 64.00; H, 10.17. Found: C, 64.19; H, 10.44.

(4aα,5α,8α,8aβ)-5-[(*tert*-Butyldimethylsilyl)oxy]octahydro-8-hydroxy-4a,8-dimethyl-2(1*H*)-naphthalenone (8). To 360 mL of 0.62 M MeMgI in ether was added dropwise a solution of 19.79 g (55.6 mmol) of silyl ether **7** in 360 mL of dry ether. The reaction mixture was stirred at rt for 42 h, after which time the excess MeMgI was quenched by careful addition of saturated aqueous NH_4Cl. After addition of 500 mL of water, the two-phase mixture was separated and the aqueous layer was extracted with five 150-mL portions of CH_2Cl_2. The combined organic layers were washed with 300 mL of brine, dried, and evaporated under reduced pressure. The remaining residue was taken up in 500 mL of acetone, and 10 mL of water and three drops of concentrated HCl were added. After stirring at rt for 20 min, 5 mL of saturated aqueous $NaHCO_3$ was added. The reaction mixture was concentrated under reduced pressure, taken up in 500 mL of water, and extracted with five 200-mL portions of CH_2Cl_2. The combined organic layers were washed with 200 mL of brine, dried, and evaporated under reduced pressure. Recrystallization from diisopropyl ether and flash chromatography of the mother liquid on silica gel (10:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 15.06 g (83%) of pure **8**: mp 143–145 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.00 (s, 3 H), 0.03 (s, 3 H), 0.83 (s, 9 H), 0.90–2.80 (m, 12 H), 1.10 (s, 3 H), 1.20 (s, 3 H), 3.26 (dd, J = 4, 10 Hz, 1 H); MS, m/e (rel intensity) 311 (M^+ – 15, 1.6), 293 (1), 269 (31), 251 (13), 177 (100), 159 (18), 135 (41), 131 (31), 119 (22), 75 (46); calcd for $C_{17}H_{31}O_3Si$ (M^+ – 15) m/e 311.2042, found m/e 311.2049. Anal. Calcd for $C_{18}H_{34}O_3Si$: C, 66.20; H, 10.49. Found: C, 66.11; H, 10.67.

(1α,4α,4aα,7β,8aβ)- and (1α,4α,4aα,7α,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]decahydro-1,4a-dimethyl-1,7-naphthalenediols (9 and 10). To a solution of 3.26 g (10.0 mmol) of ketone **8** in 80 mL of dry THF was added dropwise 25 mL of 1 M L-Selectride in THF at –78 °C. The solution was warmed to 0 °C over 1 h, and then a mixture of 10 mL of water and 35 mL of EtOH was added. After stirring for 20 min, 10 mL of 6 M NaOH and 25 mL of 30% H_2O_2 were added and stirring was continued for 16 h. The mixture was then concentrated under reduced pressure and the resulting residue was taken up in 150 mL of water. The aqueous layer was extracted with four 100-mL portions of ether. The combined organic layers were dried and evaporated under reduced pressure to afford 3.28 g (100%) of a 1:1.1 mixture of **9** and **10**, respectively, according to GC analysis. Analytical samples of **9** and **10** were obtained by flash chromatography on silica gel (8:1 petroleum ether (bp 40–60 °C)/EtOAc). Physical and spectral data of **9** and **10** follow.

9: mp 119–121 °C (from petroleum ether (bp 80–100 °C)); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.02 (s, 6 H), 0.70–2.10 (m, 13 H), 0.84 (s, 9 H), 0.97 (s, 3 H), 1.09 (s, 3 H), 3.26 (dd, J = 4, 10 Hz, 1 H), 4.17 (m, $W_{1/2}$ = 9 Hz, 1 H); MS, m/e (rel intensity) 271 (M^+ – 57, 5), 253 (25), 179 (8), 161 (100), 131 (15), 119 (15), 105 (13), 75 (20); calcd for $C_{14}H_{27}O_3Si$ (M^+ – 57) m/e 271.1729, found m/e 271.1733. Anal. Calcd for $C_{18}H_{36}O_3Si·H_2O$: C, 62.38; H, 11.05. Found: C, 62.26; H, 11.09.

