Chemistry of Natural Compounds and Bioorganic Chemistry

The synthesis of (±)-pallescensin A

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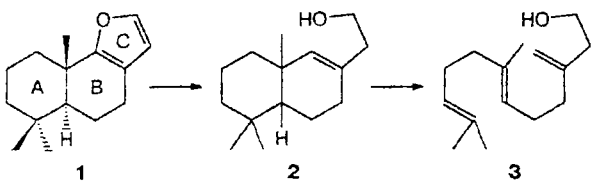
The racemic form of the metabolite of the *Dysidea* sea sponge, furanoterpenoid pallescensin A, was synthesized by cationic cyclization of the sulfonyl-substituted linear sesquiterpene precursor.

Key words: furanoterpenoid, pallescensin A; derivative of farnesol, cationic cyclization.

Previously,[1] we have attempted to synthesize the racemic form of the metabolite of the *Dysidea* sea sponge,[2] pallescensin A (**1**). We planned to prepare the key intermediare needed for this synthesis, *viz.*, appropriately functionalized octaline **2**, by the cationic cyclization (CC) of the available linear sesquiterpene alcohol **3**.



1 **2** **3**

However, realization of this scheme was hampered by an unfavorable regio- and stereochemical outcome of the CC of triene **3**; even under the optimal conditions, this reaction gave a mixture of products **5** in which undesirable regioisomers (regarding the position of the multiple bond) **5a,b** predominated (Scheme 1). Moreover, the minor component of the resulting mixture **5c**, whose primary structure was suitable for the subsequent building of the furan fragment of molecule **1**, was built, unlike the latter, from *cis*-fused rings *A* and *B*.

In view of the known[3] fact that an α-phenylsulfonyl group promotes the stabilization of type **9** carbocation to give mostly a sulfone of the allylic series, in the present work, we studied the possibility of controlling the regioselectivity of the key step in the scheme chosen for the synthesis of furanoterpenoid **1** using the appropriately functionalized trienol **4** as the substrate for CC. This compound was prepared by alkylation of the dilithium derivative **14** of hydroxysulfone **13**[4] with geranyl bromide **12**.

The cationic cyclization of triene **4** was carried out using a ~6.5-fold excess of HSO_3F in 2-nitropropane at −80 °C. The reaction yielded a complex mixture of

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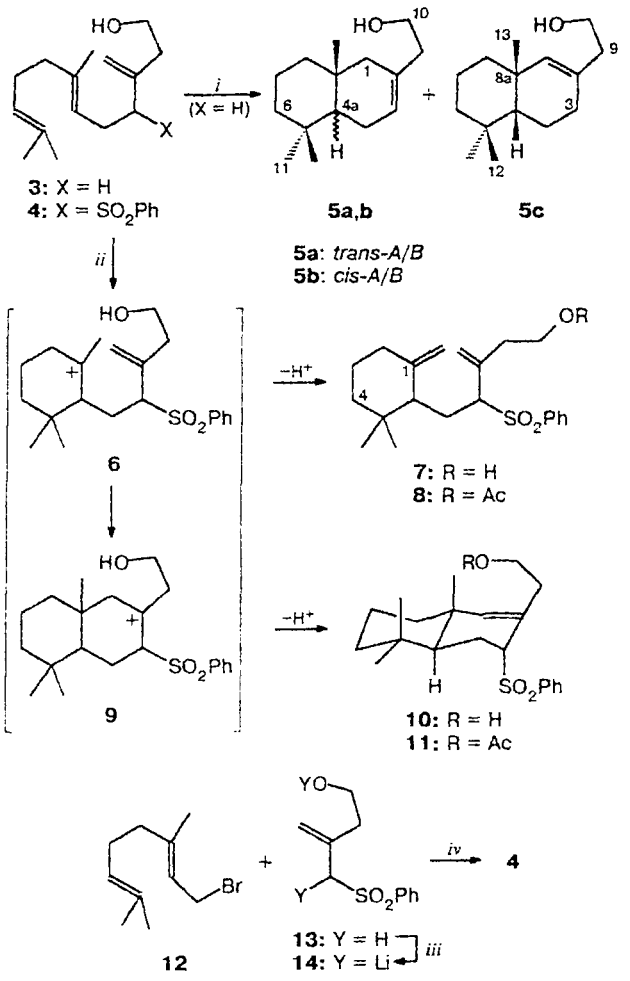
Scheme 1



