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Cycloaddition of allylsilanes. Part 20: Organosilicon-mediated total synthesis of (±)-cameroonanol☆

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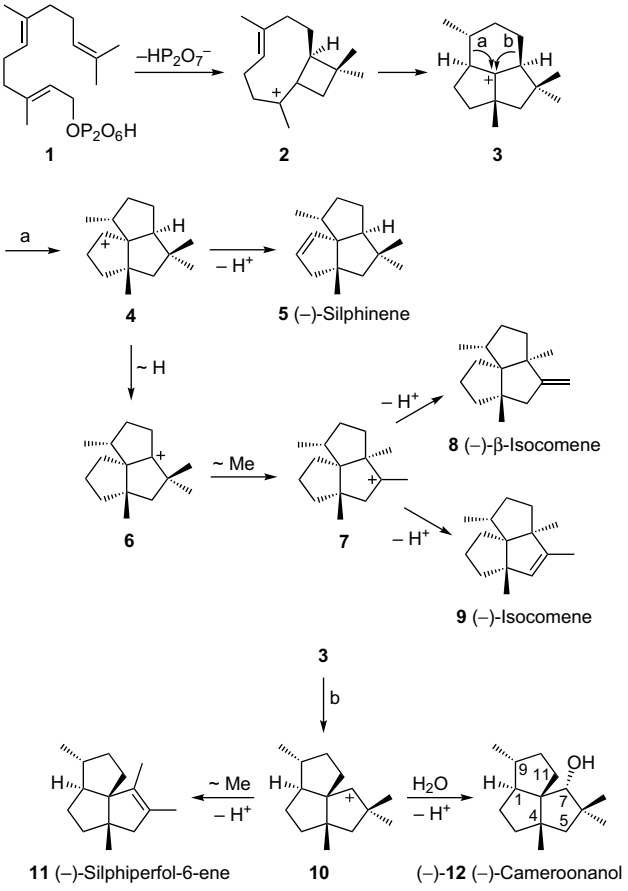
ABSTRACT

We describe a seven-step total synthesis of the triquinane sesquiterpene (±)-cameroonanol using a Lewis acid-promoted [3+2] cycloaddition of an allylsilane and a modified Fleming–Tamao oxidation as key reactions.

1. Introduction

The angular triquinanes are a group of structurally related sesquiterpenes consisting of three annelated cyclopentanes. Biogenetically they derive from farnesyl pyrophosphate **1** (Scheme 1).[2] Cyclization of farnesyl pyrophosphate **1** to the carbenium ion **2** followed by a sequence of various rearrangement steps affords the presilphiperfolanyl cation **3**, which is considered as the crucial precursor in the biogenesis of angular triquinanes. Wagner–Meerwein rearrangement of **3** following path 'a' provides the carbenium ion **4**. Elimination of a proton provides (−)-silphinene **5**. Whereas shift of the angular hydrogen to the carbenium ion **6** followed by a methyl shift affords the carbenium ion **7**. Elimination of a proton leads either to (−)-β-isocomene **8** or to (−)-isocomene **9**. Wagner–Meerwein rearrangement of **3** following path 'b' affords the carbenium ion **10**. Shift of a methyl group and subsequent elimination of a proton provide (−)-silphiperfol-6-ene **11**. Nucleophilic attack of water at the carbenium ion **10** leads to (−)-cameroonanol (−)-**12**.[3] (−)-Cameroonanol (−)-**12** has been isolated in 1998 by Weyerstahl et al. on their investigation of the essential oil of *Echinops giganteus* var. *lelyi*, an endemic species of Cameroon and Nigeria.[3] Although a large variety of sesquiterpenes has been found in the essential oil of *E. giganteus*, (−)-cameroonanol (−)-**12** appeared to represent the major factor of its patchouli-like, woody fragrance. The structure and absolute configuration have been assigned based on NMR spectroscopy, comparison with other compounds from the same source and rearrangement to derivatives of known structure.[2b,3]

Because of their unique structure, triquinane sesquiterpenes became attractive synthetic targets for demonstrating the utility and scope of novel methodologies for cyclopentane annelations.[4,5]



Scheme 1. Biosynthetic route to the angular triquinane sesquiterpenes.

☆ See Ref. 1.

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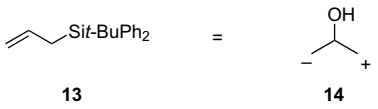


Scheme 2. Allyl-*tert*-butyldiphenylsilane **13** as synthetic equivalent for the 2-hydroxy-substituted 1,3-dipole **14**.

In 2000, Coates et al. described the first total synthesis of (±)-cameroonanol (±)-**12**.[6] We reported the second total synthesis of (±)-cameroonanol (±)-**12** in 2007.[7] Our methodology combines the Lewis acid-promoted [3+2] cycloaddition of allyl-*tert*-butyldiphenylsilane **13** with a subsequent modified Fleming–Tamao oxidation. Thus, allyl-*tert*-butyldiphenylsilane **13** is exploited as synthetic equivalent for the 2-hydroxy-substituted 1,3-dipole **14** (Scheme 2).[8–10]

Lewis acid-promoted [3+2] cycloadditions of allylsilanes found diverse applications in organic synthesis.[8–10] In the present paper, we describe full experimental details of our improved synthetic route to (±)-cameroonanol (±)-**12**.

2. Results and discussion

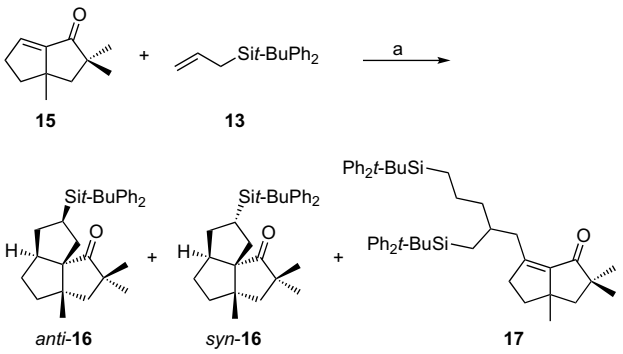
The triquinane framework was assembled in the first step by the titanium tetrachloride-promoted [3+2] cycloaddition of allyl-*tert*-butyldiphenylsilane **13** (Scheme 3).