10: mp 189–191 °C (from petroleum ether (bp 100–140 °C)); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.00 (s, 6 H), 0.70–2.10 (m, 13 H), 0.86 (s, 9 H), 1.02 (s, 3 H), 1.10 (s, 3 H), 3.13 (dd, J = 4, 10 Hz, 1 H), 3.55 (m, $W_{1/2}$ = 21 Hz, 1 H); MS, m/e (rel intensity) 271 (M^+ – 57, 6), 253 (8), 179 (15), 161 (100), 131 (23), 119 (16), 105 (16), 75 (22); calcd for $C_{14}H_{27}O_3Si$ (M^+ – 57) m/e 271.1729, found m/e 271.1725. Anal. Calcd for $C_{18}H_{36}O_3Si$: C, 65.80; H, 11.04. Found: C, 66.06; H, 11.22.

(1α,4α,4aα,7β,8aβ)- and (1α,4aα,7α,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]decahydro-1,4a-dimethyl-1,7-naphthalenediol 7-(Methanesulfonates) (2 and 11). To a stirred solution of 3.28 g (10.0 mmol) of a 1:1.1 mixture of **9** and **10** in 75 mL of dry pyridine was added 1.22 mL (15.75 mmol) of MsCl. The reaction mixture was stirred for 2 h at 40 °C and then concentrated under reduced pressure. The resulting residue was taken up in 200 mL of CH_2Cl_2 and washed successively with 50-mL portions of 10% aqueous H_2SO_4, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried and the solvent was removed under reduced pressure. The remaining residue was flash chromatographed on silica gel (8:1 to 2:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 2.042 g (50%) of β-mesylate **11** and 1.856 g (46%) of α-mesylate **2**. Spectral and physical data of the mesylates **2** and **11** follow.

2: mp 45 °C dec (from petroleum ether (bp 40–60 °C)); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.00 (s, 3 H), 0.01 (s, 3 H), 0.75–2.15 (m, 12 H), 0.85 (s, 9 H), 0.99 (s, 3 H), 1.12 (s, 3 H), 2.98 (s, 3 H), 3.25 (dd, J = 4.1, 11.4 Hz, 1 H), 5.07 (m, $W_{1/2}$ = 9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ –5.04 (q), –4.17 (q), 11.82 (q), 17.81 (s), 25.60 (3 q), 26.61 (2 t), 26.88 (t), 29.38 (q), 33.38 (t), 38.32 (q), 39.02 (s), 39.26 (t), 43.30 (d), 70.67 (s), 79.01 (d), 80.20 (d); MS, m/e (rel intensity) 349 (M^+ – 57, 4), 311 (1.5), 254 (11), 161 (100), 131 (15), 119 (14), 105 (28), 75 (19); calcd for $C_{15}H_{29}O_5SSi$ (M^+ – 57) m/e 349.1505, found m/e 349.1494. Anal. Calcd for $C_{19}H_{38}O_5SSi$: C, 56.11; H, 9.42. Found: C, 56.01; H, 9.52.

11: mp 91–93 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 200 MHz) δ –0.03 (s, 3 H), 0.00 (s, 3 H), 0.83 (s, 9 H), 0.92–2.17 (m, 12 H), 1.01 (s, 3 H), 1.11 (s, 3 H), 2.98 (s, 3 H), 3.15 (dd, J = 4.0, 11.5 Hz, 1 H), 4.63 (m, $W_{1/2}$ = 22 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ –5.10 (q), –4.18 (q), 12.41 (q), 17.79 (s), 25.58 (3 q), 26.89 (t), 27.56 (t), 27.97 (t), 29.67 (q), 37.42 (t), 38.62 (s), 38.73 (q), 39.19 (t), 48.50 (d), 70.76 (s), 79.24 (d), 82.26 (d); MS, m/e (rel intensity) 311 (M^+ – 95, 1.5), 254 (13), 161 (100), 131 (10), 119 (13), 105 (25), 75 (17); calcd for $C_{18}H_{35}O_2Si$ (M^+ – 95) m/e 311.2406, found m/e 311.2408. Anal. Calcd for $C_{19}H_{38}O_5SSi$: C, 56.11; H, 9.42. Found: C, 56.30; H, 9.68.

