Synthesis and Odor of Chiral Partial Structures of Khusimone

Part 3[1])

Short Communication

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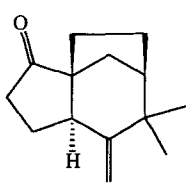
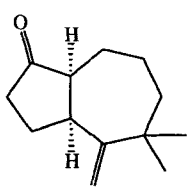
Khusimone (**1**), one of the main odor-donating compounds of vetiver oil, is subject of the following study on structure/odor relationship. The omittance of the methano bridge of the tricyclic khusimone should lead to the bicyclic partial structure (–)-**2**. Unexpectedly, (–)-**2** could not be obtained since epimerization favored (–)-**16**. The stereochemical key step of the synthesis of the hydrazulene nucleus is based on a highly diastereoselective conjugate addition to a chiral oxocyclopent-1-ene-1-carboxylate.

Introduction. – In continuation of our studies [1–4] on the question whether it is possible to generate a well-balanced vetiver odor also from a bicyclic partial structure of (–)-khusimone (**1**), which is one of the main odor-donating compounds of the essential oil of *Vetiveria zizanoides*, finally we focused our interest on the olfactory consequences of omitting the methano bridge. This degradation of the tricyclic nor-sesquiterpene leads to structure (–)-**2**. The synthetic approach to (–)-**2** should be realized as depicted in *Scheme 1*.

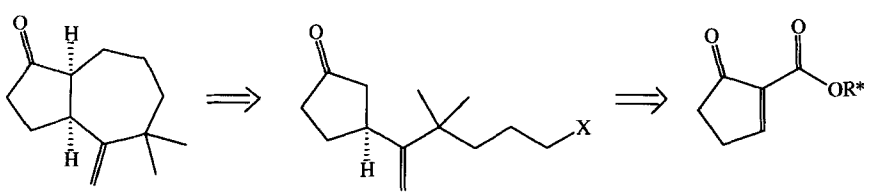


(–)-**1**



(–)-**2**

Scheme 1



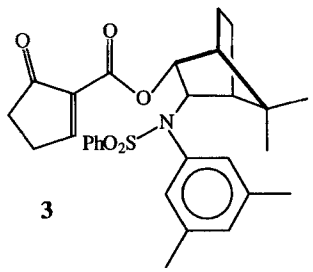
(–)-**2**

[1]) Part 2: [1].

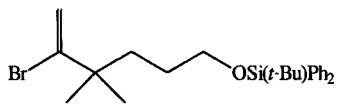
[2]) Part of the Ph. D. thesis [2].

[3]) Part of Diploma work [3].

Results and Discussion. – Based on retrosynthetic considerations, we used as starting materials bromo compound **4** and the chiral olefinic oxo ester **3** [4–7].



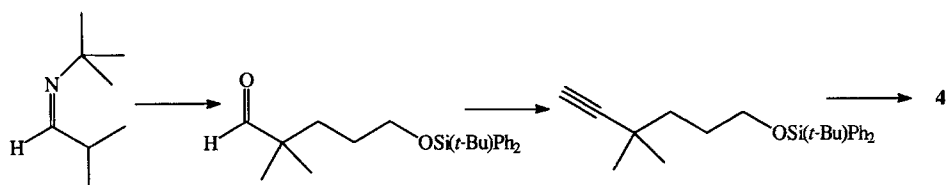
3



4

Employing the already successful methodology [4], the synthesis of **4** started from the *N*-(*tert*-butyl)-imine derivative **5** of isobutyraldehyde (*Scheme 2*). After alkylation and hydrolysis of **5**, the resulting aldehyde **6** was converted to the alkyne **7**. Successive treatment with *B*-bromo-9-BBN (*B*-bromo-9-borabicyclo[3.3.1]nonane) yielded **4**.