Paquette et al. have used the bicyclo[3.3.0]octenone **15** as precursor in their synthesis of silphinene.[4b] We prepared compound **15** using a modification of Paquette's original procedure reported by Coates et al.[6] The Lewis acid–Lewis base complex of titanium tetrachloride and compound **15** has been generated at −20 °C. Subsequent addition of allyl-*tert*-butyldiphenylsilane **13** at −78 °C afforded the triquinane **16** as a 7:1 mixture of the *anti* and the *syn* diastereoisomer (*syn* and *anti* denote the relative stereochemistry of the silyl substituent to the carbonyl function). As a minor by-product we isolated the bicyclo[3.3.0]octenone **17** (6% yield). Compound **17** is quite unusual and has been isolated as a single diastereoisomer. It is presumed to result from addition of a second equivalent of allyl-*tert*-butyldiphenylsilane **13** at the intermediate siliranium ion and subsequent 1,5-hydride shift instead of cyclization. The mechanism of formation as well as the stereochemistry of **17** are currently under investigation. Based on our previous findings,[8g,8h] the relative configuration of the silyl group of the triquinane **16** has been assigned by the chemical shift of the ^{13}C NMR signal for the CH group in the cyclopentane ring α to silicon. Moreover, an X-ray crystal structure determination at a later stage of the synthesis confirmed this assignment. For our synthetic route towards (±)-cameroonanol (±)-**12**, we could use the diastereoisomeric mixture of triquinane **16**.

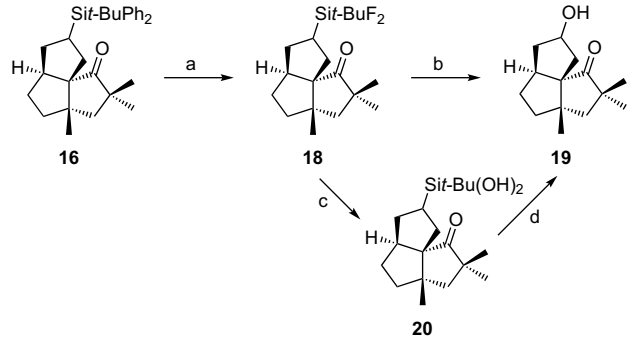
In the following step, the silyltriquinane had to be converted into a hydroxytriquinane. Organosilanes, like dimethylphenylsilanes and alkoxysilanes, can be readily transformed into the corresponding hydroxy compounds by oxidative cleavage of the carbon–silicon bond via the well-established Fleming–Tamao oxidation.[11] We have developed a modified Fleming–Tamao oxidation, especially for the oxidative cleavage of sterically highly hindered organosilicon compounds containing the *tert*-butyldiphenylsilyl and the diisopropylphenylsilyl group.[12] The oxidative cleavage of the *tert*-butyldiphenylsilyl group proceeds smoothly if a double protodesilylation is achieved in the first step. Protodesilylation of the triquinanes **16** using the boron trifluoride–acetic acid complex for 2 days at 83 °C to the intermediate *tert*-butyldifluorosilyl compound **18** followed by oxidation with buffered hydrogen peroxide for 3 days at 65 °C provided the desired hydroxytriquinane **19** (Scheme 4). Replacement of hydrogen peroxide by water in the second step transformed the intermediate difluorosilyl compound **18** into the *tert*-butyldihydroxysilyl compound **20**. At this stage, an unequivocal confirmation of the relative stereochemistry of our triquinanes has been obtained by crystallization of the major diastereoisomer *anti*-**20** and X-ray crystal structure determination (Fig. 1). The formation of compound **20** emphasizes the replacement of both phenyl groups with fluorine in the first step to afford **18** by double protodesilylation. Subsequent double nucleophilic substitution of the difluorosilyl compound **18** with water affords the dihydroxysilyl compound **20**. Oxidative cleavage of **20** led to the hydroxytriquinane almost quantitatively. Based on our earlier study on the oxidative cleavage of the methyldiphenylsilyl group,[12] we have proposed that the cleavage of the *tert*-butyldiphenylsilyl group by the modified Fleming–Tamao oxidation proceeds via dihydroxysilanes as intermediates. The present results confirm our mechanistic proposal for cleavage of the *tert*-butyldiphenylsilyl group.

Using TPAP (tetrapropylammonium perruthenate) and *N*-methylmorpholine *N*-oxide as stoichiometric oxidant,[13] oxidation of carbinol **19** led to the diketone **21** in 84% yield (Scheme 5). Using PCC (pyridinium chlorochromate) and Celite® as reagents,[14] the diketone **21** was obtained in 94% yield. Celite®, which has the same effect on oxidations with PCC as molecular sieves,[15] leads to shorter reaction times and easier work-up. A simple filtration over silica gel removes the chromium residues.

We envisaged a regio- and stereoselective alkylation of the diketone **21** for introduction of the methyl group at C-9. Using a bulky lithium base, preferential deprotonation should take place at C-9 because of the steric hindrance at C-11 caused by the annulated cyclopentanone. Electrophilic attack at the resulting 9,10-enolate should occur from the *exo*-face and thus give rise to the desired diastereoselectivity. Deprotonation using lithium diisopropylamide and subsequent treatment with iodomethane in the presence of DMPU (*N*,*N*′-dimethyl-1,3-propylene urea) and catalytic amounts of dimethylzinc afforded the mono-*C*-alkylated



Scheme 3. Reagents and conditions: (a) 1. $TiCl_4$, CH_2Cl_2, −20 °C, 10 min; 2. **13**, −78 °C, 24 h, 43% **16** (ratio of *anti*-**16**/*syn*-**16**=7:1), 6% **17**.



Scheme 4. Reagents and conditions: (a) $BF_3 \cdot 2AcOH$, 1,2-$C_2H_4Cl_2$, reflux, 46 h; (b) CsF, $KHCO_3$, H_2O_2, THF/MeOH (1:1), reflux, 3 days, 59% (two steps); (c) CsF, $KHCO_3$, H_2O, THF/MeOH (1:1), reflux, 12 h, 27% (two steps); (d) CsF, $KHCO_3$, H_2O_2, THF/MeOH (1:1), reflux, 7 days, 96%.