Elimination Reactions of the Mesylates 2 and 11 with Sodium *tert*-Amylate in Toluene. a. A solution of 1.051 g (2.59 mmol) of α-mesylate **2** in 40 mL of dry toluene was degassed and refluxed under an argon atmosphere. To this refluxing solution was added 7.4 mL (10 equiv) of sodium *tert*-amylate (3.5 M in toluene) at once. The reaction mixture was refluxed for an additional 10 min[21] and then, after cooling to 0 °C, 10 mL of water and 40 mL of brine were added. The two-phase mixture was separated and the aqueous layer was extracted with six 50-mL portions of petroleum ether (bp 40–60 °C). The combined organic layers were dried and evaporated under reduced pressure. The remaining residue was flash chromatographed on silica gel (50:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.697 g (87%) of a 11.5:1 mixture of double-bond isomers **3** and **12**, respectively, according to GC analysis. Almost pure samples of **3** and **12** were obtained by flash chromatography on silica gel (100:1 petroleum ether (bp 40–60 °C)/EtOAc).

(1α,4α,4aα,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,4a,5,6,8a-octahydro-1,4a-dimethyl-1-naphthalenol (3): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.00 (s, 3 H), 0.02 (s, 3 H), 0.80–2.15 (m, 10 H), 0.86 (s, 9 H), 0.98 (s, 3 H), 1.18 (s, 3 H), 3.25 (dd, J

(20) Conia, M. J.-M. *Bull. Soc. Chim.* **1950**, *17*, 537.

(21) According to TLC analysis the reaction was completed within 2 min.

= 4.1, 11.3 Hz, 1 H), 5.64–5.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −4.87 (q), −3.98 (q), 12.03 (q), 18.05 (s), 23.09 (t), 25.84 (3 q), 27.34 (t), 29.21 (q), 35.09 (t), 38.36 (s), 38.71 (t), 49.95 (d), 70.89 (s), 78.50 (d), 124.11 (d), 129.35 (d); MS, *m/e* (rel intensity) 253 (M^+ − 57, 2), 161 (100), 131 (20), 119 (10), 105 (20), 75 (19); calcd for $C_{14}H_{25}O_2Si$ (M^+ − 57) *m/e* 253.1624, found *m/e* 253.1617.

(1α,4α,4aα,8aβ)-4-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,4a,5,8,8a-octahydro-1,4a-dimethyl-1-naphthalenol (12): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.75–2.12 (m, 10 H), 0.86 (s, 9 H), 0.96 (s, 3 H), 1.10 (s, 3 H), 3.23 (dd, *J* = 3.9, 11.4 Hz, 1 H), 5.49–5.75 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −4.86 (q), −3.91 (q), 12.09 (q), 18.06 (s), 22.51 (t), 25.83 (3 q), 27.11 (t), 29.76 (q), 38.17 (s), 39.14 (t), 41.49 (t), 46.10 (d), 70.73 (s), 79.97 (d), 125.30 (d), 125.47 (d); MS, *m/e* (rel intensity) 295 (M^+ − 15, 0.4), 253 (17), 161 (100), 131 (18), 119 (27), 105 (67), 75 (37); calcd for $C_{14}H_{25}O_2Si$ (M^+ − 57) *m/e* 253.1624, found *m/e* 253.1630.

b. The β-mesylate **11** (0.406 g, 1.00 mmol) was treated with 10 equiv of sodium *tert*-amylate in toluene as described above for the elimination of the α-mesylate **2**. Workup and flash chromatography on silica gel (50:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded a mixture (0.176 g, 57%) of **3** and **12** in a ratio of 6.5:1, respectively, according to GC analysis.

c. In a similar way, a 1:1.1 mixture of **2** and **11** gave a 8.4:1 mixture of **3** and **12**, respectively, in 66% yield.