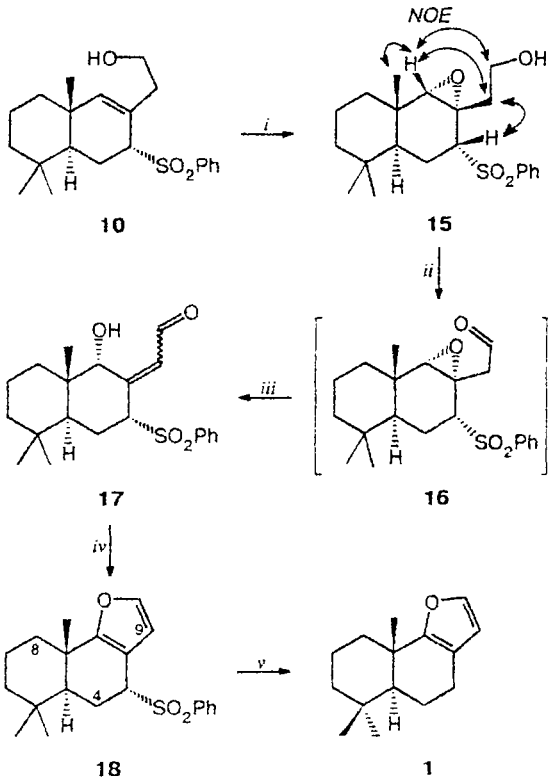
Reagents and conditions: *i.* $F_3B \cdot OEt_2$; *ii.* HSO_3F/Pr^iNO_2, −80 °C; *iii.* Bu^nLi/THF/HMPA, −70 °C; *iv.* THF, −60 °C.

mono- and bicyclic alcohols, which were acetylated without additional purification, because the acetates thus formed can be more easily distinguished by chromatography. During the separation of the resulting mixture of acetates by preparative HPLC, we found that substituted octaline **11**, in which the position of the double bond and the character of ring fusion corresponded to those needed for the subsequent synthesis of furanoterpenoid **1** according to our scheme, was present in this mixture as one of major components. The yield of acetate **11** was ~35% based on the initial triene **4** used in the reaction. This mixture was also found to contain monocyclic acetate **8** (yield ~38%); the corresponding alcohol **7** must have resulted from termination of the CC at the step of carbocation **6** due to its deprotonation. In addition, a fraction (~13%) consisting of an unresolved mixture of at least four products was isolated; apparently, these compounds were regio- and stereoisomers of acetates **8** and **11**. This is indicated by the fact that the ^1H NMR spectrum of this mixture contains a set of signals for exocyclic methine protons and for the protons of methyl groups, whose chemical shifts are close to those observed in the spectra of compounds **8** and **11**. It should be noted that the attempts to increase the yield of the latter compound by increasing the excess of the cyclizing reagent or by conducting the reaction for longer periods or at higher temperatures were unsuccessful; these attempts led only to the accumulation of resinous products.

The structures of the previously unknown acetates **8** and **11** and of alcohol **10** obtained by hydrolysis of the latter were determined using their ^1H and ^{13}C NMR, IR, and mass spectra and elemental analyses and also by comparing their spectral characteristics with those published previously[1] for related compounds. In particular, the conclusion about the relative configuration of the substituents and the geometry of ring fusion in octaline **11** was based on the magnitudes of the spin-spin coupling constants of the HC(3), HC(4), and HC(4a) protons. For the former proton, two vicinal constants, $J_{HC(3)-HC(4)} = 10$ Hz and $J_{HC(3)-HC(4')} = 8$ Hz, are observed, which is typical of equatorial—axial and equatorial—equatorial couplings, whereas in the case of HC(4a), one of the constants is equal to 14 Hz, which suggests its axial orientation. According to these results, acetate **11** exists in solution predominantly in the "steroid" conformation shown in Scheme 1 with a quasi-axial arrangement of the allylic phenylsulfonyl group. This is consistent with the same preferred orientation of this group found previously[5] for the series of cyclohexenes.

