was removed under reduced pressure to provide 2.43 g of a light yellow oil. Analysis of this sample was carried out on a Waters Associate HPLC with a Partisil ODS-2 column monitoring a mobile phase of $MeOH/H_2O/HOAc$ (200:200:4) at 280 nm. Standard solutions of **25** were used to generate a standard curve based on peak area from which the presence of Boc-Et-Tyr (**25**) was substantiated and a yield of 13% was determined.

Direct N-Ethylation of *t*-Boc-L-tyrosine through Use of a Trimethylsilyl Ether Intermediate. A magnetically stirred solution of Boc-L-Tyr (100 g, 35.5 mmol) in 150 mL of dry THF was cooled to −70 °C under Ar. A solution of *t*-BuLi in pentane (35.5 mL, 71 mmol) was then added dropwise over a 25-min period. After the resulting heterogeneous mixture was stirred for 0.5 h, trimethylsilyl chloride (35.5 mmol, 3.86 g) dissolved in 10 mL of THF was added dropwise (5 min) to the agitated mixture. The reaction temperature was allowed to warm at 0 °C before recooling to −70 °C and adding an additional 18 mL (35.5 mmol) of *t*-BuLi to the reaction. After the mixture was stirred at this temperature for 30 min, it was warmed to −20 °C and stirred at this temperature for an additional 30 min before adding triethyloxonium tetrafluoroborate (35.5 mmol, 6.7 g). The reaction was warmed to room temperature, stirred for 24 h, diluted with CH_2Cl_2 (600 mL), and extracted with 0.5 N $KHSO_4$ (3 × 200 mL). The aqueous washes were extracted with CH_2Cl_2 (150 mL). The combined CH_2Cl_2 extracts were dried (Na_2SO_4) and filtered, and all solvent was stripped off to provide 12.5 g of a pale yellow oil. As described in the previous experiment, HPLC analysis was used to determine that the desired product (**25**) was produced directly in 22% yield.

Acknowledgment. We thank Dr. R. Mazur for his interest and useful suggestions and Drs. S. Djuric and R. Garland for helpful comments.

Registry No. 7, 13734-34-4; **11**, 94732-05-5; **12**, 70961-24-9; **13**, 368-39-8; **14**, 94799-50-5; **15**, 94732-06-6; **16**, 94732-07-7; **17**, 94732-08-8; **18**, 94732-09-9; **20**, 94732-10-2; **21**, 2130-96-3; **23**, 94732-11-3; **24**, 94732-12-4; **25**, 94732-13-5; **26**, 94732-14-6; **27**, 3978-80-1; **29**, 94732-15-7; **30**, 94732-16-8; Tyr-OMe·HCl, 3417-91-2; Boc-D-Met, 5241-66-7; Me_3SiCl, 75-77-4; Boc-DL-Phe, 4530-18-1; *tert*-butyldimethylsilyl chloride, 18162-48-6.

Basidiomycete Sesquiterpenes: The Silica Gel Induced Degradation of Velutinal Derivatives

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Derivatives of the pentacyclic sesquiterpene velutinal, occurring as fatty acid esters in *Lactarius* species and in other *Basidiomycetes*, form a number of previously isolated furanoid sesquiterpenes when degraded by silica gel. On the basis of the structure of isolated intermediates and products, a mechanism for the degradation is proposed.