Scheme 2

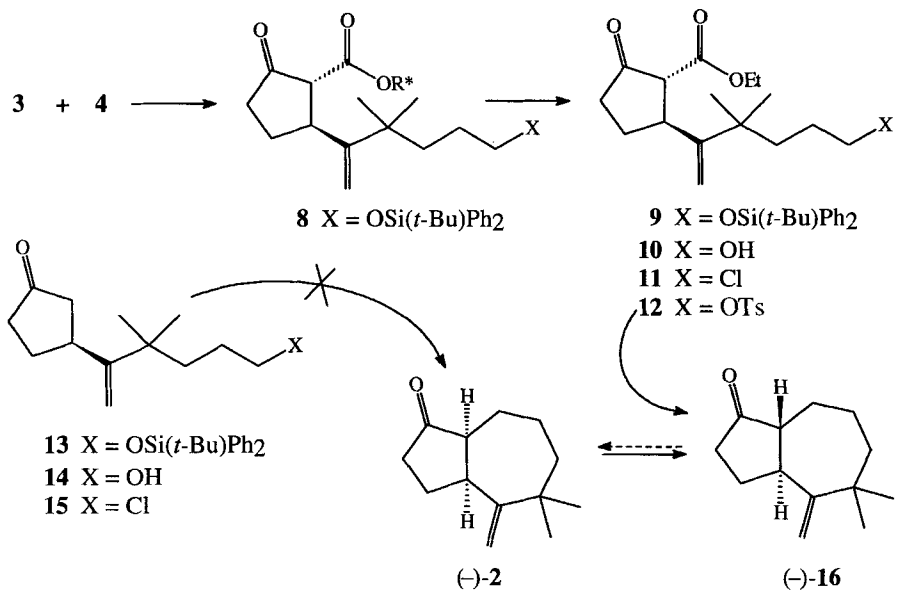


5 **6** **7**

The stereochemical key step was realized by converting **4** into the organolithium compound by reaction with 2 equiv. *t*-BuLi, followed by $MgBr_2 \cdot Et_2O$, $CuBr \cdot Me_2S$, and $BF_3 \cdot Et_2O$, and subsequent conjugate addition to the chiral ester **3** (*Scheme 3*). This method, which consumes only 1 equiv. of **4** led, in high yields (*ca.* 80%), to **8** (*Gilman*'s reagent led to only very low yields of **8**; *ca.* 5%), and, in accordance to [4–7], no diastereoisomeric impurities could be detected *via* ^1H- and ^{13}C-NMR. Transesterification (→ **9**) and decarbethoxylation led to the chiral ketone **13**. In the following, chloride **15** should be submitted to cyclization. Unexpectedly, this led only in traces to (−)-**16**, moreover, (−)-**2** could not be detected at all. The use of toluene-4-sulfonates as much better leaving group failed completely. Only the apparently more reactive β-oxo ester **12** allowed intramolecular cyclization by treatment with *t*-BuOK (KH, $LiN(SiMe_3)_2$ failed as did the use of the appropriate chloride **11** as starting material). Subsequent decarboxylation of the resulting bicyclic β-oxo ester again afforded only (−)-**16**. It is obvious that equilibrium *via* keto-enol tautomerism favors (−)-**16** to such a great extent that (−)-**2** could not be isolated. Accordingly, stirring of (−)-**16** for 24 h with NaOMe in MeOH did not change the ratio in favor of the epimer (−)-**2**.

Confirmation of the structure of (−)-**16** as well as assignment of resonances was achieved by a combination of different NMR techniques, such as NOE-difference spec-

Scheme 3



troscopy [8], APT [9], HMQC [10], COSY-45 [11], and long-range INEPT [12] experiments with selective excitation. Comparison of the ^{1}H- and ^{13}C-chemical shifts of (–)-**16** with those found for its two demethylidene congeners (replacement of the seven-membered ring of (–)-**16** by a six-membered ring) described in [4] reveals excellent correspondence with the *trans*-fused isomer. This is an additional strong hint for *trans*-configuration of H–C(3a) and H–C(8a) in (–)-**16**.

Compound (–)-**16** exhibits an intense woody and camphoraceous odor. In summary, the odorous impression is a pleasent one but lacks the typical vetiver odor descriptors.

We are indepted to Mr. *W. Höppner* and *V. Hausmann*, perfumers of *Dragoco-Vienna*, for the organoleptic analysis.

Experimental Part

General: See [4]. For experimental details for the synthesis of the new compounds **4**–**15**, see cognate preparations; yields were similar to those obtained for congeneres described in [4].