(1aα,3aα,4α,7α,7aβ,7bα)-1,1-Dibromo-4-[(*tert*-butyldimethylsilyl)oxy]decahydro-3a,7-dimethyl-1*H*-cyclopropa[*a*]naphthalen-7-ol (13). To a solution of 1.514 g (4.88 mmol) of a 7:1 mixture of **3** and **12** in 40 mL of dry toluene was added 14 mL of sodium *tert*-amylate (3.5 M in toluene). To this mixture was added a solution of 2.13 mL (24.4 mmol) of $HCBr_3$ in 10 mL of dry toluene dropwise under vigorous stirring. When the addition was complete, the reaction mixture was allowed to stir for an additional 20 min, after which time 200 mL of brine was added. The two-phase mixture was separated and the aqueous layer was extracted with five 100-mL portions of petroleum ether (bp 40–60 °C). The combined organic layers were dried and evaporated under reduced pressure. The remaining residue was flash chromatographed on silica gel (70:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 1.786 g (76%) of dibromide **13**, which solidified on standing, and 0.263 g (11%) of another dibromide **14**. Physical and spectroscopic data of **13** and **14** follow.

13: mp 81–83 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ −0.01 (s, 3 H), 0.02 (s, 3 H), 0.45–2.20 (m, 12 H), 0.87 (s, 9 H), 0.92 (s, 3 H), 1.26 (s, 3 H), 3.15 (dd, *J* = 4, 10 Hz, 1 H); MS, *m/e* (rel intensity) 427 (13), 425 (24), 423 (M^+ − 57, 12), 335 (16), 333 (30), 331 (15), 254 (22), 253 (16), 252 (23), 251 (12), 131 (100); calcd for $C_{15}H_{25}O_2Br_2Si$ (M^+ − 57) *m/e* 422.9992, found *m/e* 422.9984. Anal. Calcd for $C_{19}H_{34}O_2Br_2Si$: C, 47.30; H, 7.10. Found: C, 47.04; H, 7.12.

14: mp 106–107 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.00 (s, 6 H), 0.50–2.57 (m, 12 H), 0.86 (s, 9 H), 0.90 (s, 3 H), 1.05 (s, 3 H), 3.12 (dd, *J* = 4, 10 Hz, 1 H); MS, *m/e* (rel intensity) 427 (38), 425 (73), 423 (M^+ − 57, 38), 335 (22), 333 (47), 331 (23), 254 (17), 253 (21), 252 (18), 251 (18), 145 (36), 131 (100), 95 (51), 75 (100); calcd for $C_{15}H_{25}O_2Br_2Si$ (M^+ − 57) *m/e* 422.9992, found *m/e* 422.9990. Anal. Calcd for $C_{19}H_{34}O_2Br_2Si$: C, 47.30; H, 7.10. Found: C, 47.35; H, 7.25.

(1aα,3aα,4α,7α,7aβ,7bα)-4-[(*tert*-Butyldimethylsilyl)oxy]decahydro-1,1,3a,7-tetramethyl-1*H*-cyclopropa[*a*]naphthalen-7-ol (15). To a suspension of 4.28 g (47.9 mmol) of dry copper(I) cyanide in 90 mL of dry ether was added 54.4 mL (87 mmol) of MeLi (1.6 M in ether) at −78 °C. The mixture was gradually warmed to 0 °C over 45 min. The mixture was then cooled to −15 °C and a solution of 2.097 g (4.35 mmol) of dibromo compound **13** and 1.9 mL (4.35 mmol) of HMPA in 80 mL of dry ether was added dropwise. Stirring was continued for an additional 45 min, after which time 15 mL of MeI was added. The mixture was stirred for another 5 min and then poured into a mixture of 90 mL of saturated aqueous NH_4Cl and 10 mL of concentrated NH_4OH. The two-phase mixture was separated and the aqueous layer was extracted with five 50-mL portions of CH_2Cl_2. The combined organic layers were washed with brine, dried, and evaporated under reduced pressure. The remaining residue was flash chromatographed on silica gel (60:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.926 g (60%) of pure dimethylated product **15**, which solidified on standing: mp 64–65 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ −0.06 (s, 3 H), −0.04 (s, 3 H), 0.10–2.20 (m, 12 H), 0.80 (s, 12 H), 0.93 (s, 3 H), 0.98 (s, 3 H), 1.06 (s, 3 H), 3.08 (dd, *J* = 4, 10 Hz, 1 H); MS, *m/e* (rel intensity) 352 (M^+, 0.2), 295 (1.6), 203 (100), 149 (12), 147 (13), 131 (17), 123 (10), 119 (8), 105 (12), 75 (20); calcd for $C_{17}H_{31}O_2Si$ (M^+ − 57) *m/e* 295.2093, found *m/e* 295.2096. Anal. Calcd for $C_{21}H_{40}O_2Si$: C, 71.53; H, 11.43. Found: C, 71.22; H, 11.66.