The further transformation of the homoallylic alcohol **10** into the target furanoterpenoid **1** was accomplished according to the scheme that we used previously[1] for the preparation of related compounds. The epoxidation of olefin **10** by *m*-chloroperbenzoic acid (MCPBA) proved to be stereospecific and gave hydroxy epoxide **15** (Scheme 2). The oxidation of alcohol **15** by the pyridinium complex of CrO_3 carried out in the next step yielded labile aldehyde **16**; upon contact with SiO_2, this compound, used without purification, transformed into a mixture of hydroxyaldehydes (*E*/*Z*)-**17** (*cf.* Ref. 1). The formation of labile hydroxyaldehydes **17** was confirmed by the ^1H NMR spectrum. The spectrum of a freshly prepared sample exhibited signals for the protons of the aldehyde group (δ 9.75) shifted upfield, as is normally observed for conjugated aldehydes, and also signals for the CHS-group protons (δ 3.75), methine protons (δ 5.5), and for the double set of protons of the methyl groups at δ 0.6—1.1. Hydroxyaldehydes **17** readily undergo cyclization to give furanoterpenoid **18**. This transformation occurs even during storage of a solution of **17** in $CDCl_3$ at room temperature. When the mixture of hydroxyaldehydes **17** is heated for a short period with a catalytic amount of *p*-toluenesulfonic acid in benzene, this transformation

Scheme 2



Reagents and conditions: *i.* MCPBA/CH_2Cl_2, 25 °C; *ii.* CrO_3/Py/CH_2Cl_2, 25 °C; *iii.* SiO_2, 25 °C; *iv.* TsOH/PhH, 80 °C; *v.* Li/NH_3/THF, −78 °C.

occurs rapidly. Finally, the ultimate step of the synthesis of furanoterpenoid **1** involved reductive desulfonylation of sulfone **18** by Li in NH_3.

Epoxide **15** and tricyclic sulfone **18** prepared for the first time were characterized by spectral data and by elemental analysis. The conclusion about the stereochemistry of the former compound was based on a 2D NOESY experiment (see Scheme 2). It should also be noted that, like octaline **11**, sulfones **15** and **18** exist in conformations in which the sulfonyl group is axial. This is indicated by the magnitudes (<10 Hz) of the vicinal spin-spin coupling constant of the HCS-group proton with both HC(4) protons, measured in the ^1H NMR spectra of these compounds. The spectral characteristics (^1H and ^{13}C NMR) of the (±)-pallescensin A **1** sample synthesized by this scheme were virtually identical to those reported[2,6] for the optically active form of this furanoterpenoid.

Experimental

Melting points (not corrected) were determined using a Koffler unit. IR spectra were recorded on a Specord M-80 instrument as KBr pellets. ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$ were measured on Bruker AC-200 and Bruker WM-250 spectrometers. Mass spectra (EI, 70 eV) were obtained on Varian MAT CH-6 and Varian MAT 311A instruments. The R_f values are given for a fixed SiO_2 layer (Silufol). HPLC was performed on a column with Silasorb 600 (10 μ, 250×24 mm) using a heptane—AcOEt mixture (22 : 1, v/v, 7 mL min^{-1}) as the eluent and a refractometric detector.