*5-[(*tert*-Butyl)diphenylsilyloxy]-2,2-dimethylpentanal* (**6**). IR (NaCl, liquid film): 1730. ^{1}H-NMR (80 MHz, $CDCl_3$): 0.96 (*s*, 2 Me); 0.97 (*s*, 3 Me); 1.08–2.24 (*m*, 4 H); 3.59 (*m*, CH_2O); 7.28 (*m*, 6 H, H–C(3), H–C(4), H–C(5) of Ph); 7.59 (*m*, 4 H, H–C(2), H–C(6) of Ph); 9.36 (*s*, CHO). ^{13}C-NMR (75 MHz, $CDCl_3$): 206.0 (C=O); 135.5 (arom. C(2), C(6)); 133.8 (arom. C(1)); 129.5 (arom. C(4)); 127.5 (arom. C(3), C(5)); 63.9 (C(5)); 45.4, 33.3, 27.3 (C(2), C(3), C(4)); 26.8 (Me_3C); 21.2 (Me_2C); 19.1 (Me_3C). M.: 312 (23), 311 (92), 233 (21), 200 (22), 199 (100), 197 (10), 183 (13), 181 (10), 139 (26).

*6-[(*tert*-Butyl)diphenylsilyloxy]-3,3-dimethylhex-1-yne* (**7**). IR (NaCl, liquid film): 3305. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.98 (*s*, 3 Me); 1.12 (*s*, 2 Me); 1.30–1.79 (*m*, 4 H); 1.98 (*s*, HC≡C); 3.61 (*t*, J = 6.3, CH_2O); 7.32 (*m*, 6 H, H–C(3), H–C(4), H–C(5) of Ph); 7.60 (*m*, 4 H, H–C(2), H–C(6) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.6 (arom. C(2), C(6)); 134.1 (arom. C(1)); 129.5 (arom. C(4)); 127.6 (arom. C(3), C(5)); 91.8 (C(2));

67.7 (C(1)); 64.2 (C(6)); 39.3, 30.7, 28.5 (C(3), (C(4), (C(5)); 29.1 (Me_2C); 26.8 (Me_3C); 19.2 (Me_3C). MS: 308 (13), 307 (47), 229 (37), 200 (18), 199 (100), 183 (15), 181 (15), 163 (17), 137 (10).

*2-Bromo-6-[(*tert*-butyl)diphenylsilyloxy]-3,3-dimethylhex-1-ene* (**4**). IR (NaCl, liquid film): 1620, 1590. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.05 (*s*, 3 Me); 1.15 (*s*, 2 Me); 1.47 (*m*, 4 H); 3.65 (*m*, CH_2O); 5.45 (*d*, J = 2.1, 1 H, CH_2=C); 5.55 (*d*, J = 2.1, 1 H, CH_2=C); 7.38 (*m*, 6 H, H–C(3), H–C(4), H–C(5) of Ph); 7.68 (*m*, 4 H, H–C(2), H–C(6) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.6 (C(2)); 135.6 (arom. C(2), C(6)); 134.1 (arom. C(1)); 129.5 (arom. C(4)); 127.6 (arom. C(3), C(5)); 115.7 (C(1)); 64.2 (C(6)); 42.4, 37.2, 27.7 (C(3), C(4), C(5)); 27.1 (Me_2C); 26.9 (Me_3C); 19.2 (Me_3C). MS: 389 (12), 387 (12), 263 (19), 261 (20), 199 (14), 181 (16), 109 (100), 81 (16), 67 (49).