(1aα,3aα,4α,7α,7aβ,7bα)-Decahydro-1,1,3a,7-tetramethyl-1*H*-cyclopropa[*a*]naphthalene-4,7-diol (16). To a solution of 0.881 g (2.50 mmol) of monoprotected diol **15** in 40 mL of acetonitrile was added 2.5 mL of 40% aqueous HF. The mixture was stirred for 100 min and then poured into 150 mL of saturated aqueous $NaHCO_3$. After extraction of the aqueous layer with six 50-mL portions of CH_2Cl_2, the combined organic layers were dried and evaporated under reduced pressure. Flash chromatography of the resulting residue on silica gel (5:1 petroleum ether (bp 40–60 °C)/EtOAc) afforded 0.563 g (95%) of diol **16** as white crystals: mp 149–150 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.50–0.75 (m, 2 H), 0.88 (s, 3 H), 1.00 (s, 3 H), 1.03 (s, 3 H), 1.12 (s, 3 H), 1.25–2.15 (m, 11 H), 3.13 (dd, *J* = 4, 10 Hz, 1 H); MS, *m/e* (rel intensity) 238 (M^+, 6), 220 (39), 205 (16), 202 (15), 187 (16), 163 (43), 162 (100), 135 (27), 123 (30), 121 (30); calcd for $C_{15}H_{26}O_2$ (M^+) *m/e* 238.1933, found *m/e* 238.1930. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.19; H, 11.04.

(1aα,3aα,4α,7α,7aβ,7bα)-Decahydro-1,1,3a,7-tetramethyl-1*H*-cyclopropa[*a*]naphthalene-4,7-diol 4-(4-Methylbenzenesulfonate) (4). A solution of 0.559 g (2.35 mmol) of diol **16** and 0.896 g (4.70 mmol) of TsCl in 25 mL of dry pyridine was stirred for 3.5 d. The reaction mixture was diluted with 250 mL of CH_2Cl_2 and washed successively with one 100-mL portion of 10% aqueous H_2SO_4, two 50-mL portions of saturated aqueous $NaHCO_3$, and one 100-mL portion of brine. The organic layer was dried and the solvent was removed under reduced pressure. The crude product was flash chromatographed on silica gel (15:1 petroleum ether (bp 40–60 °C)/EtOAc) to give 0.903 g (98%) of tosylate **4** as white crystals: mp 120–121 °C (from diisopropyl ether); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.35–0.80 (m, 2 H), 0.86 (s, 3 H), 0.95–2.30 (m, 10 H), 1.05 (s, 3 H), 1.07 (s, 3 H), 1.13 (s, 3 H), 2.44 (s, 3 H), 4.20 (dd, *J* = 4, 10 Hz, 1 H), 7.30 (d, *J* = 8 Hz, 2 H), 7.76 (d, *J* = 8 Hz, 2 H); MS, *m/e* (rel intensity) 392 (M^+, 1.8), 374 (15), 220 (45), 202 (68), 172 (100), 91 (56). Anal. Calcd for $C_{22}H_{32}O_4S$: C, 67.31; H, 8.21. Found: C, 67.23; H, 8.03.

Alloaromadendren-4β-ol (5). The tosylate **4** (0.392 g, 1.00 mmol) was treated with sodium *tert*-amylate (2 equiv) for 30 min as described for the elimination of the α-mesylate **2**. Workup and flash chromatography on silica gel (150:1 petroleum ether (bp 40–60 °C)/EtOAc) gave, in order of elution, 0.015 g (7%) of cyclic ether **17**, 0.155 g (70%) of olefin **5**, and 0.015 g (7%) of compound **18**. Spectroscopic and physical data of **5**, **17**, and **18** follow.

