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Synthesis of (±)-Abiet-5-en-7-one

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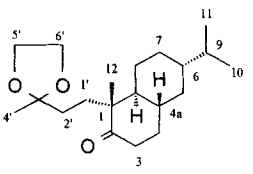
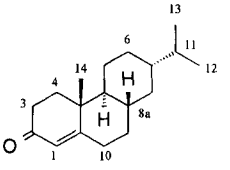
Dedicated to Prof. M. Herberhold on the Occasion of his 60th Birthday.

Pachystazone has been isolated from the aerial parts of *Salvia pachystachys* Trautv. [1] and the roots of *Salvia candidissima* Vahl. subsp. *occidentalis* Hedge [2] (Labiatae) and assumed to possess the structure of (±)-abiet-5-en-7-one ((±)-**11**). In the frame of our investigations on plant disease resistance inducing compounds [3] we were interested in (±)-**11** and have, therefore, synthesized this compound.

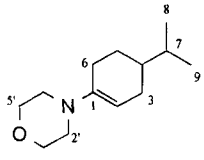
4-Isopropylcyclohexanone [4] was converted to the enamine (±)-**1**. The reaction of (±)-**1** with methyl vinyl ketone yielded the diastereomeric (±)-4-isopropyl-2-(3-oxobutyl)-cyclohexanones (±)-**2** and (±)-**3**. The intramolecular aldol condensation of (±)-**2** and (±)-**3** gave (±)-**4** which was alkylated [5, 6] with 1-bromo-3-butanone ethylene acetal to (±)-**5**. Birch reduction [7] of (±)-**5** followed by methylation resulted in the formation of (±)-**6**. After removal of the acetal protecting group an aldol condensation lead to (±)-**7** which was dimethylated to (±)-**8**. The (±)-abiet-5-en-3-one (±)-**8** reacted with $TsNHNH_2$ to the hydrazone (±)-**9** which was reduced with catecholborane [8, 9] to (±)-**10**. Allylic oxidation of (±)-abiet-5-ene ((±)-**10**) with CrO_3/DMP [10] gave (±)-abiet-5-en-7-one ((±)-**11**).



(±)-**6** (66%)

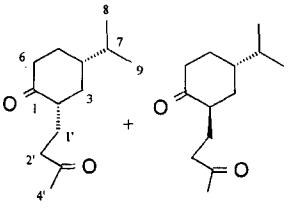


(±)-**7** (93%)



(±)-**1**

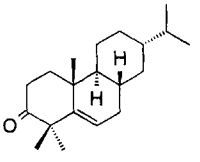
C_6H_6, rfl., 4h



(±)-**2** (±)-**3** (73%)

t-BuOK, t-BuOH

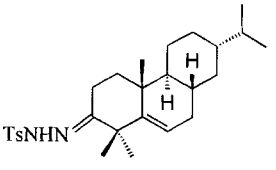
MeI, r. t., 1h



$TsNHNH_2$, AcOH

60°C, 12h

(±)-**8** (72%)



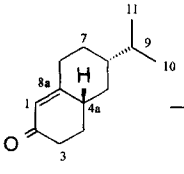
1. catecholborane, r. t., 4h

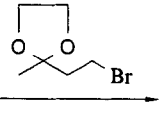
2. Me_4NOAc, r. t., 12h

(±)-**9** (98%)

0.4 N NaOMe

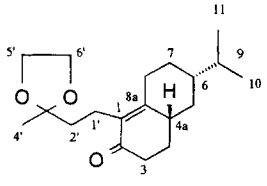
MeOH, rfl., 4h





NaH, DMSO, r. t., 24h

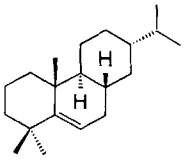
(±)-**4** (82%)



1. Li/NH_3, -78° C, 45 min

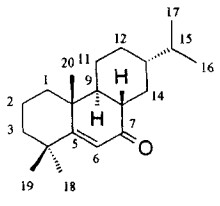
2. MeI, r. t., 12h

(±)-**5** (63%)



CrO_3/DMP

CH_2Cl_2, -20° C, 5h



(±)-**10** (73%)

(±)-**11** (53%)

Table 1 ^{13}C NMR spectral data of (±)-**11**, **16** and **pachystazone** [1] in $CDCl_3$