7,11-Dimethyl-3-methylene-4-phenylsulfonyldodeca-6*E*,10-dien-1-ol (4). A 1.2 *M* solution of Bu^nLi (31.7 mL) in hexane (38.04 mmol) was added at −70 °C (Ar) over a period of 10 min to a vigorously stirred solution of sulfone **13** [4] (3.86 g, 17.3 mmol) in 50 mL of THF and 9 mL of HMPA. After 20 min of stirring, a solution of bromide **12**[7] (4.88 g, 22.5 mmol) in 20 mL of THF was added over a period of 5 min. The reaction mixture was kept at −60 °C for 1 h, warmed to 0 °C, and quenched with saturated NH_4Cl. Ether was added, and the organic layer was separated, washed with water, dried with Na_2SO_4, and concentrated *in vacuo*, and the residue (7.2 g) was chromatographed on 150 g of SiO_2. Elution with a hexane—ether (7 : 3) mixture gave 4.13 g (66%) of compound **4** as colorless oil, R_f 0.32 (hexane—ether, 2 : 1). ^1H NMR, δ: 1.51, 1.57 and 1.66 (all br.s, 9 H, Me); 1.9—2.8 (m, 8 H, CH_2); 3.57 (dd, 1 H, HCS, J = 11.4 and 3.9 Hz); 3.68 (m, 2 H, H_2CO); 4.92 and 5.02 (both br.t, 2 H, HC=C, J = 7 Hz); 5.24 and 5.28 (both br.s, 2 H, H_2C=C); 7.5—7.9 (m, 5 H, H arom.). ^{13}C NMR, δ: 16.0, 17.5, 26.3 (Me); 26.3, 27.3, 39.3, 39.8 (CH_2); 50.4 (CHO); 69.6 (CHS); 118.8 and 123.9 (H<u>C</u>=C); 120.1 (H_2<u>C</u>=C); 131.69, 137.45, 137.53 (C=); 128.11, 129.0, 133.6, 138.9 (C arom.). Found (%): C, 69.22; H, 8.38; S, 8.66. $C_{21}H_{30}O_3S$. Calculated (%): C, 69.57; H, 8.34; S, 8.84.

2-(2-Acetoxyethyl)-5,5,8aβ-trimethyl-3α-phenylsulfonyl-3,4,4aα,5,6,7,8,8a-octahydronaphthalene (11) and 2-(5-acetoxy-3-methylene-2-phenylsulfonylpent-1-yl)-3,3-dimethyl-1-methylenecyclohexane (8). A solution of triene **4** (2.82 g, 7.8 mmol) in 30 mL of Pr^iNO_2 cooled to −80 °C was added over a period of 10 min to a solution of HSO_3F (5.08 g, 50.5 mmol) in 40 mL of Pr^iNO_2 vigorously stirred at −80 °C (Ar). The reaction mixture was kept for 25 min at −80 °C, quenched with a solution of NEt_3 (16.02 g, 0.16 mol) in 20 mL of Pr^iNO_2, warmed to 0 °C over a period of 30 min, and treated with ether and water. The aqueous layer was separated and extracted with ether. The combined organic layer was washed with water, dried with Na_2SO_4, and concentrated *in vacuo* to give ~3 g of a substance; the product was dissolved in a mixture of pyridine (1.28 g, 16.1 mmol) and Ac_2O (1.64 g, 16.1 mmol). The reaction mixture was kept at 25 °C for 20 min, quenched with a saturated aqueous solution of $NaHCO_3$, and extracted with ether. The usual workup of the ethereal extract gave ~3.2 g of a product, which was chromatographed on 100 g of SiO_2. Elution with a hexane—ether (4 : 1) mixture yielded 2.77 g of a fraction with R_f 0.35 (hexane—ether, 4 : 1), which was separated by HPLC. This gave (in the order of elution) 1.1 g (35%) of acetate **11** and 1.2 g (38%) of acetate **8**.

Acetate **11** — colorless prisms, m.p. 89—90 °C (hexane). IR, ν/cm^{-1}: 538, 570, 600, 664, 680, 740, 754, 780, 1030, 1045, 1080, 1128, 1140, 1170, 1200, 1220, 1241, 1268, 1300, 1378, 1440, 1460, 1475, 1735, 1744, 2800—3100. ^1H NMR, δ: 0.41, 0.71 and 0.76 (all s, 9 H, Me); 0.91 (dd, 1 H, HC(4a), J = 14.0 and 3.0 Hz); 1.0—1.4 (m, 6 H, CH_2); 1.55 (ddd, 1 H, HC(4), J = 14.0, 14.0, and 10.0 Hz); 1.89 (ddd, 1 H, HC(4), J = 14.0, 8.0, and 3.0 Hz); 2.01 (s, 3 H, MeCO); 2.50 (ddd, 1 H, HC(9), J = 15.0, 9.0, and 6.5 Hz); 3.09 (ddd, 1 H, HC(9), J = 15.0, 6.0, and 4.5 Hz); 4.02 (dd, 1 H, HCS, J = 10.0 and 8.0 Hz); 4.15 (ddd, 1 H, HCO, J = 11.0, 6.5, and 4.5