5: mp 57.5–59 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.50–0.67 (m, 2 H), 0.90–1.87 (m, 7 H), 0.96 (s, 3 H), 1.01 (s, 3 H), 1.22 (s, 3 H), 1.93–2.18 (m, 1 H), 2.25–2.40 (m, 2 H), 2.67 (br q, *J* = 10.1 Hz, 1 H), 4.83 (br s, 1 H), 4.87 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.85 (q), 17.17 (s), 21.43 (t), 21.79 (d), 25.31 (d), 26.85 (t), 26.85 (q), 28.74 (q), 37.88 (t), 40.40 (t), 44.62 (d), 47.26 (d), 80.26 (s), 108.63 (t), 150.65 (s); MS, *m/e* (rel intensity) 220 (M^+, 6), 205 (10), 202 (100), 187 (59), 159 (26), 146 (49), 117 (45), 107 (51), 93 (40), 91 (37), 43 (49); calcd for $C_{15}H_{24}O$ (M^+) *m/e* 220.1827, found *m/e* 220.1835. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.97. Found: C, 81.60; H, 11.29.

17: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.48–0.75 (m, 2 H), 0.99 (s, 3 H), 1.04 (s, 3 H), 1.10 (s, 3 H), 1.20–1.82 (m, 8 H), 1.24 (s, 3 H), 1.86 (br s, 1 H), 2.06 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.47 (q), 17.31 (s), 18.41 (q), 20.83 (t), 22.49 (d), 23.50 (t), 24.97 (d), 28.83 (q), 29.37 (q), 35.09 (t), 40.87 (t), 46.90 (d), 51.33 (d), 81.83 (s), 85.43 (s); MS, *m/e* (rel intensity) 220 (M^+, 15), 205 (6), 202 (5), 187 (6), 177 (10), 162 (100), 147 (50), 134 (37), 119 (67), 109 (32), 85 (48), 43 (47); calcd for $C_{15}H_{24}O$ (M^+) *m/e* 220.1827, found *m/e* 220.1828.

18: mp 57–59 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.21–0.36 (m, 1 H), 0.80–1.40 (m, 3 H), 0.86 (s, 3 H), 0.95 (d, *J* = 7 Hz, 3 H), 1.01 (s, 3 H), 1.55 (br s, 3 H), 1.60–1.92 (m, 2 H), 2.10–2.72 (m, 5 H), 5.18–5.31 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.44 (q), 15.77 (s), 16.54 (q), 19.70 (q), 25.17 (t), 26.99 (t), 27.20 (d), 27.79 (d), 29.54 (q), 36.87 (t), 41.07 (t), 45.67 (d), 122.12 (d), 138.02 (s), 216.93 (s); MS, *m/e* (rel intensity) 220 (M^+, 50), 205 (6), 202 (2),

177 (38), 149 (44), 148 (35), 110 (54), 95 (100), 82 (65), 43 (32); calcd for $C_{15}H_{24}O$ (M^+) m/e 220.1827, found m/e 220.1830. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.97. Found: C, 81.58; H, 10.91.