Introduction

The velutinal esters **1a** and **1b** were recently isolated during a search for the chemical entities responsible for the so called sulphovanillin reaction, which is used as a diagnostic test in systematic mycology,[1] and independently during a search for the elusive precursors of previously isolated *Lactarius* sesquiterpenes.[2] In several *Lactarius* species the velutinal esters probably function as the "ammunition" in a chemical defense system, in which they are enzymatically converted to toxic sesquiterpenes within minutes whenever the mushroom is injured.[3] Unaffected specimens of these *Lactarius* species contain no sesquiterpenes in significant amounts besides the velutinal esters.[1,2] A number of previously reported sesquiterpenes from *Lactarius* species are in fact artifacts, formed during extraction and workup of the extracts. Free velutinal **1c**, its esters (**1a** and **1b**), and methyl acetal **1d** are labile compounds which on adsorption on silica gel form a number of furanoid sesquiterpenes[4] of lactarane and secolactarane type which have been isolated previously from different Basidiomycetes.[5] Rapid degradation also takes place on dissolving compounds **1a–d** in reagent grade methanol, as under other conditions where traces of acid are present.[6] The furanoid sesquiterpenes are formed via intermediate dihydrofurans. These profurans are very easily converted to furans by acidic catalysis, although many of them are stable enough to be isolated. In this paper we report a detailed investigation of the products formed when the three velutinal derivatives **1a**, **1c**, and **1d** are degraded by silica gel and in reagent grade methanol, and we suggest a mechanistic interpretation of the product patterns. The origin of a number of reported sesquiterpenes of *Lactarius* and *Russula*, whether they are true metabolites, secondary enzymatic products, or chemical artifacts, still remains to be established, and in that context the chemistry of velutinal is of central interest.

Materials and Methods

Hemiacetal esters **1a,b** were isolated, respectively, from an EtOAc extract of *L. vellereus* and from an EtOAc extract of *L. necator*, both species were collected in the south of Sweden during the autumns of 1982 and 1983. Apart

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[1] Favre-Bonvin, J.; Gluchoff-Fiasson, K.; Bernillon, J. *Tetrahedron Lett.* **1982**, *23*, 1907.

[2] Sterner, O.; Bergman, R.; Kessler, E.; Nilsson, L.; Oluwadiya, J.; Wickberg, B. *Tetrahedron Lett.* **1983**, *24*, 1415.

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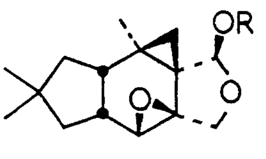
[6] De Bernardi, M.; Vidari, G.; Vita-Finzi, P.; Gluchoff-Fiasson, K. *Tetrahedron Lett.* **1982**, *23*, 4623.



a: R=Stearoyl
b: R=6-Ketostearoyl
c: R=H
d: R=CH_3

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Figure 1. Velutinal derivatives.