	(±)-11	16	pachyst.		(±)-11	16	pachyst.
1	39.7	39.8	36.1	11	25.5		18.9
2	37.5	37.8	18.9	12	29.0		33.4
3	17.9	18.1	35.6	13	43.4		36.4
4	36.7	36.5	37.8	14	30.1		28.6
5	178.6	176.9	159.1	15	32.8		37.0
6	123.6	123.9	125.2	16	19.7		23.2*
7	202.0	202.9	198.0	17	19.7		23.2*
8	45.6	45.6	35.2	18/28	31.7*	31.6*	24.6*
9	51.7	52.1	35.2	19/29	30.6*	30.3*	18.4*
10	38.7	38.8	37.8	20/19	20.1	19.6	24.6*

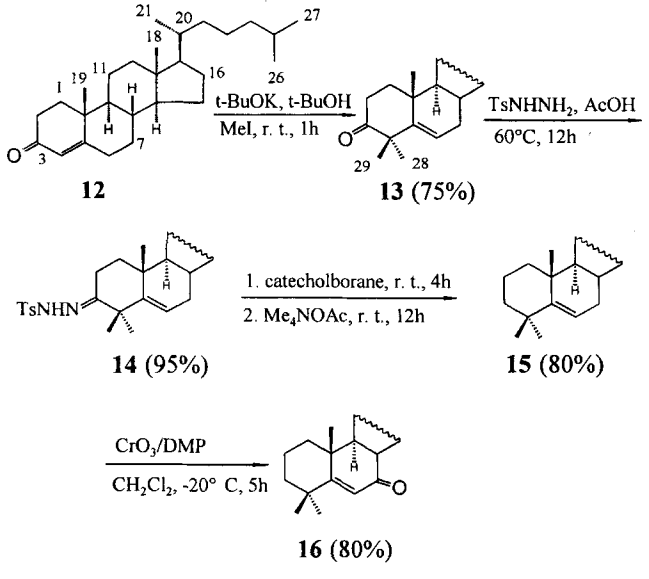
* Assignments with an asterisk are interchangeable.

The comparison of the ^{13}C NMR data (Table 1) of the synthesized (±)-**11** and the isolated pachystazone [1] showed clearly that both are two different compounds.

Our results were checked by the synthesis of the known 4,4-dimethylcholest-5-en-7-one (**16**) [11]: Cholest-4-en-3-one (**12**) was methylated with MeI to 4,4-dimethylcholest-5-en-3-one (**13**) [12]. The reaction of **13** with $TsNHNH_2$ gave 4,4-dimethyl-3-tosylhydrazonocholest-5-ene (**14**) which was reduced with catecholborane to 4,4-dimethylcholest-5-ene (**15**) [13]. Oxidation of **15** with CrO_3/DMP yielded 4,4-dimethylcholest-5-en-7-one (**16**).

The ^{13}C-chemical shifts of the A/B ring systems of (±)-**11** and **16** revealed a very good accordance. So the structure of pachystazone could not be as depicted in formula (±)-**11**. In the ^{13}C NMR spectrum of 3β-hydroxy-5α-cholest-7-en-6-one [14] the signals at δ: 199.8, 123.0 and 163.9 were observed for C-6, C-7 and C-8. The ^{13}C NMR signals of pachystazone at δ: 198.0, 125.2 and 159.1 could represent the carbons C-6, C-7 and C-8 of abiet-7-en-6-one.

The assignments of the ^1H and ^{13}C NMR data were based on ^1H, ^1H, ^1H COSY, ^{13}C, ^{13}C APT and ^1H, ^{13}C COSY-experiments.



Experimental

Melting points were measured on a Reichert hot stage microscope and are reported without correction. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ on a Bruker AC 300 spectrometer. Chemical shifts are given in parts per million (δ-scale), coupling constants (*J*) in Hertz. ^1H-chemical shifts were referenced to the residual $CHCl_3$ signal (7.24). ^{13}C-chemical shifts were referenced to $CDCl_3$ (77.0). Assignments of the NMR signals with * or † are interchangeable. MS were recorded at 70 eV on a Varian MAT-313 spectrometer.

Thin layer chromatography was carried out on precoated plates of Polygram^R SILG/UV_{254} (layer thickness 0.25 mm, Macherey–Nagel). Spots were visualized by UV (254 nm) and spraying with phosphomolybdic acid reagent followed by heating. Column chromatography (CC) was performed on Merck silica gel 60 (70–230 mesh ASTM). CH_2Cl_2 was distilled under nitrogen from P_2O_5. CrO_3 was dried over P_2O_5 before use.