*(1*R*,2*S*,3*R*,4*S*)-3-[*N*-(3,5-Dimethylphenyl)-N-(phenylsulfonyl)amino]-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl (1*R*,2*S*)-2-{5-[(*tert*-Butyl)diphenylsilyloxy]-2,2-dimethyl-1-methylidenepentyl}-5-oxocyclopentanecarboxylate* (**8**). Yield after CC (petroleum ether/AcOEt 8:2): 3.95 g (78%). Colorless crystals. M.p. 63–64°. IR (KBr): 1760, 1730, 1640, 1610, 1600, 1170, 1090. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.58 (*s*, Me); 0.91 (*s*, Me); 0.98 (*s*, Me); 1.03 (*s*, *t*-Bu); 1.08 (*s*, Me); 1.14 (*s*, Me); 1.20–1.88 (*m*, 11 H); 1.98 (br. *s*, MeC_6H_3); 2.16–2.64 (*m*, MeC_6H_3, 2 aliph. H); 3.36–3.80 (*m*, CH_2O, H–C(1), H–C(2)); 3.85 (*d*, J = 7.0, H–C(3′)); 5.03 (*s*, 1 H, C=CH_2); 5.10 (*s*, 1 H, C=CH_2); 5.24 (*d*, J = 7.0, H–C(2′)); 5.58 (*s*, H–C(2) of $Me_2C_6H_3$); 6.83 (*s*, H–C(4) of $Me_2C_6H_3$); 7.15 (*s*, H–C(6) of $Me_2C_6H_3$); 7.18–7.59 (*m*, 11 arom. H); 7.60–7.78 (*m*, 4 H, H–C(2), H–C(6) of Ph_2Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.7 (C(5)); 167.6 (COO); 156.3 (=$CCMe_2$); 138.5 (C(1) of $PhSO_2$); 137.3 (C(1) of $Me_2C_6H_3$); 135.5 (C(2), C(6) of Ph_2Si); 134.1 (C(1) of Ph_2Si); 132.2 (C(4) of $PhSO_2$); 129.4, 129.3, 128.2, 127.9, 127.5 (arom. C); 109.5 (CH_2=); 82.5 (C(2′)); 67.3 (C(3′)); 64.6 (CH_2O); 62.5 (C(1)); 50.7 (C(1′)); 48.4 (C(4′)); 47.4 (C(7′)); 40.6 (C(2)); 39.2, 38.7 (=$CCMe_2$ or C(4)); 37.0 (CH_2); 32.2, 31.3, 27.8, 27.78 (C(3), C(5′), C(6′), CH_2); 27.6, 27.0 (Me_2C); 26.9 (Me_3C); 21.4, 21.1, 20.7 (arom. Me, 2 Me); 19.2 (Me_3C); 11.3 (Me). MS: 751 (6), 750 (27), 748 (59), 747 (100), 746 (6), 745 (7), 415 (6), 414 (6), 413 (21), 142 (3). Anal. calc. for $C_{54}H_{69}NO_6SSi$ (888.29): C 73.02, H 7.83, N 1.58; found: C 72.76, H 8.04, N 1.53.

*Ethyl (1*R*,2*S*)-2-{5-[(*tert*-Butyl)diphenylsilyloxy]-2,2-dimethyl-1-methylidenepentyl}-5-oxocyclopentanecarboxylate* (**9**). IR (NaCl, liquid film): 1760, 1730, 1660, 1635, 1595, 1115. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02 (*s*, Me); 1.046 (*s*, *t*-Bu); 1.051 (*s*, Me); 1.23 (*t*, J = 6.9, Me); 1.30–1.74 (*m*, 5 H, CH_2CH_2C=O, $CH_2CH_2CH_2O$, CH_2CH_2O); 2.12–2.38 (*m*, 2 H, CH_2C=O, CH_2CH_2C=O); 2.39–2.58 (*m*, 1 H, CH_2C=O); 3.10–3.34 (*m*, H–C(1), H–C(2)); 3.48–3.76 (*m*, CH_2OSi); 4.13 (*dq*, J = 0.9, 6.9, CH_2OC=O); 5.0 (*s*, 1 H, CH_2=C); 5.05 (*s*, 1 H, CH_2=C); 7.23–7.49 (*m*, 6 H, H–C(3), H–C(4), H–C(5) of Ph); 7.55–7.80 (*m*, 4 H, H–C(2), H–C(6) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.6 (C(5)); 169.2 (COO); 157.4 (C(1′)); 135.6 (arom. C(2), C(6)); 134.0 (arom. C(1)); 129.5 (arom. C(4)); 127.6 (arom. C(3), C(5)); 109.0 (CH_2=); 64.4 (C(5′)); 63.2 (C(1)); 61.3 (CH_2O); 42.0 (C(2)); 39.2 (C(2′)); 39.0 (C(4)); 36.6 (CH_2); 32.1 (C(3)); 27.9 (CH_2); 27.3, 26.8 (Me_2C); 26.9 (Me_3C); 19.2 (Me_3C); 14.2 (Me). MS: 394 (1), 392 (30), 391 (86), 281 (26), 199 (100), 183 (18), 181 (17), 175 (9), 105 (6), 55 (7). Anal. calc. for $C_{32}H_{44}O_4Si$ (520.78): C 73.80, H 8.52; found: C 73.67, H 8.57.