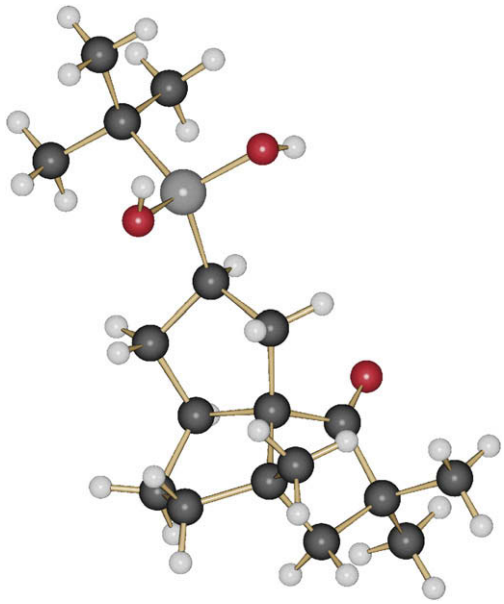


Figure 1. Molecular structure of *anti*-**20** in the crystal: triclinic, $P\bar{1}$.

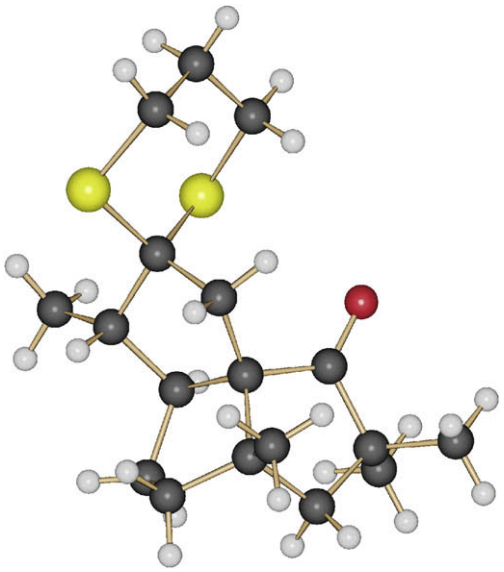
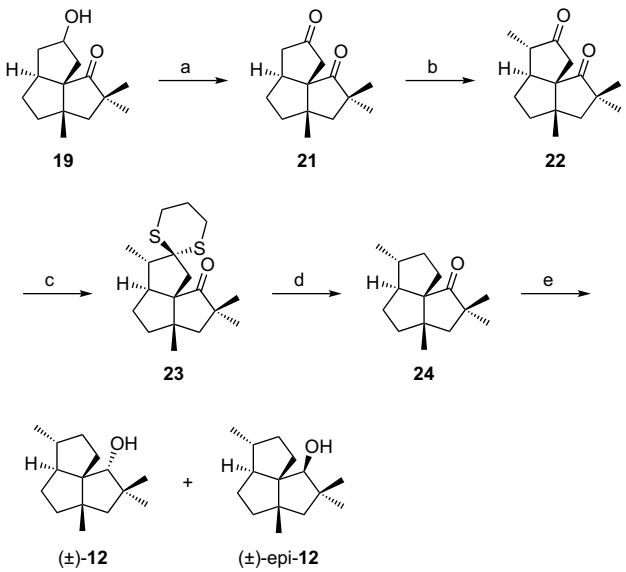


Figure 2. Molecular structure of **23** in the crystal: triclinic, $P\bar{1}$.

compound **22** as major product. Addition of catalytic amounts of dimethylzinc, originally described by Noyori, was essential for the regio- and stereoselective methylation.[16] According to a GC–MS chromatogram the crude product contained about 60% of the desired monomethylated product **22**, two monomethylated isomers, two dialkylated products, and some starting material **21**. Simple flash chromatography on silica gel using hexane/*tert*-butyl methyl ether (10:1) as eluent provided pure **22** in 54% yield. The relative configuration was assigned by 2D NMR spectroscopy (COSY, HSQC, HMBC, and NOESY). A chemoselective deoxygenation of the carbonyl group at C-7 was feasible by exploiting the sterical hindrance of the carbonyl group at C-10 caused by two neighboring quaternary carbon centers. Thus, thioketalization of compound **22** by reaction with boron trifluoride and 1,3-propanedithiol led regioselectively to the dithioketal **23**. An X-ray crystal structure analysis of compound **23** unambiguously confirmed the regio- and stereochemical assignment for the methylation (Fig. 2).



Scheme 5. Reagents and conditions: (a) PCC, Celite, CH_2Cl_2, 25 °C, 5 h, 94%; (b) 1. BuLi, *i*-Pr_2NH, THF, −5 °C, 6 h; 2. MeI, $ZnMe_2$, DMPU, THF, −78 to 25 °C, 40 h, 54%; (c) $HS(CH_2)_3SH$, $BF_3\cdot Et_2O$, CH_2Cl_2, 25 °C, 24 h, 83%; (d) Raney-Ni, EtOH, 25 °C, 4 h, 71%; (e) DIBAL-H, CH_2Cl_2, −78 °C, 20 h, 88% [ratio of (±)-**12**/(±)-*epi*-**12**=3.7:1].

Raney-nickel hydrogenation of the dithioketal **23** afforded (±)-cameroonanone (±)-**24**. Previously, Weyerstahl et al. obtained (−)-cameroonanone (−)-**24** by oxidation of natural (−)-cameroonanol (−)-**12**.[3] (±)-Cameroonanone (±)-**24** served as an intermediate in the synthetic route described by Coates et al.[6] Both groups described a low diastereoselectivity for the reduction of cameroonanone **24** to cameroonanol **12**. We have investigated the diastereoselectivity of the reduction of (±)-cameroonanone (±)-**24** to (±)-cameroonanol (±)-**12** by variation of the reaction conditions (Table 1).