4-Isopropylcyclohexanone was purchased from Lancaster Synthesis GmbH (Mühlheim am Main) and cholest-4-en-3-one (**12**) from Fluka Chemie AG (Buchs, Switzerland).

(±)-*1-(N-Morpholino)-4-isopropylcyclohexene* (±)-1

A solution of 24.0 g (0.17 mmol) of 4-isopropylcyclohexanone, 19.2 ml (0.22 mmol) of morpholine and 150 mg (0.70 mmol) of *p*-toluenesulphonic acid in 70 ml of benzene was refluxed for 8 h by using of a Dean–Stark trap. Benzene was evaporated and the residue was distilled *in vacuo* and 31.7 g (89%) of (±)-**1** was obtained. R_f = 0.62 (cyclohexane/EtOAc, 3:1). *b. p.* 68 °C (0.01 Torr). – ^1H NMR: δ4.61 (m, H-2), 2.07 (m, H-3ax), 2.97 (m, H-3eq), 1.20 (m, H-4), 1.19 (m, H-5ax), 2.03 (H-5eq), 1.20 (m, H-6ax), 2.00 (m, H-6eq), 1.42 (m, H-7), 0.84 (d, *J* = 6.7, 3H-8*), 0.85 (d, *J* = 6.7, 3H-9*), 3.66 (m, H-2', H-6'), 2.76 (m, H-3', H-5'). – ^{13}C NMR: δ 145.4 (C-1), 100.1 (C-2), 28.1 (C-3), 40.4 (C-4), 27.4 (C-5), 26.6 (C-6), 32.2 (C-7), 19.7 (C-8), 20.0 (C-9), 67.0 (C-2', C-6'), 48.5 (C-3', C-5'). – MS: *m/z*(%) 209 (100) [M+], 194 (90), 180 (40), 166 (90), 139 (70), 109 (60), 108 (90).

(±)-*4-Isopropyl-2-(3-oxobutyl)-cyclohexanone* (±)-2, (±)-3

31.0 g (0.15 mol) of (±)-**1** and 20 ml (0.25 mol) of methyl vinyl ketone in 100 ml of anhydrous benzene were refluxed for 4 h. Benzene was evaporated and the residue dissolved in 100 ml of cyclohexane. This solution was washed with 5% hydrochloric acid and then with saturated $KHCO_3$ solution. The organic phase was dried with Na_2SO_4 and evaporated to dryness. The residue was distilled *in vacuo* and 23.0 g (73%) of a mixture of (±)-**2** and (±)-**3** was obtained as colour- less oil. CC of 4 g of the mixture with cyclohexane/EtOAc (5:1) as eluant gave 3.9 g of (±)-**2** and 150 mg of (±)-**3**. R_f = 0.60 (cyclohexane/EtOAc, 1:1). *b. p.* 86 – 88 °C (0.1 Torr). – ^1H NMR of (±)-**2**: δ 2.30 (m, H-2), 1.10 (ddd, *J* = 11.8, 11.8, 11.8, H-3ax), 1.99 (m, H-3eq), 1.58 (m, H-4), 1.43 (m, H-5ax), 1.96 (m, H-5eq), 2.45 (m, 2H-6), 1.49 (m, H-7), 0.85 (d, *J* = 6.7, 3H-8*), 0.86 (d, *J* = 6.7, 3H-9*), 1.35 (m, H-1'), 1.96 (m, H-1'), 2.32 (m, 2H-2'), 2.08 (s, 3H-4'). – ^{13}C NMR of (±)-**2**: δ 209.0 (C-1), 48.6 (C-2), 37.5 (C-3), 43.0 (C-4), 23.7 (C-5), 41.2 (C-6), 31.9 (C-7), 19.7 (C-8*), 19.9 (C-9*), 30.6 (C-

1'), 41.6 (C-2'), 213.2 (C-3'), 29.7 (C-4'). – MS: *m/z*(%) 210 (100) [M+], 167 (30), 153 (80), 97 (70), 43 (100).