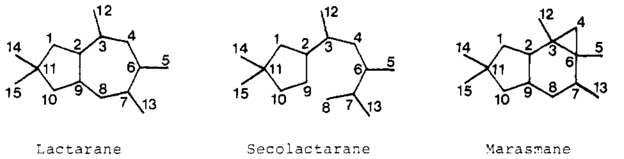


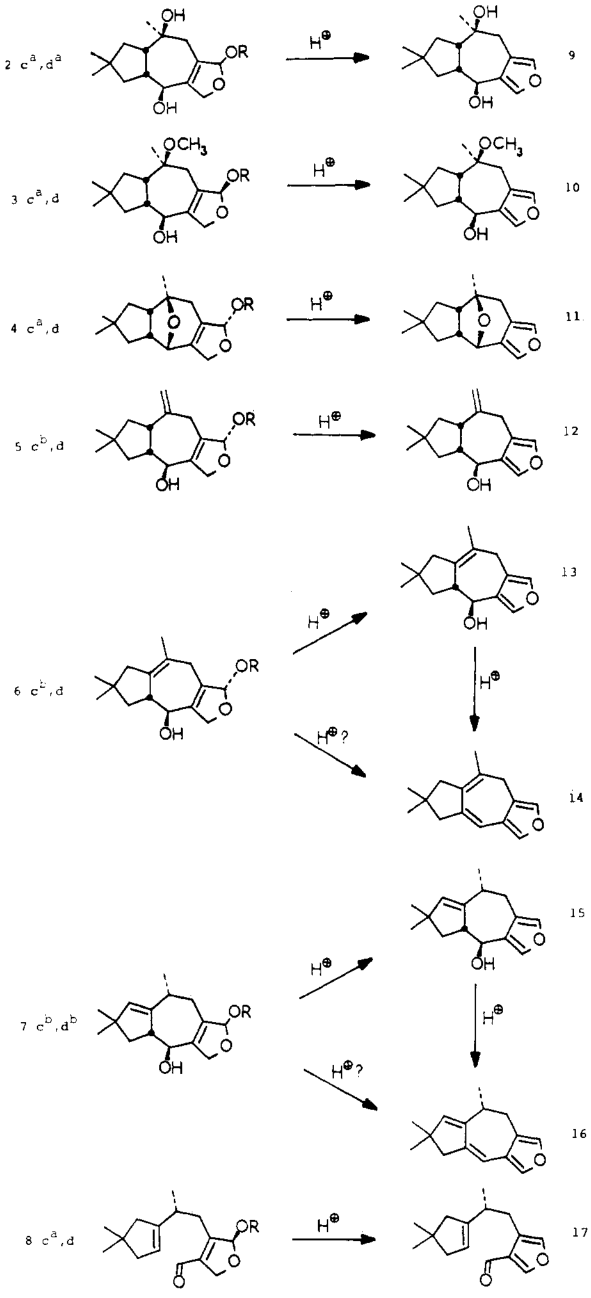
Figure 2. The numbering system for the lactarane, secolactarane, and marasmane skeletons.

from the acid residue, **1b** gave exactly the same products as **1a** and will therefore not be treated separately henceforth. Free hemiacetal **1c** and methyl acetal **1d** were prepared by transesterification of **1a** or **1b** in $EtO^-/EtOH$[2] and by solvolysis in HPLC grade methanol.[1] When degraded on silica gel, the velutinal derivative was adsorbed on a 10-fold amount of Merck, Kieselgel 60 (water content 5%) and kept under nitrogen atmosphere for 2 h, while degradation in methanol was accomplished by dissolving the velutinal derivative in a 100-fold amount of reagent grade methanol for 30 min at room temperature. 10% hexane was added to the methanol to improve dissolution. The degradation products were isolated by SiO_2 and Al_2O_3 chromatography. In order to be able to detect all relatively stable dihydrofurans that are formed when compounds **1a,c,d** are degraded, the following technique based on two-dimensional (2-D) TLC was used: The degradation mixture was applied at a corner of a square silica gel plate and developed in the first direction. When the degradation by silica gel was investigated, the velutinal derivative itself was applied to the plate, which then was left for 15 min before development. After the first development the plate was sprayed with acetic acid to induce the aromatization of the dihydrofurans, dried, and then developed in the second direction in order to separate the furan end products.

Results and Discussion

The following product patterns were obtained when the three velutinal derivatives were degraded by silica gel (structural formulas given in Scheme I; for atom numbering see Figure 2): Compound **1a** gave **2c**, **4c**, **5c**, **6c**, **8c**, **9**, **11**, **12**, **13**, **14**, **15**, **16**, and **17**. Compound **1c** gave **2c**, **4c**, **5c**, **6c**, **8c**, **9**, **12**, **13**, and **15**. Compound **1d** gave **2d**, **4d**, **5d**, **6d**, **8d**, **9**, **12**, **13**, and **15**. Besides the velutinal derivatives, the furans **9**,[7] **11**[8] (furan ether A), **12**,[9] **13**,[7] **15**[8] (furosardonin A), and **17**[10] (lactaral) have been reported previously, while dihydrofurans **2c**, **2d**, **4c**, **4d**, **5d**, **6d**, **8c**, and **8d** and furans **14** and **16** are new compounds. Hydroxydihydrofurans **5c** and **6c** were isolated as a mixture which could not be resolved without further degradation to the furans. The presence of both compounds, however, was indicated by a spectral comparison of the mixture with the corresponding methyl acetals **5d** and **6d** and also by the 2-D TLC experiment described above. Compounds **7c,d** were not isolated, although their existence was indicated by 2-D TLC experiments as described above. Apparently they are exceptionally unstable.