By reduction of (±)-cameroonanone (±)-**24** with lithium aluminum hydride in diethyl ether at 0 °C, Coates et al. obtained a ratio of 1.4:1 for (±)-cameroonanol (±)-**12** and (±)-*epi*-cameroonanol (±)-*epi*-**12**.[6] Using the same reaction conditions, Weyerstahl et al. reported a ratio of 2.3:1 by reduction of (−)-cameroonanone (−)-**24**.[3] Using tetrahydrofuran as solvent, we have determined a ratio of 2.7:1, however, at a lower yield. Finally, using diisobutylaluminum hydride at −78 °C as reducing agent,[17] we have obtained (±)-cameroonanol (±)-**12** and (±)-*epi*-cameroonanol (±)-*epi*-**12** in a ratio of 3.7:1 and 88% yield. A separation of the two epimeric alcohols (±)-**12** and (±)-*epi*-**12** has been achieved by flash chromatography on silica gel (eluent: pentane/diethyl ether, 25:1) to provide pure (±)-cameroonanol (±)-**12**. The spectroscopic data of our synthetic (±)-cameroonanol (±)-**12** were in full agreement with those reported by Weyerstahl for the natural product.[3]

Table 1
Results for the reduction of (±)-cameroonanone **24** to (±)-cameroonanol (±)-**12** and (±)-*epi*-cameroonanol (±)-*epi*-**12**

Reagent	Solvent	*T* [°C]	Yield [%]	Ratio[a]
$LiAlH_4$	Et_2O	0	86	1.4:1[b]
$LiAlH_4$	Et_2O	0	81	2.3:1[c]
$LiAlH_4$	THF	0	67	2.7:1
DIBAL-H	CH_2Cl_2	−78 to rt	61	3.2:1
DIBAL-H	CH_2Cl_2	−78	88	3.7:1

[a] Ratio of (±)-cameroonanol (±)-**12** and (±)-*epi*-cameroonanol (±)-*epi*-**12** as determined by gas chromatography.
[b] Result for the reduction of (±)-**24** reported by Coates et al.[6]
[c] Result for the reduction of (−)-**24** reported by Weyerstahl et al.[3]

3. Conclusion

The Lewis acid-promoted [3+2] cycloaddition of allyl-*tert*-butyldiphenylsilane is a useful method for the stereoselective construction of tricyclopentanoid frameworks. Using our modified Fleming–Tamao oxidation, the resulting silylcyclopentanes can be converted to cyclopentanols. Thus, this sequence of reactions provides a direct route to cyclopentanoid natural products. In the present work, the triquinane sesquiterpene (±)-cameroonanol (±)-**12** has been obtained in seven linear steps and 5% overall yield based on bicyclo[3.3.0]octenone **15**. Moreover, isolation of the *tert*-butyldihydroxysilyl derivative **20** provided circumstantial evidence for the mechanism previously proposed by us for the oxidative cleavage of the *tert*-butyldiphenylsilyl group via the modified Fleming–Tamao oxidation. Formation of the disilyl-substituted bicyclo[3.3.0]octenone **17** shows another interesting novel aspect of the Lewis acid-promoted reactions of allylsilanes with enones.

4. Experimental section

4.1. General

All reactions were carried out in dry solvents under an inert atmosphere (argon or nitrogen). THF and diethyl ether were dried using a solvent purification system (MBraun-SPS). Chemicals were used as received from commercial sources. Flash chromatography: Merck silica gel (0.040–0.063 mm). Melting points: Electrothermal IA9100. UV spectra: Perkin–Elmer Lambda 2 (UV/VIS spectrometer). IR spectra: Thermo Nicolet Avatar 360 FT-IR; ν in cm^{-1}. NMR spectra: Bruker DRX 500; chemical shifts δ in parts per million, coupling constants *J* in hertz. Mass spectra: Finnigan MAT-95 (electron impact EI, ionization potential: 70 eV) or by GC/MS-coupling using an Agilent Technologies 6890N GC System equipped with a 5973 Mass Selective Detector (EI, 70 eV). Elemental analyses: EuroVector EuroEA3000. X-ray analyses: Bruker-Nonius Kappa CCD with an Oxford Cryosystems cooling device and STOE IPDS 2 image plate; Software: Collect (Nonius BV, 1999), Dirax/lsq (Duisenberg, 1992), SHELXS-97 (Sheldrick, G. M., 1900), EvalCCD (Duisenberg et al., 2003), SADABS version 2.10 (Sheldrick, G. M., Bruker AXS Inc., 2002), SHELX97-2 (Sheldrick, G. M., 1997).

4.2. (3a,5a,7,8a)-7-*tert*-Butyldiphenylsilyl-2,2,3a-trimethyldecahydrocyclopenta[*c*]pentalen-1-one (*anti*-16), (3a,5a,7,8a)-7-*tert*-butyldiphenylsilyl-2,2,3a-trimethyldecahydrocyclopenta[*c*]pentalen-1-one (*syn*-16), and 8-([5-*tert*-butyldiphenylsilyl]-[2-*tert*-butyldiphenylsilylmethyl]pentyl)-3,3,5-trimethylbicyclo[3.3.0]oct-1(8)-en-2-one (17)

A 1 M solution of titanium tetrachloride in dichloromethane (7.31 mL, 7.31 mmol) was added to a solution of 3,3,5-trimethylbicyclo[3.3.0]oct-1(8)-en-2-one (**15**) (1.00 g, 6.09 mmol) in anhydrous dichloromethane (40 mL) at −20 °C. After stirring for 10 min, the mixture was cooled to −78 °C, allyl-*tert*-butyldiphenylsilane (**13**) (3.42 g, 12.2 mmol) was added, and the mixture was stirred at −78 °C for 24 h. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride and stirred vigorously until it turned yellow (approx. 10 min). The aqueous layer was separated and extracted with dichloromethane three times. The combined organic layers were dried over sodium sulfate and the solvent was removed. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 40:1) afforded as the less polar fraction a diastereoisomeric mixture of *anti*-**16** and *syn*-**16** (ratio: 7:1) as a colorless oil, yield: 1.17 g (43%). The more polar fraction was the bicyclo[3.3.0]octenone **17**, colorless oil, yield: 284 mg (6%).