*Ethyl (1*R*,2*S*)-2-(5-Hydroxy-2,2-dimethyl-1-methylidenepentyl)-5-oxocyclopentanecarboxylate* (**10**). IR (NaCl, liquid film): 3440, 1755, 1720, 1640. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*s*, Me); 1.10 (*s*, Me); 1.26 (*dt*, J = 3.0, 7.1, Me); 1.31–1.65 (*m*, H–C(3), $CH_2CH_2CH_2O$, CH_2CH_2O); 2.05 (*m*, 1 H); 2.32–2.51 (*m*, 3 H, H–C(3), H–C(4)); 3.26 (*m*, H–C(1), H–C(2)); 3.59 (*m*, CH_2O); 4.15 (*m*, CH_2OC=O); 5.03 (*d*, J = 2.3, 1 H, CH_2=C); 5.06 (*d*, J = 2.3, 1 H, CH_2=C). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.4 (C(5)); 169.4 (COO); 157.0 (C(1′)); 109.1 (CH_2=); 62.9 (C(1)); 63.0, 61.4 (C(5′), CH_2O); 41.7 (C(2)); 39.1, 38.8 (C(4), C(2′)); 36.3 (CH_2); 32.1 (C(3)); 27.8 (CH_2); 27.4, 26.6 (Me_2C); 14.0 (Me). MS: 282 (1, M^+), 236 (4), 177 (22), 155 (36), 121 (27), 109 (62), 79 (36), 69 (36), 67 (37), 55 (100). HR-MS: calc. for $C_{16}H_{26}O_4^+$: 282.1831; found: 282.183 ± 0.0014.

*Ethyl (1*R*,2*S*)-2-[2,2-Dimethyl-1-methylidene-5-(*p*-tolylsulfonyl)pentyl]-5-oxocyclopentanecarboxylate* (**12**). IR (NaCl, liquid film): 1760, 1725, 1655, 1635, 1600, 1360, 1175. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.01 (*s*, Me); 1.05 (*s*, Me); 1.24 (*t*, J = 7.2, Me); 1.36–1.64 (*m*, H–C(3), $CH_2CH_2CH_2O$, CH_2CH_2O); 2.23–2.55 (*m*, 3 H, H–C(3), H–C(4)); 2.45 (*s*, MeC_6H_4); 3.16–3.26 (*m*, H–C(1), H–C(2)); 4.00 (*m*, CH_2OSO_2); 4.11 (*m*, CH_2O); 5.02 (*s*, CH_2=); 7.35 (*d*, J = 8.1, H–C(3), H–C(5) of Ph); 7.78 (*d*, J = 8.1, H–C(2), H–C(6) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 211.2 (C(5)); 169.1 (COO); 156.6 (C(1′)); 144.6 (C(1) of Ph); 133.2 (C(4) of Ph); 129.7 (C(3), C(5) of Ph); 127.8 (C(2), C(6) of Ph); 109.5 (CH_2=); 70.9 (CH_2OSO_2); 63.0 (C(1)); 61.3 (CH_2O); 41.6 (C(2)); 39.1, 38.8 (C(4), C(2′)); 35.8 (CH_2); 32.1 (C(3)); 27.0, 26.6 (Me_2C); 24.4 (CH_2); 21.6 (MeC_6H_4); 14.1 (Me). MS: 436 (2, M^+), 390 (11), 363 (23), 177 (93), 155 (76), 109 (91), 107 (44), 91 (100), 67 (41), 55 (77).