Scheme I. Degradation Products of Velutinal Derivatives 1a-d[c]



[a] Isolated as the C-5 Epimeric mixture. [b] Not isolated. [c] c, R = H; d, R = CH_3.

The formation of the dehydrated products **14** and **16**, the first of which is formed in small amounts (ca 0.1%), was indicated also by 2-D TLC experiments to occur via acid-catalyzed dehydration of the corresponding hydroxydihydrofurans prior to aromatization. When pure furosardonin A (**15**) or furan alcohol **13** are treated with stearic acid or acetic acid on a silica gel plate, no dehydrated furans **14** or **16** are formed. The same treatment of the mixture of **5c** and **6c** gives small amounts of the corresponding dehydrated furans. Stronger acids, like *p*-TSA, easily induce the dehydration of **13** and **15** to **14** and **16**. Thus the hydroxydihydrofurans lose water to form the C-8

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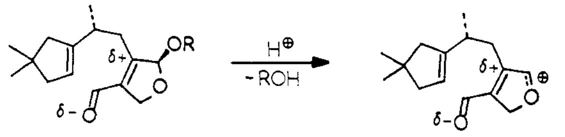
(10) Magnusson, G.; Thoren, S. *Tetrahedron* **1974**, *30*, 1431.



8 c,d

Figure 3. Aromatization of **8c,d** is counteracted by the electron-withdrawing aldehyde.

to C-9 double bond more readily than the furan alcohols.

When the degradation was performed in methanol, mostly the same patterns of products were obtained. Compounds **1a** and **1c**, however, gave **3c** and **10** instead of **2c** and **9**, while compound **1d** gave **3d** and **10** instead of **2d** and **9**. Dihydrofurans **3c** and **3d** are also new compounds, while **10** has been reported previously.[11] When the furan **10** was isolated initially from *L. vellereus*,[11] it was noticed that extraction of the mushrooms with hexane led to the dihydroxyfuran **9**, while extraction with methanol gave the methyl ether **10** and extraction with ethanol gave the corresponding ethyl ether. Hence compound **10** was considered to be an extraction artifact.

As seen above, there are differences between the product patterns when velutinal ester **1a**, free velutinal **1c**, and methyl acetal **1d** are degraded on silica gel. While **1c** and **1d** form analogous products, the pattern of products from **1a** differs considerably. An explanation for the diverging behavior of the velutinal esters **1a** and **1b** is found in the pivotal role of the furan precursors **2–8** and in their relative stability in the degradation conditions. Seco derivatives **8c,d**, with the stabilizing effect of the electron-withdrawing aldehyde (Figure 3) are the most stable. However **4c,d** are comparably stable and resist silica gel for at least 2 h, while, at the other extreme, **7c,d** are to labile to be isolated. The striking difference in stability between the internal ether **4** and compound **2** for example, suggests that subtle conformational changes may exert an important effect. The additional acidity of the fatty acids liberated from **1a** and **1b** is thus needed to catalyze the aromatization of profurans **4** and **8** as well as dehydration of alcohols **6** and **7** to dienes **14** and **16**.

The configuration of C-5 requires comment. All hydroxydihydrofurans were obtained as nonseparable epimer mixtures while most methoxydihydrofurans preferred the configuration opposite to **1d**. The methoxydihydrofurans were obtained firstly in the β-configuration, but during workup **4d**, **5d**, and **6d** epimerized to the more stable α-configuration. **3d** epimerized so slowly that the β-epimer could be isolated. **8d** did not epimerize at all, and **2d** was obtained as an epimer mixture. Besides the products discussed above, a large number of minor products are also formed on silica. These are believed to be mainly dimeric acetals and the nature and amount of these depend upon the quality and amount of silica gel used for degradation.