(4aSR,6SR)-6-Isopropyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone ((±)-**4**)

160 ml of 0.8N NaOMe solution was added dropwise to 19.0 g (0.1 mol) of the mixture of (±)-**2** and (±)-**3** in 160 ml of MeOH at *r. t.* and then refluxed for 4 h. The reaction mixture was neutralized with 5% hydrochloric acid and the solvent evaporated. The residue was extracted twice with 100 ml of Et_2O. The combined ethereal phases were dried with Na_2SO_4 and the ether was evaporated. The residue was chromatographed (CC) with cyclohexane/EtOAc (1:1) as eluant and yielded 17.2 g (82%) of (±)-**4** as colourless oil. R_f = 0.49 (cyclohexane/EtOAc, 3:1). – ^{1}H NMR: δ 5.77 (s, H-1), 2.31 (m, 2H-3), 1.60 (m, H-4ax), 2.07 (m, H-4eq), 2.30 (m, H-4a), 0.91 (m, H-5ax), 1.89 (m, H-5eq), 1.34 (m, H-6), 1.11 (dddd, J = 12.3, 12.3, 12.3, 4.1, H-7ax), 1.87 (m, H-7eq), 2.23 (m, H-8ax), 2.49 (H-8eq), 1.44 (m, H-9), 0.85 (d, J = 6.7, 3H-10, 3H-11). – ^{13}C NMR: δ 124.0 (C-1), 200.0 (C-2), 36.6 (C-3), 29.3 (C-4), 37.7 (C-4a, C-5), 43.1 (C-6), 29.8 (C-7), 35.3 (C-8), 167.2 (C-8a), 32.3 (C-9), 19.7 (C-10, C-11). – MS: *m/z* (%) 192 (100) [M+], 164 (90) [M+ – H_2O], 149 (95), 94 (50).

(4aSR,6SR)-1-[3',3'-(Ethylenedioxy)-butyl]-6-isopropyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone ((±)-**5**)

A solution of 4.0 g (20.8 mmol) of (±)-**4** in 50 ml of DMSO was added to 552 mg (23.0 mmol) of NaH in 50 ml of anhydrous DMSO. The mixture was stirred for 1 h at *r. t.*, then 4.48 g (23.0 mmol) of 1-bromo-3-butanone ethylene acetal in 25 ml of DMSO was added dropwise and the solution stirred for 24 h at *r. t.*. The reaction mixture was diluted with 100 ml of saturated NH_4Cl solution and extracted three times with 100 ml of Et_2O. The combined ethereal phases were dried with Na_2SO_4 and evaporated. CC of the residue with cyclohexane/EtOAc (2:1) as eluant gave 4.02 g (63%) of (±)-**5** as yellow oil. R_f = 0.67 (cyclohexane/EtOAc, 1:1). – ^{1}H NMR: δ 0.86 (d, J = 6.7, 3H-10, 3H-11), 1.32 (s, 3H-4'), 3.91 (m, 2H-5', 2H-6'). – ^{13}C NMR: δ 132.8 (C-1), 199.0 (C-2), 36.6 (C-3), 28.9 (C-4), 38.6 (C-4a), 38.4 (C-5), 43.2 (C-6), 30.2 (C-7), 30.8 (C-8), 159.9 (C-8a), 32.4 (C-9), 19.8 (C-10, C-11), 38.4 (C-1'), 19.7 (C-2'), 109.8 (C-3'), 23.5 (C-4'), 64.6 (C-5', C-6'). – MS: *m/z*(%) 306 (10) [M+], 87 (100).

(1RS,4aSR,6SR,8aSR)-1-[3',3'-(Ethylenedioxy)-butyl]-6-isopropyl-1-methyl-3,4,4a,5,6,7,8,8a-octahydro-2(1H)-naphthalenone ((±)-**6**)

To 113 mg (16.2 mmol) of Li in 100 ml of liquid NH_3 was added dropwise a solution of 920 mg (3.0 mmol) of (±)-**5** in 23 ml of THF. The mixture was stirred for 45 min at –78 °C, NH_3 was evaporated, 1.87 ml (30 mmol) of MeI added and allowed to stand for 12 h at *r. t.*. The reaction mixture was diluted with 50 ml of H_2O and extracted three times with 60 ml of Et_2O. The combined ethereal phases were dried with Na_2SO_4 and evaporated to dryness. CC of the residue with cyclohexane/EtOAc (7:1) as eluant yielded 638 mg (66%) of (±)-**6** as colourless oil. R_f = 0.49 (cyclohexane/EtOAc, 5:1). – ^{1}H NMR: δ 1.14 (m, H-4a), 1.06 (m, H-6), 1.39 (m, H-9), 0.83 (d, J = 6.8, 3H-10, 3H-11), 1.01 (s, 3H-12), 1.33 (s, 3H-4'), 3.92 (m, 2H-5', 2H-6'). – ^{13}C NMR: δ 50.4 (C-1), 215.1 (C-2), 38.2 (C-3), 28.7 (C-4), 46.9 (C-4a), 37.3 (C-5), 43.5 (C-6), 29.2 (C-7), 33.7 (C-8), 35.8 (C-8a), 32.6 (C-9), 19.7 (C-10, C-11), 20.9 (C-12), 25.7 (C-1'), 33.2 (C-2'), 110.3 (C-3'), 23.4 (C-4'), 64.4 (C-5'*), 64.5 (C-6'*). – MS: *m/z*(%) 322 (5) [M+], 307 (20), 87 (100).