*(3*S*)-3-{5-[(*tert*-Butyl)diphenylsilyloxy]-2,2-dimethyl-1-methylidenepentyl}cyclopentanone* (**13**). IR (NaCl, liquid film): 1750, 1640, 1595, 1110. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.04 (*s*, Me, *t*-Bu); 1.06 (*s*, Me); 1.28–1.60 (*m*, $CH_2CH_2CH_2O$, CH_2CH_2O); 1.76 (*m*, 1 H); 1.96–2.24 (*m*, 3 H); 2.30–2.50 (*m*, 2 H); 2.77 (*m*, 1 H); 3.52–3.76 (*m*, CH_2O); 4.95 (*s*, 1 H, CH_2=C); 4.98 (*s*, 1 H, CH_2=C); 7.28–7.47 (*m*, 6 H, H–C(3), H–C(4), H–C(5) of Ph);

7.56–7.79 (*m*, 4 H, H–C(2), H–C(6) of Ph). ^{13}C-NMR (75 MHz, $CDCl_3$): 219.0 (C(1)); 158.8 (C(1′)); 135.5 (arom. C(2), C(6)); 133.9 (arom. C(1)); 129.5 (arom. C(4)); 127.6 (arom. C(3), C(5)); 108.0 (CH_2=); 64.3 (C(5′)); 48.2 (C(2)); 39.4, 39.1 (C(5), C(2′)); 37.6 (C(3)); 36.7 (CH_2); 32.2 (C(4)); 28.0 (CH_2); 27.3, 27.0 (Me_2C); 26.8 (Me_3C); 19.2 (Me_3C). MS: 394 (1), 392 (29), 391 (88), 281 (27), 199 (100), 183 (18), 181 (18), 175 (18), 105 (14), 55 (18). Anal. calc. for $C_{29}H_{40}O_2Si$ (448.72): C 77.63, H 8.98; found: C 77.38, H 9.17.

(3S)-3-(5-Hydroxy-2,2-dimethyl-1-methylidenepentyl)cyclopentanone (**14**). IR (NaCl, liquid film): 3440, 1750, 1670, 1640. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, Me); 1.09 (*s*, Me); 1.32–1.55 (*m*, $CH_2CH_2CH_2O$, CH_2CH_2O); 1.67–2.29 (*m*, 5 H); 2.32–2.55 (*m*, 2 H); 2.83 (*m*, 1 H); 3.49–3.71 (*m*, CH_2O); 4.99 (*s*, 1 H, CH_2=C); 5.01 (*s*, 1 H, CH_2=C). ^{13}C-NMR (75 MHz, $CDCl_3$): 219.4 (C(1)); 158.6 (C(1′)); 108.1 (CH_2=); 63.2 (C(5′)); 48.1 (C(2)); 39.4, 39.0 (C(5) or C(2′)); 37.5 (C(3)); 36.6 (CH_2); 32.2 (C(4)); 28.0 (CH_2); 27.1, 26.9 (Me_2C). MS: 210 (16, M^+), 152 (20), 151 (31), 109 (50), 93 (33), 83 (100), 81 (39), 79 (39), 67 (56), 55 (78). HR-MS: calc. for $C_{13}H_{22}O_2^+$: 210.1620; found: 210.1617 ± 0.0021.

(3S)-3-(5-Chloro-2,2-dimethyl-1-methylidenepentyl)cyclopentanone (**15**). IR (NaCl, liquid film): 1750, 1640, 1155, 900. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*s*, Me); 1.10 (*s*, Me); 1.42–2.32 (*m*, 8 H); 2.34–2.62 (*m*, 2 H); 2.82 (*m*, 1 H); 3.51 (*t*, *J* = 6.0, CH_2Cl); 5.01 (*s*, CH_2=C). ^{13}C-NMR (75 MHz, $CDCl_3$): 218.8 (C(1)); 158.3 (C(1′)); 108.5 (CH_2=); 48.1 (C(2)); 45.6, 39.4, 39.0, 37.8 (C(5), C(2′), C(5′), CH_2); 37.5 (C(3)); 32.3 (C(4)); 28.1 (CH_2); 27.1, 27.0 (Me_2C). MS: 228 (1, M^+), 152 (77), 110 (32), 109 (40), 107 (32), 95 (32), 83 (100), 81 (30), 67 (42), 55 (70).