The formation of the dihydrofurans can mechanistically be rationalized as depicted in Scheme II. The proposed mechanism requires that the configuration at C-3, relative to C-9, is as indicated in the formulae. Furan alcohol **15** isolated here was found to be identical (spectral data and optical rotation) to furosardonin A, which previously has been assigned tentatively the epimeric configuration at C-3.[8] In order to establish the C-3 configuration of furosardonin A, the steric energy of all likely conformers of both epimers (i.e., **15** and **18**) was calculated by the molecular mechanics computer program MM-2.[12] These results are shown in Table I.

Scheme II. Degradation Mechanism

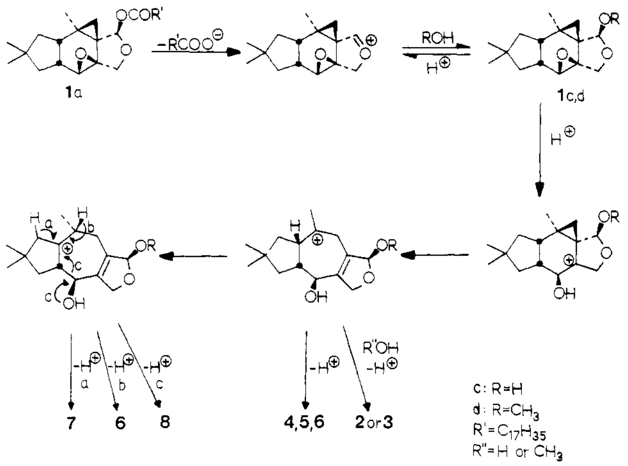
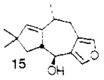
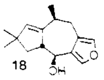


Table I. The Relative Steric Energy (kcal/mol) of All Likely Conformers of the C-3 Epimers of Furosardonin A (15 and 18)

	conformation			
	C-3 Me e C-8 OH e	C-3 Me e C-8 OH a	C-3 Me a C-8 OH e	C-3 Me a C-8 OH a
 15	23.43	24.87	24.50	
 18	25.94		22.62	27.21

New NMR data for furosardonin A show nuclear Overhauser effects on C(1)H (14%) when the C-3 methyl group was irradiated (360 MHz) and on C(4)H (1%) when C(8)H was irradiated (300 MHz), indicating that both the C-3 methyl group and the C-8 hydroxyl group are equatorially oriented on the seven-membered ring. This is also supported by the newly estimated coupling constants (300 MHz) of C(3)H with C(4)H and C(4)H′ (2 and 12 Hz), and of C(8)H with C(9)H (10.5 Hz). While the e,e conformation of **18** is more than 3 kcal/mol less stable compared to the conformation having the C-3 methyl group axially and the C-8 hydroxyl group equatorially oriented, the e,e conformation of **15** is the most stable. For the observed NOE on C(4)H discussed above, the e,e conformation of **18** has a incompatibly long distance between C(4)H and C(8)H, and altogether this shows that the correct C-3 configuration of furosardonin A is as in **15**. Work is now under way to correlate chemically both furosardonin A (**15**) and lactaral **17** to compounds of known C-3 configuration and to compounds of known absolute configuration.

Experimental Section

General Procedures. All ^1H NMR spectra were recorded with a Nicolet NM-360 spectrometer (360 MHz), except part of the new data for furosardonin A (**15**) which were recorded with a Bruker AM-300 spectrometer (300 MHz) (separately indicated) in deuteriobenzene. The coupling constants *J* are given in Hertz. ^{13}C NMR spectra were recorded with the Nicolet spectrometer (91 MHz). Chemical shifts are reported in ppm with tetramethylsilane as internal standard throughout. Deuteriochloroform (filtered through Na_2CO_3 to remove any acidic impurities) was used as solvent if not otherwise stated. Melting points were obtained with a Kofler hot-stage apparatus and are uncorrected. IR spectra were determined with a Perkin-Elmer 257 spectro-

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[11] Magnusson, G.; Thoren, S.; Dahmen, J.; Leander, K. *Acta Chem. Scand. Ser. B.* 1974, *28*, 841.