Compound ***16***: IR (neat): ν=3071, 2959, 2933, 2858, 1722, 1471, 1427, 1392, 1380, 1362, 1307, 1273, 1194, 1153, 1107, 999, 986, 910, 820, 764, 737, 702, 649, 608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.82 (s, 3H), 0.98 (dd, *J*=9.6, 1.3 Hz, 1H), 1.06 (s, 3H), 1.081 (s, 9H), 1.085 (s, 3H), 0.94–1.27 (m, 2H), 1.40–1.44 (m, 1H), 1.56 (d, *J*=13.9 Hz, 1H), 1.58–1.74 (m, 2H), 1.66 (d, *J*=13.9 Hz, 1H), 1.92 (ddd, *J*=12.8, 5.8, 2.2 Hz, 1H), 2.14–2.21 (m, 2H), 2.48–2.50 (m, 1H), 7.31–7.40 (m, 6H), 7.59–7.67 (m, 4H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$), *anti*-**16**: δ=18.57 (C), 24.55 (CH_3), 25.35 (CH), 27.34 (CH_3), 27.87 (CH_3), 28.47 ($3CH_3$), 29.45 (CH_2), 35.57 (CH_2), 38.36 (CH_2), 40.01 (CH_2), 44.94 (C), 47.21 (C), 48.03 (CH_2), 55.03 (CH), 70.98 (C), 127.28 (2CH), 127.36 (2CH), 128.88 (2CH), 134.32 (C), 134.44 (C), 136.54 (2CH), 136.56 (2CH), 229.55 (C=O); *syn*-**16**: δ=18.04 (C), 22.31 (CH_3), 26.37 (CH_3), 26.89 (CH_2), 28.47 ($3CH_3$), 28.60 (CH), 29.83 (CH_3), 30.64 (CH_2), 31.19 (CH_2), 41.75 (CH_2), 45.16 (C), 45.56 (CH), 46.70 (CH_2), 48.90 (C), 68.11 (C), 127.45 (2CH), 134.82 (C), 135.29 (C), 136.13 (2CH), 136.25 (2CH), 136.54 (2CH), 136.56 (2CH), 223.41 (C=O). MS (EI): *m*/*z* (%)=444 (1, M^+), 387 (100), 199 (12), 197 (6), 183 (45), 181 (6), 135 (10), 105 (3), 83 (6), 81 (10). HRMS *m*/*z* calcd for $C_{30}H_{40}OSi$: 444.2848, found: 444.2857.

Compound ***17***: UV ($CHCl_3$): λ=227, 265 (ε=11.530 cm^2 $mmol^{-1}$) nm. IR (neat): ν=3071, 3048, 2929, 2858, 1701, 1642, 1471, 1427, 1391, 1362, 1260, 1193, 1106, 999, 910, 866, 820, 736, 701, 606 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.66–0.73 (m, 2H), 0.80–1.18 (m, 6H), 0.956 (s, 9H), 0.960 (s, 9H), 1.05 (s, 3H), 1.188 (s, 3H), 1.194 (s, 3H), 1.44–1.48 (m, 1H), 1.58–1.69 (m, 2H), 1.82 (dd, *J*=12.0, 6.3 Hz, 1H), 1.86 (d, *J*=12.8 Hz, 1H), 2.03 (dd, *J*=17.5, 8.4 Hz, 1H), 2.15 (dd, *J*=12.9, 7.5 Hz, 1H), 2.24 (dd, *J*=12.9, 6.6 Hz, 1H), 2.46 (ddd, *J*=17.3, 10.9, 6.3 Hz, 1H), 7.29–7.39 (m, 12H), 7.49–7.52 (m, 4H), 7.58–7.61 (m, 4H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=10.02 (CH_2), 14.23 (CH_2), 18.06 (C), 18.30 (C), 21.09 (CH_2), 25.67 (CH_3), 26.89 (CH_3), 27.83 ($3CH_3$), 27.87 ($3CH_3$), 28.26 (CH_3), 32.51 (CH), 36.41 (CH_2), 38.65 (CH_2), 40.71 (CH_2), 44.15 (CH_2), 49.42 (C), 50.07 (C), 51.44 (CH_2), 127.41 (2CH), 127.45 (2CH), 127.48 (4CH), 128.86 (2CH), 128.92 (2CH), 128.96 (2CH), 134.98 (C), 135.14 (C), 135.88 (2C), 136.23 (4CH), 136.26 (2CH), 147.22 (C), 153.95 (C), 207.60 (C=O). MS (EI): *m*/*z* (%)=667 (10, $M^+-C_4H_9$), 429 (5), 401 (8), 387 (100), 199 (24), 197 (10), 183 (14), 135 (20). HRMS: *m*/*z* calcd for $C_{45}H_{55}OSi_2$ ($M^+-C_4H_9$): 667.3791, found: 667.3799.

4.3. (3a,5a,8a)-7-Hydroxy-2,2,3a-trimethyldecahydrocyclopenta[*c*]pentalen-1-one (19)

Method A. Boron trifluoride–acetic acid complex (2.5 g, 1.8 mL, 13.14 mmol) was added to a solution of *anti*-/*syn*-**16** (584 mg, 1.31 mmol) in anhydrous 1,2-dichloroethane (30 mL) and the mixture was heated at reflux for 46 h. After cooling to room temperature, the mixture was neutralized by addition of a saturated sodium bicarbonate solution. The aqueous layer was separated, extracted with diethyl ether three times, and the combined organic layers were dried over magnesium sulfate. The solvent was removed and the residue was dissolved in THF (25 mL). Cesium fluoride (1.2 g, 7.88 mmol), $KHCO_3$ (264 mg, 2.60 mmol), methanol (25 mL), and a solution of hydrogen peroxide in water (35%, 2.3 mL, 22.34 mmol) were added. The mixture was heated at reflux for 3 days. After cooling to room temperature, water (100 mL) was added. The aqueous layer was separated and extracted with diethyl ether three times. The combined organic layers were washed with a saturated aqueous solution of iron(II) sulfate, dried over magnesium sulfate, and the solvent was removed. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 1:1) afforded the carbinol **19** as a colorless oil, yield: 170 mg (59%).

IR (neat): ν=3432, 2955, 2868, 1726, 1462, 1380, 1358, 1307, 1274, 1219, 1091, 1059, 995 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=1.04 (s, 3H), 1.07 (s, 3H), 1.09 (s, 3H), 1.24 (dt, *J*=12.2, 8.9 Hz, 1H), 1.41 (dd,

J=12.6, 8.7 Hz, 1H), 1.46 (m, 1H), 1.59–1.79 (m, 4H), 1.83–1.91 (m, 1H), 1.95 (ddd, J=12.6, 6.0, 1.6 Hz, 1H), 2.13–2.18 (m, 2H), 2.33 (dq, J=1.4, 8.8 Hz, 1H), 4.41 (m, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=24.72 (CH_3), 27.39 (CH_3), 28.10 (CH_3), 30.39 (CH_2), 39.68 (CH_2), 39.80 (CH_2), 42.56 (CH_2), 44.79 (C), 47.86 (C), 48.10 (CH_2), 49.19 (CH), 68.60 (C), 73.59 (CH), 228.28 (C=O). MS (EI): m/z (%)=222 (22, M^+), 207 (100), 179 (9), 167 (6), 165 (76), 152 (7), 151 (19), 149 (5), 95 (8), 94 (13), 79 (11), 77 (5). HRMS m/z calcd for $C_{14}H_{22}O_2$: 222.1620, found: 222.1611.