(±)-Alloaromadendrane-4β,10α-diol (1). To a solution of 0.060 g (0.27 mmol) of olefin **5** in 5 mL of CH_2Cl_2 were added 5 mL of acetone, 5 mL of water, 0.005 g of 18-crown-6, and 0.100 g of $NaHCO_3$. The mixture was stirred vigorously and 1.36 mL of 0.29 M Oxone (0.79 mmol of $KHSO_5$) in water was added dropwise at 0 °C. Stirring was continued for an additional 80 min, after which time 5 mL of 10% aqueous $Na_2S_2O_3$ and 10 mL of saturated aqueous $NaHCO_3$ were added. The aqueous layer was extracted with seven 25-mL portions of CH_2Cl_2. The combined organic layers were dried and evaporated under reduced pressure. The remaining residue, according to GCMS and ^1H NMR analysis, a 4.3:1 mixture of the epoxides **19** [^1H NMR (main peaks, $CDCl_3$) δ 0.94 (s, 3 H), 1.02 (s, 3 H), 1.18 (s, 3 H), 2.50 (d, J = 4 Hz, 1 H), 2.95 (d, J = 4 Hz, 1 H); MS, m/e (rel intensity) 236 (M^+, 0.1), 221 (1), 218 (4), 203 (3), 187 (4), 175 (6), 163 (8), 145 (16), 133 (14), 121 (15), 105 (28), 81 (60), 55 (30), 43 (100)] and **20** [^1H NMR (main peaks, $CDCl_3$) δ 0.94 (s, 3 H), 1.04 (s, 3 H), 1.15 (s, 3 H), 2.40 (d, J = 4 Hz, 1 H), 2.88 (d, J = 4 Hz, 1 H); MS, m/e (rel intensity) 236 (M^+, 0.3), 221 (0.4), 218 (2), 203 (2), 187 (3), 175 (6), 160 (8), 145 (21), 134 (17), 105 (27), 81 (44), 55 (27), 43 (100)], respectively, was taken up in 5 mL of dry ether and an excess $LiAlH_4$ was added. The mixture was stirred at rt for 17 h, diluted with 75 mL of CH_2Cl_2, and then carefully quenched with a few drops of saturated aqueous Na_2SO_4. The mixture was dried and concentrated under reduced pressure. The remaining residue was flash chromatographed on silica gel (6:1 to 2:1 petroleum ether (bp 40–60 °C)/EtOAc) to give, in order of elution, 0.011 g (16%) of 4β,10β-diol **22**, 0.012 g (18%) of the cyclic hydroxy ether **21**, and 0.030 g (46%) of 4β,10α-diol **1**. Physical and spectroscopic data of **1**, **21**, and **22** follow.

1: mp 120–120.5 °C (from n-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.48–0.68 (m, 2 H), 0.95 (s, 3 H), 1.00–1.95 (m, 11 H), 1.03 (s, 3 H), 1.24 (s, 3 H), 1.32 (s, 3 H), 2.23 (br q, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, m/e (rel intensity) 238 (M^+, 0.3), 220 (3), 205 (5), 202 (3), 187 (4), 177 (4), 162 (11), 149 (9), 147 (14), 139 (100), 121 (26), 81 (39), 43 (52); calcd for $C_{15}H_{26}O_2$ (M^+) m/e 238.1933, found m/e 238.1928. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.30; H, 11.20.

21: mp 137–138 °C (from diisopropyl ether); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.49 (d, J = 9.4 Hz, 1 H), 0.60–0.77 (m, 1 H), 0.90–1.89 (m, 10 H), 0.97 (s, 3 H), 1.01 (s, 3 H), 1.24 (s, 3 H), 2.19 (br s, 1 H), 3.31 (d, J = 9.5 Hz, 1 H), 3.37 (d, J = 9.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.41 (q), 17.48 (s), 18.15 (q), 20.67 (t), 22.08 (d), 23.26 (t), 25.38 (d), 29.35 (q), 35.57 (t), 36.17 (t), 44.65 (d), 50.94 (d), 68.96 (t), 83.81 (s), 85.76 (s); MS, m/e (rel intensity) 236 (M^+, 3), 218 (32), 205 (16), 160 (40), 147 (58), 145 (62), 134 (100), 105 (38), 91 (33), 43 (46); calcd for $C_{15}H_{24}O_2$ (M^+) m/e 236.1776, found m/e 236.1775. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.23. Found: C, 76.51; H, 10.37.

22: mp 109 °C (from n-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ 0.60–0.75 (m, 1 H), 0.87 (br d, J = 7.4 Hz, 1 H), 0.93–1.47 (m, 3 H), 0.96 (s, 3 H), 1.05 (s, 3 H), 1.09 (s, 3 H), 1.20 (s, 3 H), 1.64–2.00 (m, 8 H), 2.20 (dt, J = 8.9, 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, m/e (rel intensity) 238 (M^+, 0.3), 220 (7), 205 (4), 202 (4), 192 (5), 187 (4), 177 (5), 162 (7), 147 (10), 139 (100), 121 (60), 81 (34), 43 (46); calcd for $C_{15}H_{26}O_2$ (M^+) m/e 238.1933, found m/e 238.1930. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.24; H, 11.22.