[12] Allinger, N. L.; "Advances in Physical Organic Chemistry"; Academic Press: London, 1976; Vol. 1, p 1.

photometer. Optical rotations were measured with a Perkin-Elmer 1541 automatic polarimeter (1-dm cell). UV spectra were recorded with a Cary 219 spectrophotometer in ethanol if not otherwise stated. Mass spectra (EI) were recorded with a Varian MAT 112 at 70 eV. Elemental analyses were carried out by the elemental analysis laboratory of this institution. All solvents used for chromatography were freshly destilled. TLC experiments were performed on Merck Kieselgel 60 F_{254} SiO_2 plates (prewashed with diethyl ether), developed with EtOAc/hexane mixtures, and visualized by spraying with anisaldehyde/sulfuric acid and warming to 120 °C, and on Merck Aluminiumoxid 60 F_{254} neutral Type F Al_2O_3 plates (prewashed with diethyl ether), developed with methylene chloride, and visualized by spraying with molybdate phosphoric acid and warming to 120 °C. Preparative separations were performed on Merck Kieselgel 60 (water content 5%) and Merck Lobar prepacked columns SiO_2 columns eluated with EtOAc/hexane mixtures, and on Merck Aluminiumoxid 90, standardized, activity II–III (water content 4%) Al_2O_3 columns eluated with methylene chloride. All preparative columns were prewashed with diethyl ether and hexane.

1,3,4,4a,5,6,7,7a,8,9-Decahydro-1,4,8-trihydroxy-6,6,8-trimethylazuleno[5,6-*c*]furan (2c). 2c (epimeric mixture 1:1) was obtained as crystalline white solid, mp 130–132 °C, by SiO_2 and Al_2O_3 chromatography of the SiO_2 degradation products of **1a** and **1c**: $[\alpha]^{22}{}_D$ −1.6° (*c* 1.0, ethanol). Elemental Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.1; H, 9.02. Found: C, 67.0; H, 9.03. UV no maximum above 210 nm; IR (KBr) 3320, 2960, 2950, 2880, 1470, 1380, 1130, 1050, 990 cm^{-1}.

1,3,4,4a,5,6,7,7a,8,9-Decahydro-4,8-dihydroxy-1-methoxy-6,6,8-trimethylazuleno[5,6-*c*]furan (2d). **2d** (epimeric mixture 1:1) was obtained as a crystalline white solid, mp 121–124 °C, by SiO_2 and Al_2O_3 chromatography of the SiO_2 degradation products of **1d**: $[\alpha]^{22}{}_D$ +15.3° (*c* 1.2, ethanol). Elemental Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.0; H, 9.28. Found: C, 67.6; H, 9.16. UV no maximum above 210 nm; IR (KBr) 3220, 2960, 2940, 1470, 1380, 1250, 1090, 1030, 1000, 960, 900, 760 cm^{-1}.

1,3,4,4a,5,6,7,7a,8,9-Decahydro-1,4-dihydroxy-8-methoxy-6,6,8-trimethylazuleno[5,6-*c*]furan (3c). **3c** (epimeric mixture 1:1) was obtained as a colorless oil by SiO_2 and Al_2O_3 chromatography of the products obtained when **1a** and **1c** were degraded in reagent grade methanol: $[\alpha]^{22}{}_D$ −2.4° (*c* 0.8, ethanol). Elemental Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.0; H, 9.28. Found: C, 67.8; H, 9.58. UV no maximum above 210 nm; IR (KBr) 3380, 2950, 2880, 1470, 1370, 1070, 990, 890 cm^{-1}.