4.4. (3a,5a,7,8a)-7-*tert*-Butyldihydroxysilyl-2,2,3a-trimethyldecahydrocyclopenta[*c*]pentalen-1-one (20)

Boron trifluoride–acetic acid complex (15.5 g, 11.5 mL, 82.50 mmol) was added to a solution of *anti*-/*syn*-**16** (3.41 g, 7.67 mmol) in anhydrous 1,2-dichloroethane (100 mL) and the mixture was heated at reflux for 46 h. After cooling to room temperature, the mixture was neutralized by addition of a saturated sodium bicarbonate solution. The aqueous layer was separated, extracted with diethyl ether three times, and the combined organic layers were dried over magnesium sulfate. The solvent was removed and the residue was dissolved in THF (70 mL). CsF (7.5 g, 53.0 mmol), $KHCO_3$ (1.7 g, 16.4 mmol), methanol (70 mL), and water (15 mL) were added and the mixture was heated at reflux for 12 h. After cooling to room temperature, water (100 mL) was added. The aqueous layer was separated and extracted with diethyl ether three times. The combined organic layers were dried over magnesium sulfate and the solvent was removed. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 1:1) afforded the dihydroxysilane **20** as colorless crystals, yield: 670 mg (27%), mp 146 °C.

IR (ATR): ν=3391, 2933, 2856, 1726, 1705, 1465, 1380, 1360, 1310, 1275, 1197, 1154, 1128, 1082, 987, 919, 886, 833, 816, 762, 612 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ=0.86 (s, 9H), 1.00 (s, 3H), 1.01 (s, 3H), 1.05 (s, 3H), 1.13–1.18 (m, 1H), 1.25–1.35 (m, 2H), 1.40 (t, J=12.8 Hz, 1H), 1.55–1.71 (m, 5H), 1.78–1.83 (m, 1H), 1.98 (m, 1H), 2.31 (q, J=8.7 Hz, 1H), 5.59 (s, 1H), 5.62 (s, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=18.45 (C), 24.54 (CH_3), 25.97 ($3CH_3$), 26.89 (CH), 27.40 (CH_3), 28.11 (CH_3), 29.67 (CH_2), 34.45 (CH_2), 37.64 (CH_2), 39.97 (CH_2), 44.96 (C), 47.41 (C), 47.91 (CH_2), 54.97 (CH), 71.25 (C), 229.47 (C=O). ^{29}Si NMR (99 MHz, DMSO-d_6): δ=−12.81. MS (EI): m/z (%)=324 (3, M^+), 307 (7), 306 (29), 291 (7), 267 (100), 251 (2), 249 (8), 211 (12), 193 (4), 187 (18), 183 (13), 147 (10), 77 (16). HRMS: m/z calcd for $C_{18}H_{32}O_3Si$: 324.2121, found: 324.2092. Anal. Calcd for $C_{18}H_{32}O_3Si$: C 66.62, H 9.94. Found: C 66.78, H 9.96.

4.4.1. *Crystal data for anti-**20***

$C_{18}H_{32}O_3Si$, crystal size: 0.51×0.47×0.08 mm^3, M_r=324.53 g mol^{-1}, triclinic, space group $P\bar{1}$, λ=0.71073 Å, a=12.186(3), b=15.114(1), c=16.730(4) Å, α=103.50(1)°, β=95.17(2)°, γ=104.16(1)°, V=2869.5(10) Å^3, Z=6, ρ_{calcd}=1.127 g cm^{-3}, μ=0.133 mm^{-1}, T=198(2) K, θ range=3.52–22.50°; reflections collected: 43,390, independent: 7450 (R_{int}=0.0522). The structure was solved by direct methods and refined by full-matrix least-squares on F^2; R_1=0.0407, wR_2=0.1006 [$I>2\sigma(I)$]; maximal residual electron density: 0.464 e Å^{-3}. CCDC 636590 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.5. (3a,5a,8a)-7-Hydroxy-2,2,3a-trimethyldecahydrocyclopenta[*c*]pentalen-1-one (19)

Method B. Methanol (10 mL), cesium fluoride (168 mg, 1.11 mmol), and $KHCO_3$ (37 mg, 370 μmol) were added to a solution of the dihydroxysilyl compound **20** (60 mg, 185 μmol) in THF (10 mL). After addition of aqueous hydrogen peroxide (35%; 293 μL, 3.70 mmol), the reaction mixture was heated at reflux for 7 days. Subsequently, the mixture was cooled to room temperature and water (10 mL) was added. The aqueous layer was separated and extracted with diethyl ether three times. The combined organic layers were washed with a saturated aqueous solution of iron(II) sulfate, dried over magnesium sulfate, and the solvent was removed. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 1:1) provided the carbinol **19** as a colorless oil, yield: 39.5 mg (96%).

Spectroscopic data, see above.

4.6. (3a,5a,8a)-2,2,3a-Trimethyldecahydrocyclopenta[*c*]-pentalene-1,7-dione (21)

A solution of the carbinol **19** (837 mg, 3.80 mmol) in dichloromethane (50 mL) was added to a suspension of PCC (1.80 g, 8.36 mmol) and Celite® (4.6 g) in dichloromethane (70 mL). The resulting mixture was stirred at room temperature for 5 h. Removal of the chromium residues by filtration over silica gel (*tert*-butyl methyl ether) and evaporation of the solvent afforded **21** as a light yellow oil, yield: 787 mg (94%).

IR (neat): ν=2959, 2935, 2870, 1746, 1468, 1402, 1382, 1360, 1276, 1227, 1171, 1096, 1056, 1020, 895 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.06 (s, 3H), 1.11 (s, 3H), 1.16 (s, 3H), 1.46–1.49 (m, 1H), 1.65–1.69 (m, 1H), 1.75–1.80 (m, 1H), 1.78 (s, 2H), 1.91–2.00 (m, 2H), 2.28 (dd, J=18.6, 1.8 Hz, 1H), 2.53–2.62 (m, 2H), 2.81 (m, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=25.59 (CH_3), 27.13 ($2CH_3$), 31.07 (CH_2), 41.69 (CH_2), 43.49 (CH_2), 43.92 (CH_2), 45.61 (C), 46.52 (CH), 47.35 (C), 49.76 (CH_2), 66.86 (C), 217.06 (C=O), 225.86 (C=O). MS (EI): m/z (%)=220 (36, M^+), 205 (15), 178 (23), 165 (100), 164 (13), 137 (25), 109 (15), 94 (22), 79 (12). HRMS m/z calcd for $C_{14}H_{20}O_2$: 220.1463, found: 220.1459.