Hz); 4.38 (ddd, 1 H, HCO, J = 11.0, 9.0, and 6.0 Hz); 5.50 (s, 1H, HC(1)); 7.5—7.9 (m, 5 H, HC arom.). ^{13}C NMR, δ: 18.8 and 20.9 (Me); 19.7 (C-7); 21.0 (MeCO); 22.5 (C-4); 32.5 (Me-11); 32.9 (C-5); 34.6 (C-8); 35.2 (C-8a); 40.0 and 42.0 (C-6, C-9); 49.4 (C-4a); 62.7 (CHS); 65.7 (CH_2O); 122.8 (C-2); 137.0 (C-1); 171.0 (C=O); 129.0, 129.4, 133.7, 148.2 (C arom.).Found (%): C, 68.43; H, 7.87; S, 7.84. $C_{23}H_{32}O_4S$. Calculated (%): C, 68.28; H, 7.97; S, 7.93.

Acetate **8** — colorless oil, R_f 0.35 (hexane—ether, 4 : 1). IR, ν/cm^{-1}: 538, 562, 615, 688, 720, 755, 910, 1035, 1083, 1148, 1241, 1304, 1362, 1385, 1445, 1640, 1740, 2800—3100. ^{1}H NMR, δ: 0.80 and 0.86 (both s, 6 H, Me); 1.1—2.4 (m, 11 H, CH_2, CH); 2.01 (s, 3 H, MeCO); 3.60 (dd, 1 H, HCS, J = 12.5 and 3.0 Hz); 4.12 (m, 2 H, CH_2O); 4.40, 4.76, 4.94, and 5.14 (all br.s. 4 H, H_2C=); 7.5—7.9 (m, 5 H, HC arom.). ^{13}C NMR, δ: 19.1 (C-5); 21.0 (MeCO); 23.3, 23.6 (Me); 28.4 (C-1'); 33.6 (C-3); 34.6 (C-6); 35.1 (C-4'); 40.5 (C-4); 49.8 (C-2); 61.9 (CH_2O); 69.5 (CHS); 110.2, 119.8 (H_2C=); 136.7, 147.8 (C=); 170.9 (C=O); 128.6, 129.3, 133.6, 148.1 (C arom.). MS, m/z: 263 $[M-PhSO_2]^+$, 203 $[M-PhSO_2-MeCO_2]^+$.

2-(2-Hydroxyethyl)-5,5,8aβ-trimethyl-3α-phenylsulfonyl-3,4,4aα,5,6,7,8,8a-octahydronaphthalene (10). A solution of compound **11** (0.25 g, 0.62 mmol) and KOH (38 mg, 0.68 mmol) in 1 mL of methanol was kept at 25 °C for 10 min (Ar); then the mixture was diluted with ether and neutralized with 10% HCl. The aqueous layer was separated and extracted with ether. The usual workup of the combined organic layer gave ~0.25 g of a substance, which was then chromatographed on 3 g of SiO_2. Elution with a hexane—ether (1 : 1) mixture gave 0.22 g (97%) of compound **10** as a colorless oil, R_f 0.31 (hexane—ether, 1 : 4). ^{1}H NMR, δ: 0.45, 0.70, and 0.75 (all s, 9 H, Me); 1.0—1.6 (m, 8 H, CH, CH_2); 1.73 (ddd, 1 H, HC(4), J = 14.2, 7.9, and 3.0 Hz); 2.4 (m, 1 H, HC(9)); 3.09 (dt, 1 H, HC(9), J = 15.2 and 4.8 Hz); 4.12 (dd, 1 H, HCS, J = 9.1 and 7.8 Hz); 3.75 (m, 2 H, H_2CO); 5.55 (br.s, 1 H, HC(1)); 7.5—7.9 (m, 5 H, HC arom.). MS, m/z: 221 $[M-PhSO_2]^+$, 220, 203, 187, 177, 150, 148, 139, 135, 133, 125, 121, 119, 117, 108, 106, 105, 97, 95, 92, 91, 82, 80, 76.