1,3,4,4a,5,6,7,7a,8,9-Decahydro-4-hydroxy-1,8-dimethoxy-6,6,8-trimethylazuleno[5,6-*c*]furan (3d). **3d** was obtained as a white crystalline solid, mp 62–64 °C, by SiO_2 and Al_2O_3 chromatography of the products obtained when **1d** was degraded in reagent grade methanol: $[\alpha]^{22}{}_D$ −51.0° (*c* 1.2, ethanol). Elemental Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.9; H, 9.52. Found: C, 69.2; H, 9.59. UV no maximum above 210 nm; IR (KBr) 3390, 2930, 2920, 1470, 1380, 1140, 1090, 1060, 960, 910, 850, 740, 640 cm^{-1}.

4,8-Epoxy-1,3,4,4a,5,6,7,7a,8,9-decahydro-1-hydroxy-6,6,8-trimethylazuleno[5,6-*c*]furan (4c). The hemiacetal (epimeric mixture 1:1) is in equilibrium with the hydroxy aldehyde (approximately 10% in chloroform). This is indicated by IR and UV data, as well as by NMR data (given for the aldehyde group only). **4c** was obtained as a colorless oil by SiO_2 chromatography of the SiO_2 degradation products of **1a** and **1c**: $[\alpha]^{22}{}_D$ +98.1° (*c* 1.2, diethyl ether). Elemental Anal. Calcd for $C_{15}H_{22}O_3$: C, 72.0; H, 8.86. Found: C, 71.8; H, 9.08. UV 243 nm (2800); IR (KBr) 3400, 2960, 2940, 2870, 1670, 1470, 1370, 1030, 830 cm^{-1}.

4,8-Epoxy-1,3,4,4a,5,6,7,7a,8,9-decahydro-1-methoxy-6,6,8-trimethylazuleno[5,6-*c*]furan (4d). **4d** was obtained as a white crystalline solid, mp 54–58 °C, by SiO_2 chromatography of the SiO_2 degradation products of **1d**: $[\alpha]^{22}{}_D$ +30.0° (*c* 1.3, diethyl ether). Elemental Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.7; H, 9.15. Found: C, 72.8; H, 9.25. UV no maximum above 210 nm; IR (KBr) 2960, 2930, 2870, 1470, 1450, 1380, 1370, 1200, 1100, 1030, 880 cm^{-1}.

1,3,4,4a,5,6,7,7a,8,9-Decahydro-4-hydroxy-1-methoxy-6,6-dimethyl-8-methyleneazuleno[5,6-*c*]furan (5d). **5d** was obtained as a colorless oil by SiO_2 and Al_2O_3 chromatography of the SiO_2 degradation products of **1d**. Too small amounts of the pure compound were obtained to obtain elemental analysis and ^{13}C NMR: $[\alpha]^{22}{}_D$ +18° (*c* 0.1, diethyl ether); UV no maximum above 210 nm; IR (KBr) 3440, 2960, 2870, 1640, 1470, 1370, 1100, 1030, 900 cm^{-1}.

1,3,4,4a,5,6,7,9-Octahydro-4-hydroxy-1-methoxy-6,6,8-trimethylazuleno[5,6-*c*]furan (6d). **6d** was obtained as a colorless oil by SiO_2 and Al_2O_3 chromatography of the SiO_2 degradation products of **1d**: $[\alpha]^{22}{}_D$ +15.6° (*c* 3.3, diethyl ether). Elemental Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.7; H, 9.15. Found: C, 72.9; H, 9.19. UV no maximum above 210 nm; IR (KBr) 3410, 2960, 2870, 1470, 1370, 1040 cm^{-1}.