(4aRS,4bSR,7SR,8aSR)-7-Isopropyl-4a-methyl-4,4a,4b,5,6,7,8,8a,9,10-decahydro-2(3H)-phenanthrenone ((±)-**7**)

300 mg (0.93 mmol) of (±)-**6** in 20 ml of 0.7% methanolic HCl was refluxed for 5 h. 30 ml of saturated $KHCO_3$ solution was added, the mixture extracted three times with 40 ml of CH_2Cl_2. The combined CH_2Cl_2 phases were dried with Na_2SO_4 and yielded after evaporation 225 mg (93%) of (±)-**7** as colourless oil. R_f = 0.62 (cyclohexane/EtOAc, 2:1). – ^{1}H NMR: δ 5.70 (s, H-1), 0.68 (ddd, J = 12.0, 12.0, 12.0, H-8ax), 1.65 (m, H-8eq), 0.83 (d, J = 6.8, 3H-12, 3H-13), 1.10 (s, 3H-14). – ^{13}C NMR: δ 123.7 (C-1), 199.7 (C-2), 33.9 (C-3), 35.5 (C-4), 38.6 (C-4a), 53.3 (C-4b), 25.5 (C-5), 29.7 (C-6), 43.5 (C-7), 37.6 (C-8), 36.7 (C-8a), 34.6 (C-9), 33.0 (C-10), 171.8 (C-10a), 32.7 (C-11), 19.7 (C-12*), 19.8 (C-13*), 17.6 (C-14). – MS: *m/z*(%) 260 (80) [M+], 218 (50), 124 (100).

(±)-*Abiet-5-en-3-one* ((±)-**8**)

30 mg (0.76 mmol) of *K* was dissolved in 3 ml of *t*-BuOH under nitrogen. To this solution 100 mg (0.38 mmol) of (±)-**7** in 2 ml of *t*-BuOH was added, and after 30 min 0.1 ml (1.60 mmol) of MeI was added dropwise at *r. t.*. After stirring for 1 h at *r. t.* the reaction was stopped by addition of 4 ml of 5% aqueous HCl and the solution extracted with 40 ml of CH_2Cl_2. The organic phase was washed with H_2O, dried with Na_2SO_4 and eva-porated. CC of the residue with cyclohexane/EtOAc (2:1) gave 79 mg (72%) of (±)-**8** as a colourless resin. R_f = 0.80 (cyclohexane/EtOAc, 2:1). – ^{1}H NMR: δ 5.48 (m, H-6), 1.65 (m, H-7ax), 2.09 (m, H-7eq), 0.67 (ddd, J = 12.1, 12.1, 12.1, H-14ax), 1.75 (m, H-14eq), 0.81 (d, J = 6.8, 3H-16, 3H-17), 1.18 (s, 3H-18*), 1.17 (s, 3H-19*), 0.73 (s, 3H-20). – ^{13}C NMR: δ 31.6 (C-1), 33.7 (C-2), 216.9 (C-3), 48.7 (C-4), 149.5 (C-5), 119.9 (C-6), 33.7 (C-7), 31.2 (C-8), 48.6 (C-9), 36.9 (C-10), 26.1 (C-11), 29.8 (C-12), 43.6 (C-13), 38.2 (C-14), 32.7 (C-15), 19.7 (C-16, C-17), 30.2 (C-18*), 27.1 (C-19*), 17.6 (C-20). – MS: *m/z*(%) 288 (20) [M+], 273 (10), 245 (10), 124 (100).