1α,2-Epoxy-2β-(2-hydroxyethyl)-5,5,8aβ-trimethyl-3α-phenylsulfonyl-1,2,3,4,4aα,5,6,7,8,8a-decahydronaphthalene (15). MCPBA (0.3 g, 1.49 mmol) was added in portions over a period of 10 min to a solution of alcohol **10** (0.23 g, 0.63 mmol) in 5 mL of CH_2Cl_2 stirred at 25 °C (Ar). The reaction mixture was kept for 12 h at 25 °C, diluted with ether, washed with a 5% solution of KOH and water, dried with Na_2SO_4, and concentrated *in vacuo*. The residue (0.24 g) was chromatographed on 20 g of SiO_2. Elution with a hexane—ether (7 : 3) mixture gave 0.16 g (74%) of epoxide **15** as colorless prisms, m.p. 86—87 °C (hexane). IR, ν/cm^{-1}: 545, 600, 670, 695, 720, 755, 820, 855, 880, 910, 945, 970, 1000, 1085, 1145, 1180, 1205, 1290, 1305, 1320, 1370, 1385, 1395, 1450, 1460, 1550, 1585, 1720, 2800—3100. ^{1}H NMR (C_6D_6), δ: 0.46, 0.58, and 1.06 (all s, 9 H, Me); 0.8—1.6 (m, 9 H, CH, CH_2); 2.07 (dt, 1 H, HC(9), J = 15.3 and 5.6 Hz); 2.68 (s, 1 H, HC(1)); 3.06 (dt, 1 H, HC(9), J = 15.3 and 6.2 Hz); 3.81 (br.t, 1 H, HCS, J = 9.1 Hz); 3.98 (dd, 2 H, H_2CO, J = 6.2 and 5.6 Hz); 7.0 and 7.7 (both m, 5 H, HC arom.). ^{13}C NMR, δ: 17.0, 21.0 (Me); 17.9 (C-7); 22.0 (C-4); 32.4 (Me-11); 33.9 (C-5); 36.6 (C-8); 36.7 (C-6); 36.7 (C-8a); 40.3 (C-4a); 41.4 (C-9); 58.9 (H_2CO); 59.1 (C-2); 62.6 (HCS); 70.9 (C-1); 128.2, 129.1, 133.8, 138.9 (C arom.). MS, m/z: 208, 207, 189, 163, 149, 143, 133, 123, 119, 111, 109, 107, 105, 95, 93, 91, 81, 79, 78, 77, 69. Found (%): C, 66.52; H, 7.98; S, 8.39. $C_{21}H_{30}O_4S$. Calculated (%): C, 66.63; H, 7.99; S, 8.47.