4-[2-(4,4-Dimethyl-1-cyclopentenyl)propyl]-2,5-dihydro-5-hydroxy-3-furancarbaldehyde (8c). **8c** (epimeric mixture 1:1) was obtained as a colorless oil by SiO_2 chromatography of the SiO_2 degradation products of **1a** and **1c**: $[\alpha]^{26}{}_D$ +23.8° (*c* 3.3, diethyl ether). Elemental Anal. Calcd for $C_{15}H_{22}O_3$: C, 72.0; H, 8.86; O, 19.2. Found: C, 71.8; H, 9.00; O, 19.5. UV (hexane) 238 nm (9000); IR (neat) 3400, 2960, 2880, 2850, 1680, 1470, 1370, 1260, 1050, 820 cm^{-1}.

4-[2-(4,4-Dimethyl-1-cyclopentenyl)propyl]-2,5-dihydro-5-methoxy-3-furancarbaldehyde (8d). **8d** was obtained as a colorless oil by SiO_2 chromatography of the SiO_2 degradation products of **1d**: $[\alpha]^{26}{}_D$ +7.9° (*c* 4.1, diethyl ether). Elemental Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.7; H, 9.15; O, 18.1. Found: C, 72.8; H, 9.09; O, 17.9. UV (hexane) 240 nm (9400); IR (neat) 2980, 2880, 2850, 1680, 1370, 1270, 1100, 1050, 960, 740 cm^{-1}.

5,6,7,9-Tetrahydro-6,6,8-trimethylazuleno[5,6-*c*]furan (14). **14** was obtained as a colorless oil by SiO_2 chromatography of the SiO_2 degradation products of **1a**. Too small amounts were obtained to obtain elemental analysis and ^{13}C NMR: UV 288 nm (5200); IR (KBr) 2960, 2930, 2870, 1470, 1370, 1050, 880, 790 cm^{-1}.

5,6,8,9-Tetrahydro-6,6,8-trimethylazuleno[5,6-*c*]furan (16). **16** was obtained as a white crystalline solid, mp 70–71 °C, by SiO_2 chromatography of the SiO_2 degradation products of **1a**: $[\alpha]^{22}{}_D$ +12.2° (*c* 1.2, diethyl ether). Elemental Anal. Calcd for $C_{15}H_{18}O$: C, 84.1; H, 8.47. Found: C, 83.7; H, 8.47. UV 246 (4700), 290 nm (14300); IR (KBr) 2950, 2870, 2840, 1430, 1370, 1050, 880, 790 cm^{-1}.

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Registry No. **1a**, 82855-01-4; **1c**, 83481-29-2; **1d**, 94061-53-7; 5α-**2c**, 94061-54-8; 5β-**2c**, 93943-48-7; 5α-**2d**, 93943-49-8; 5β-**2d**, 94061-55-9; 5α-**3c**, 93943-50-1; 5β-**3c**, 94061-56-0; **3d**, 93943-51-2; 5α-**4c**, 93943-52-3; 5β-**4c**, 94061-57-1; **4d**, 93943-53-4; 5α-**5c**, 93943-54-5; 5β-**5c**, 94061-59-3; **5d**, 93943-55-6; 5α-**6c**, 93943-56-7; 5β-**6c**, 94061-60-6; **6d**, 93943-57-8; (5*R*)-**8c**, 93943-62-5; (5*S*)-**8c**, 93943-58-9; **8d**, 93943-59-0; **13**, 94061-58-2; **14**, 93943-60-3; **15**, 74638-12-3; **16**, 93943-61-4; **17**, 54462-53-2; **18**, 74638-12-3.

Supplementary Material Available: MS and ^1H NMR data for compounds **2c**, **2d**, **3c**, **3d**, **4c**, **4d**, **5d**, **6d**, **8c**, **8d**, **14**, and **16** and ^{13}C NMR data for compounds **2c**, **2d**, **3c**, **3d**, **4c**, **4d**, **6d**, **8c**, **8d**, and **16** (6 pages). Ordering information is given on any current masthead page.