4.7. (3a,5a,6,8a)-2,2,3a,6-Tetramethyldecahydrocyclopenta[*c*]pentalene-1,7-dione (22)

A 1.6 M solution of butyllithium in hexane (1.02 mL, 1.63 mmol) was added to a solution of diisopropylamine in anhydrous THF (5 mL) at −5 °C and the mixture was stirred at that temperature for 15 min. A solution of **21** (300 mg, 1.36 mmol) in anhydrous THF (2 mL) was added and the mixture was stirred at −5 °C for 6 h. The solution was cooled to −78 °C and DMPU (522 mg, 492 μL, 4.08 mmol) and a 1 M solution of dimethylzinc in heptane (272 μL, 272 μmol) were added. After 15 min of stirring at −78 °C, iodomethane (965 mg, 423 μL, 6.80 mmol) was added and the reaction mixture was allowed to warm up to room temperature over a period of 16 h. The reaction mixture was stirred for another 24 h at room temperature and then quenched by addition of a saturated aqueous solution of ammonium chloride (20 mL). Dichloromethane (20 mL) was added, the aqueous layer was separated, and extracted with dichloromethane three times. The combined organic layers were dried over magnesium sulfate and the solvent was evaporated. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 10:1) gave **22** as a colorless oil, yield: 171 mg (54%).

IR (ATR): ν=2960, 2933, 2870, 1729, 1458, 1380, 1288, 1171, 1091, 1042, 974, 895, 582 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.04 (s, 3H), 1.110 (d, J=7.1, 3H), 1.112 (s, 3H), 1.14 (s, 3H), 1.54–1.58 (m, 1H), 1.66–1.82 (m, 5H), 1.95 (m, 1H), 2.37 (br t, J=7.8 Hz, 1H), 2.44–2.53 (m, 2H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=14.90 (CH_3), 25.84 (CH_3), 26.25 (CH_3), 26.99 (CH_3), 29.04 (CH_2), 42.31 (CH_2), 44.07 (CH_2), 46.04 (C), 46.26 (C), 49.10 (CH), 50.18 (CH_2), 55.85 (CH), 64.41 (C), 218.76 (C=O), 226.94 (C=O). MS (EI): m/z (%)=234 (23, M^+), 219 (7), 178 (40), 165 (100), 150 (10), 137 (55), 121 (6), 114 (9), 109

(11), 107 (8), 94 (8), 79 (10). HRMS: *m*/*z* calcd for $C_{15}H_{22}O_2$: 234.1620, found: 234.1623.

4.8. (3a′,5a′,6′,8a′)-2′,2′,3a′,6′-Tetramethyl-spiro[1,3-dithiane-2,7′-decahydrocyclopenta[*c*]pentalen]-1′-one (23)

Boron trifluoride–diethyl ether complex (163 mg, 144 μL, 1.15 mmol) was added to a solution of **22** (257 mg, 1.10 mmol) and 1,3-propanedithiol (124 mg, 115 μL, 1.15 mmol) in anhydrous dichloromethane (10 mL). The mixture was stirred for 24 h at room temperature. Then, an aqueous solution of sodium hydroxide (5%; 20 mL) and dichloromethane (20 mL) were added. The organic layer was separated, washed with water, dried over magnesium sulfate, and the solvent was evaporated. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 10:1) provided **23** as colorless crystals, yield: 294 mg (83%), mp 84 °C.

IR (ATR): ν=2959, 2943, 2924, 2904, 2866, 2824, 1729, 1453, 1414, 1377, 1358, 1305, 1276, 1241, 1189, 1133, 1084, 1055, 1033, 1002, 987, 953, 929, 902, 872, 780, 717, 683, 656, 607, 567, 548 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=1.05 (s, 3H), 1.07 (s, 3H), 1.08 (s, 3H), 1.15 (d, *J*=6.8 Hz, 3H), 1.47 (dd, *J*=13.2, 6.1 Hz, 1H), 1.60–1.76 (m, 5H), 1.81–1.91 (m, 2H), 2.08–2.13 (m, 1H), 2.12 (d, *J*=14.1 Hz, 1H), 2.50 (dd, *J*=10.2, 7.8 Hz, 1H), 2.80 (dt, *J*=14.1, 3.9 Hz, 1H), 2.85 (dt, *J*=14.4, 4.1 Hz, 1H), 2.98 (d, *J*=14.1 Hz, 1H), 3.12–3.21 (m, 2H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=13.69 (CH_3), 25.27 (CH_3), 25.74 (CH_2), 26.78 (CH_2), 27.11 (CH_3), 27.52 (CH_3), 28.02 (CH_2), 28.79 (CH_2), 40.29 (CH_2), 44.29 (C), 47.14 (CH_2), 47.80 (C), 49.16 (CH_2), 52.47 (CH), 58.69 (CH), 60.77 (C), 68.16 (C), 225.62 (C=O). MS (EI): *m*/*z* (%)=324 (96, M^+), 291 (7), 255 (9), 250 (18), 240 (100), 228 (6), 217 (73), 194 (37), 166 (66), 146 (9), 134 (16), 133 (75), 119 (14), 105 (20), 93 (9), 91 (27), 79 (24). HRMS: *m*/*z* calcd for $C_{18}H_{28}OS_2$: 324.1582, found: 324.1581. Anal. Calcd for $C_{18}H_{28}OS_2$: C 66.61, H 8.70, S 19.76. Found: C 66.60, H 8.48, S 19.68.