5,5,8aβ-Trimethyl-3α-phenylsulfonyl-3,4,4aα,5,6,7,8,8a-octahydronaphtho[1,2-*b*]furan (18).* A solution of **15** (0.76 g, 2 mmol) in 8 mL of CH_2Cl_2 was added over a period of 3 min to a solution of CrO_3 (1.2 g, 12 mmol) in 15 mL of CH_2Cl_2 and 1.94 mL (1.9 g, 24 mmol) of pyridine stirred at 25 °C (Ar). The reaction mixture was kept at 25 °C for 2 h and diluted with ether; the precipitate was separated by decanting, and the solution was concentrated *in vacuo* to give 0.7 g of a substance. SiO_2 (7 g) was added to this product, and the mixture was kept at 25 °C for 5 h and extracted with ether. The extract was concentrated *in vacuo*, and the residue (0.66 g) was chromatographed on 30 g of SiO_2. Elution with a hexane—ether (3 : 2) mixture gave 0.5 g (66%) of a mixture of unstable hydroxyaldehydes **17** (^{1}H NMR data) as a colorless oil, R_f 0.41 (hexane—ether, 3 : 7). A solution of this mixture and a catalytic quantity (10 mg) of *p*-TsOH in 5 mL of benzene was refluxed for 1 h. The benzene was evaporated *in vacuo*, and the residue was chromatographed on 30 g of SiO_2. Elution with a hexane—ether (4 : 1) mixture gave 0.28 g (59%) of sulfone **18** as colorless prisms, m.p. 121—122 °C (hexane). IR, ν/cm^{-1}: 540, 555, 610, 695, 725, 735, 750, 760, 820, 870, 890, 970, 1045, 1075, 1090, 1130, 1140, 1160, 1200, 1240, 1290, 1300, 1370, 1390, 1445, 1460, 1475, 1510, 1610, 2920—3010, 3030. ^{1}H NMR, δ: 0.85, 0.92, and 1.09 (all s, 9 H, Me); 1.0—1.7 (m, 6 H, CH_2); 1.90 (ddd, 1 H, HC(4), J = 15.4, 13.0, and 7.2 Hz); 2.06 (m, 1 H, HC(4a), J = 12.9 and 3.1 Hz); 2.40 (dd, 1 H, HC(4), J = 15.2 and 3.2 Hz); 4.20 (br.d, 1 H, HC(3), J = 7.2 Hz); 6.33 (d, 1 H, HC(9), J = 1.8 Hz); 7.24 (d, 1 H, HC(10), J = 1.8 Hz); 7.45 and 7.85 (m, 5 H, HC arom.). ^{13}C NMR, δ: 18.2 (C-7); 20.5 (C-4); 20.5 and 21.1 (Me); 32.8 (C-5); 32.9 (Me-11); 34.4 (C-8); 36.1 (C-8a); 41.6 (C-6); 45.8 (C-4a); 59.7 (C-3); 106.5 (C-2); 110.9 (C-9); 140.8 (C-10); 154.1 (C-1);.128.8, 129.4, 133.6, 139.0 (C arom.). MS, m/z: 217 $[M-PhSO_2]^+$, 207, 161, 147, 131, 109, 91, 77, 64. Found (%): C, 70.05; H, 7.21, 8.97. $C_{21}H_{26}O_3S$. Calculated (%): C, 70.35; H, 7.31; S, 8.94.

(±)-Pallescensin A (1).* A solution of sulfone **18** (0.14 g, 0.4 mmol) in 3 mL of THF was added in one portion to a solution of Li (28 mg, 4 mg-at) in 15 mL of NH_3 vigorously stirred at −78 °C (Ar). The reaction mixture was kept for 15 min at −78 °C and quenched with excess NH_4Cl; NH_3 was evaporated, and the residue was treated with ether and with water. The aqueous layer was separated and extracted with ether. The usual workup of the combined organic layer gave 0.1 g of a product, which was then chromatographed on 10 g of SiO_2. Elution with hexane gave 50 mg (59%) of furan **1** as a colorless oil with R_f 0.52 (hexane). ^{1}H NMR, δ: 0.92, 0.95, and 1.20 (all s, 9 H, Me); 1.15—1.90 (m, 8 H, CH_2); 2.12 (br.d, 1 H, HC(4a), J = 12.7 Hz); 2.28—2.56 (m, 2 H, HC(3)); 6.13 (d, 1 H, HC(9), J = 1.8 Hz); 7.20 (d, 1 H, HC(10), J = 1.8 Hz) (*cf.* Refs. 2 and 6).

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* 6,6,9aβ-Trimethyl-4α-phenylsulfonyl-4,5,5aα,6,7,8,9,9a-octahydronaphtho[1,2-*b*]furan. To make comparison of the NMR spectra more convenient, the numbering of atoms in compound **18** corresponds to that in compounds **5**, **10**, **11**, and **15**.

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