(±)-Alloaromadendrane-4α,10α-diol (23). To a solution of 0.100 g (0.45 mmol) of olefin **5** in 5 mL of dry pyridine was added 0.2 mL (1.0 mmol) of $SOCl_2$ at −15 °C. The mixture was stirred for 10 min and then poured into 100 mL of aqueous 20% H_2SO_4. The aqueous solution was extracted with five 50-mL portions of CH_2Cl_2. The combined organic layers were dried and the solvent was evaporated at atmospheric pressure. The remaining residue, a mixture of three products in a ratio of 6:3:1 according to GC analysis, was epoxidized and reduced as described above for olefin **5**. The workup and flash chromatography on silica gel (2:1 petroleum ether (bp 40–60 °C)/EtOAc) gave 0.025 g (23%) of pure **23**: mp 79–80 °C (from n-hexane); ^1H NMR ($CDCl_3$, 200 MHz) δ −0.03 (t, J = 9.6 Hz, 1 H), 0.60 (ddd, J = 5.2, 9.6, 11.3 Hz, 1 H), 0.99 (s, 3 H), 1.01 (s, 3 H), 1.10–2.11 (m, 11 H), 1.16 (s, 3 H), 1.30 (s, 3 H), 2.45 (m, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz), see Table I; MS, m/e (rel intensity) 238 (M^+, 1.7), 220 (18), 205 (18), 202 (21), 187 (19), 177 (11), 162 (100), 147 (52), 134 (24), 119 (51), 107 (48), 93 (49), 81 (33); calcd for $C_{15}H_{24}O$ ($M^+ - 18$) m/e 220.1827, found m/e 220.1825. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.57; H, 10.99. Found: C, 75.77; H, 11.30.

Acknowledgment. We wish to thank Cees J. Teunis, Hugo Jongejan, and Marinus van Dijk for mass spectral data and elemental analyses and Albertus van Veldhuizen and Romano V. A. Orru for recording ^1H NMR (200 MHz) and ^{13}C NMR spectra.

Registry No. (±)-**1**, 136458-41-8; (±)-**2**, 136379-61-8; (±)-**3**, 136379-62-9; (±)-**4**, 136379-63-0; (±)-**5**, 136458-42-9; (±)-**6**, 87262-05-3; (±)-**7**, 136379-64-1; (±)-**8**, 136379-65-2; (±)-**9**, 136379-66-3; (±)-**10**, 136379-67-4; (±)-**11**, 136379-68-5; (±)-**12**, 136379-69-6; (±)-**13**, 136379-70-9; (±)-**14**, 136379-71-0; (±)-**15**, 136379-72-1; (±)-**16**, 136379-73-2; (±)-**17**, 136379-74-3; (±)-**18**, 136379-75-4; (±)-**19**, 136458-43-0; (±)-**20**, 136458-44-1; (±)-**21**, 136379-76-5; (±)-**22**, 136458-45-2; (±)-**23**, 136458-46-3.

Ozonolysis of Vinyl Ethers in the Presence of α-Diketones and α-Keto Esters

Toshihiko Tabuchi and Masatomo Nojima*

Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received May 20, 1991

Ozonolysis of vinyl ethers in the presence of α-diketones provided two types of products, i.e., a Baeyer–Villiger oxidation product and 3-acyl-1,2,4-trioxolane. The evidence suggests that the latter product is labile and, therefore, the former one might be produced by decomposition of the latter. In contrast, 1,2,4-trioxolane-3-carboxylates were stable. As a result, ozonolysis of vinyl ethers in the presence of α-keto esters yielded the expected ozonides in high yield.

The mechanism of the reaction of ozone with alkenes continues to attract considerable attention.[1] It is noted that in many cases ozonolyses of α,β-unsaturated ketones do not give the corresponding 1,2,4-trioxolanes but instead the "anomalous" products (carboxylic acid, ester, etc.).[2] In

(1) (a) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (b) Kuczkowski, R. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, 1991; Vol. 3.

(2) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1, 1982; Vol. 2.

0022-3263/91/1956-6591$02.50/0