(3aS,8aR)-5,5-Dimethyl-4-methylidenedecahydroazulene-1-one ((–)-**16**). 1. *(3aS)-8a-(Ethoxycarbonyl)-5,5-dimethyl-4-methylenedecahydroazulen-1-one*. To a cooled (0°) soln. of 118 mg (0.27 mmol) of **11** in 12 ml of abs. THF was slowly added a soln. of 91 mg (0.81 mmol) of *t*-BuOK in 2 ml of abs. THF, and the mixture was stirred at 0° for 50 min. Afterwards, the mixture was heated up slowly to 70–75°, and the temp. was maintained for additional 30 h. After cooling to 0°, aq. NH_4Cl soln. and AcOEt were added, and the org. layer was washed with brine, dried, and concentrated *in vacuo*. The crude product was purified by TLC (pentane/acetone 85:15): 16 mg (25%; recovered starting material: 12 mg). IR (NaCl, liquid film): 1745, 1710, 1630, 1195. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.01 (*s*, Me); 1.14 (*s*, Me); 1.20 (*m*, H–C(6)); 1.26 (*t*, *J* = 7.1, Me); 1.45 (*m*, H–C(8)); 1.58–1.75 (*m*, 3 H, H–C(6), H–C(7)); 2.13–2.50 (*m*, 5 H, H–C(2), H–C(3), H–C(8)); 3.77 (*m*, H–C(3a)); 4.20 (*m*, CH_2O); 4.73 (*s*, 1 H, CH_2=C(*E*)); 5.03 (*s*, 1 H, CH_2=C(*Z*)). ^{13}C-NMR (75 MHz, $CDCl_3$): 214.6 (C(1)); 170.2 (COO); 158.3 (C(4)); 106.8 (CH_2=); 63.9 (C(8a)); 61.5 (CH_2O); 44.6 (C(3a)); 38.9 (C(5)); 37.5 (C(6)); 36.6 (C(2)); 32.8 (Me); 28.8 (C(8)); 26.3 (Me); 24.6 (C(3)); 20.5 (C(7)); 14.1 (Me). MS: 264 (4, M^+), 192 (15), 191 (100), 147 (12), 133 (11), 105 (14), 91 (22), 77 (14), 67 (11), 55 (20). HR-MS: calc. for $C_{16}H_{24}O_3^+$: 264.1725; found: 264.172 ± 0.0015.

2. A mixture of 31 mg (0.12 mmol) of *(3aS)-8a-(ethoxycarbonyl)-5,5-dimethyl-4-methylidenedecahydroazulen-1-one* and 30 mg (0.72 mmol) of LiCl (dried for 18 h over P_2O_5 at 100° at 7 Torr) in 2 ml of abs. DMPU was stirred at 130° for 74 h. After cooling to r.t., the mixture was poured into 7 ml of H_2O, extracted with Et_2O, the org. layer washed with H_2O, dried, and concentrated *in vacuo*: 35 mg of crude product. TLC (CH_2Cl_2/AcOEt 98:2; plate pretreated with aq. 10% $AgNO_3$ soln.): 3 mg (13%). R_f (0.46. $[\alpha]_D$ = – 142.22 (*c* = 0.3 in EtOH). IR (NaCl, liquid film): 1745, 1635, 895. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.04 (*s*, Me_{ax}); 1.05–1.17 (*m*, H–C(8)); 1.16 (*s*, Me_{eq}); 1.15–1.29 (*m*, H–C(7)); 1.54 (*m*, H–C(6)); 1.57 (*m*, H–C(6)); 1.64–1.74 (*m*, H–C(7), H–C(8a)); 1.93 (*m*, H–C(3)); 2.10–2.20 (*m*, H–C(8)); 2.17 (*m*, H–C(2)); 2.44 (*m*, H–C(2)); 2.57 (*m*, H–C(3a)); 4.98 (*s*, 1 H, CH_2=C(*E*)); 5.01 (*s*, 1 H, CH_2=C(*Z*)). ^{13}C-NMR (75 MHz, $CDCl_3$): 219.9 (C(1)); 159.4 (C(4)); 106.5 (=CH_2); 59.3 (C(8a)); 44.5 (C(3a)); 41.7 (C(6)); 39.6 (C(5)); 38.2 (C(2)); 32.5 (Me_{ax}); 30.5 (C(8)); 28.1 (Me_{eq}); 25.7 (C(3)); 22.3 (C(7)). MS: 192 (30, M^+), 136 (100), 109 (44), 107 (51), 93 (83), 91 (58), 79 (78), 67 (58), 55 (57), 53 (45). HR-MS: calc. for $C_{13}H_{20}O^+$: 192.1514; found: 192.151 ± 0.001.

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Received September 22, 1997