4.8.1. *Crystal data for* ***23***

$C_{18}H_{28}OS_2$, crystal size: 0.46×0.34×0.28 mm^3, M_r=324.52 g mol^{-1}, triclinic, space group $P\bar{1}$, λ=0.71073 Å, *a*=7.486(2), *b*=9.117(2), *c*=13.246(3) Å, α=85.58(3)°, β=77.34(3)°, γ=87.08(3)°, *V*=878.9(4) $Å^3$, *Z*=2, ρ_{calcd}=1.226 g cm^{-3}, μ=0.301 mm^{-1}, *T*=198(2) K, θ range=3.52–25.41°; reflections collected: 11,484, independent: 3126 (R_{int}=0.0295). The structure was solved by direct methods and refined by full-matrix least-squares on F^2; R_1=0.0351, wR_2=0.0769 [$I>2\sigma(I)$]; maximal residual electron density: 0.273 e $Å^{-3}$. CCDC 636591 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.9. (±)-Cameroonanone [(3a,5a,6,8a)-2,2,3a,6-tetramethyldecahydrocyclopenta[*c*]pentalen-1-one] [(±)-24]

A suspension of Raney-nickel in water (5 g) was washed with absolute ethanol until it became active. A solution of the thioketal **23** (75 mg, 231 μmol) in absolute ethanol was added to a suspension of activated Raney-nickel in absolute ethanol (25 mL). The suspension was stirred at room temperature for 4 h, the solid was removed by filtration over silica gel (*tert*-butyl methyl ether), and the solvent was evaporated. Purification of the residue by flash chromatography on silica gel (hexane/*tert*-butyl methyl ether, 10:1) provided (±)-cameroonanone (±)-**24** as a colorless oil, yield: 36 mg (71%).

IR (ATR): ν=2951, 2933, 2866, 1725, 1458, 1378, 1358, 1304, 1272, 1223, 1194, 1128, 1087, 1067, 1038, 976, 913 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.97 (d, *J*=6.1 Hz, 3H), 1.05 (s, 3H), 1.06 (s, 3H), 1.07 (s, 3H), 1.38–1.53 (m, 4H), 1.54–1.64 (m, 3H), 1.68–1.83 (m, 4H), 1.88 (br t, *J*=7.8 Hz, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=18.83 (CH_3), 24.60 (CH_3), 27.38 (CH_3), 27.70 (CH_3), 28.81 (CH_2), 31.71 (CH_2), 36.58 (CH_2), 40.83 (CH_2), 43.26 (CH), 44.97 (C), 47.62 (C), 48.37 (CH_2), 61.17 (CH), 70.67 (C), 229.19 (C=O). MS (EI): *m*/*z* (%)=220 (52, M^+), 205 (6), 192 (7), 165 (100), 164 (75), 134 (26), 135 (30), 121 (45), 110 (61), 109 (22), 95 (22), 94 (21), 79 (20), 69 (21). HRMS: *m*/*z* calcd for $C_{15}H_{24}O$: 220.1827, found: 220.1845.

4.10. (±)-Cameroonanol [(1,3a,5a,6,8a)-2,2,3a,6-tetramethyldecahydrocyclopenta[*c*]pentalen-1-ol] [(±)-12] and (±)-*epi*-cameroonanol [(1,3a,5a,6,8a)-2,2,3a,6-tetramethyldecahydrocyclopenta[*c*]pentalen-1-ol] [(±)-*epi*-12]

A 1 M solution of diisobutylaluminum hydride (820 μL, 820 μmol) was added to a solution of (±)-cameroonanone (±)-**24** (60 mg, 272 μmol) in anhydrous dichloromethane (5 mL) at −78 °C and the mixture was stirred at that temperature for 20 h. The cooling was removed and methanol (1 mL) was added dropwise. Water (1 mL) and diethyl ether (3 mL) were added, stirring was continued for 30 min, and the precipitate was removed by filtration over silica gel (diethyl ether). The filtrate was washed with water and dried over magnesium sulfate. Evaporation of the solvent provided a diastereoisomeric mixture of (±)-cameroonanol (±)-**12** and (±)-*epi*-cameroonanol (±)-*epi*-**12** (ratio: 3.7:1) as a colorless oil, yield: 53.5 mg (88%). The diastereoisomers were separated by flash chromatography on silica gel (pentane/diethyl ether, 25:1).

*(±)-Cameroonanol [(±)-**12**]*: colorless crystals, mp 42–45 °C. IR (ATR): ν=3604, 3479, 2929, 2864, 1458, 1374, 1242, 1163, 1077, 1051, 997, 976, 910, 782, 667 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ=0.90 (s, 3H), 0.96 (s, 3H), 0.99 (d, *J*=6.6 Hz, 3H), 1.03 (s, 3H), 1.18–1.27 (m, 1H), 1.30–1.34 (m, 1H), 1.38–1.45 (m, 3H), 1.50–1.67 (m, 5H), 1.73–1.81 (m, 1H), 1.90 (t, *J*=8.2 Hz, 1H), 3.68 (br s, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=19.37 (CH_3), 23.79 (CH_3), 25.67 (CH_3), 28.99 (CH_2), 32.45 (CH_3), 35.33 (CH_2), 36.11 (CH_2), 38.64 (C), 39.97 (CH_2), 43.82 (CH), 47.56 (C), 51.36 (CH), 52.60 (CH_2), 67.10 (C), 89.71 (CH). MS (EI): *m*/*z* (%)=222 (7, M^+), 207 (11), 204 (39), 189 (27), 176 (13), 166 (40), 148 (50), 135 (100), 124 (49), 109 (24), 96 (41), 95 (36), 93 (29), 81 (32). HRMS: *m*/*z* calcd for $C_{15}H_{26}O$: 222.1984, found: 222.1971. Anal. Calcd for $C_{15}H_{26}O$: C 81.02, H 11.79. Found: C 81.05, H 11.74.

*(±)-epi-Cameroonanol [(±)-epi-**12**]*: colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ=0.81 (s, 3H), 0.91 (d, *J*=6.6 Hz, 3H), 0.96 (s, 3H), 1.03 (s, 3H), 1.19–1.88 (m, 12H), 3.35 (br s, 1H). ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ=19.01 (CH_3), 21.49 (CH_3), 25.66 (CH_2), 26.40 (CH_2), 28.44 (CH_3), 28.51 (CH_3), 36.75 (CH_2), 38.13 (CH), 41.75 (C), 43.48 (CH_2), 48.36 (C), 52.71 (CH_2), 62.73 (CH), 65.70 (C), 88.24 (CH). GC–MS (EI): *m*/*z* (%)=222 (8, M^+), 204 (41), 189 (27), 175 (34), 166 (55), 148 (42), 135 (100), 124 (46), 119 (37), 107 (40), 95 (40), 93 (40), 91 (53), 79 (45).

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