(±)-*3-Tosylhydrazonoabiet-5-ene* ((±)-**9**)

79 mg (0.27 mmol) of (±)-**8** was dissolved in 7 ml of glacial acetic acid at 60 °C. 112 mg (0.60 mmol) of *p*-$TsNHNH_2$ was added. The mixture was stirred at 60 °C for 12 h. 20 ml of H_2O was added, the tosylhydrazone filtered off and dissolved in 40 ml of CH_2Cl_2. The organic phase was treated with 10 ml of a saturated $KHCO_3$ solution, dried with Na_2SO_4 and evaporated. 121 mg (98%) of (±)-**9** was obtained as a colourless solid. R_f = 0.43 (cyclohexane/EtOAc, 4:1). *m. p.* 163–165 °C. – ^{1}H NMR: δ 5.48 (m, H-6), 1.38 (m, H-8), 0.81 (m, H-9), 1.36 (m, H-15), 0.82 (d, J = 6.7, 3H-16, 3H-17), 1.03 (s, 3H-18*), 1.24 (s, 3H-19*), 0.50 (s, 3H-20), 7.25 (d, J = 8.0, H-2', H-6'), 7.81 (d, J = 8.0, H-3', H-5'), 2.38 (s, 3H-7'), 7.42

(s, NH). – ^{13}C NMR: δ 30.0 (C-1), 21.4 (C-2), 165.2 (C-3), 42.7 (C-4), 149.1 (C-5), 119.1 (C-6), 33.7 (C-7), 31.9 (C-8), 48.5 (C-9), 36.7 (C-10), 26.1 (C-11), 29.8 (C-12), 43.6 (C-13), 38.2 (C-14), 32.7 (C-15), 19.7 (C-16*), 19.8 (C-17*), 33.6 (C-18†), 28.4 (C-19†), 18.4 (C-20), 143.7 (C-1'), 129.2 (C-2', C-6'), 128.1 (C-3', C-5'), 135.3 (C-4'), 21.5 (C-7'). – MS: *m/z*(%) 456 (10) [M$^+$], 301 (100), 272 (30).

(±)-*Abiet-5-en* ((±)-**10**)

121 mg (0.26 mmol) of (±)-**9** was dissolved in anhydrous $CHCl_3$ under nitrogen. The solution was cooled to 0 °C, 0.10 ml (1 mmol) of catecholborane was added, the mixture stirred for 30 min at 0 °C and for 4 h at *r. t.*. Then 0.2 ml of MeOH and 160 mg (1.2 mmol) of Me_4NOAc were added and the solution was stirred for 12 h at *r. t.*. 60 ml of CH_2Cl_2 and 10 ml of H_2O were added. The organic phase was separated, dried with Na_2SO_4 and evaporated. CC of the residue with cyclohexane as eluant yielded 52 mg (73%) of (±)-**10** as a colourless resin. R_f = 0.84 (cyclohexane). – ^{1}H NMR: δ 5.41 (m, H-6), *0.63 (ddd, J* = 12.1, 12.1, 12.1, H-14ax), 1.73 (m, H-14eq), 0.84 (d, *J* = 6.8, 3H-16, 3H-17), 1.10 (s, 3H-18, 3H-19), 1.00 (s, 3H-20). – ^{13}C NMR: δ 41.2 (C-1), 38.8 (C-2), 18.7 (C-3), 35.5 (C-4), 150.5 (C-5), 118.4 (C-6), 34.2 (C-7), 31.9 (C-8), 51.0 (C-9), 37.1 (C-10), 25.4 (C-11), 30.0 (C-12), 43.5 (C-13), 40.0 (C-14), 32.8 (C-15), 19.8 (C-16, C-17), 31.1 (C-18*), 32.9 (C-19*), 21.5 (C-20). –MS: *m/z*(%) 274 (70) [M$^+$], 259 (100), 189 (35), 135 (40).

(±)-*Abiet-5-en-7-one* ((±)-**11**)

190 mg (1.90 mmol) of CrO_3 was suspended in 4 ml of anhydrous CH_2Cl_2 at –20 °C under nitrogen, and 183 mg (1.90 mmol) of DMP (3.5-dimethylpyrazole) was added in one portion. The resulting mixture was stirred at –20 °C for 20 min., 52 mg (0.19 mmol) of (±)-**10** in 0.5 ml of CH_2Cl_2 was added under nitrogen, and the reaction mixture was stirred for 5 h maintaining a temperature between –10 and –20 °C. 60 ml of CH_2Cl_2 and 10 ml of 5% hydrochloric acid were added. The organic phase was separated, dried with Na_2SO_4 and evaporated. CC of the residue with cyclohexane/EtOAc (7:1) as eluant gave 29 mg (53%) of (±)-**11** as colourless resin. R_f = 0.52 (cyclohexane/EtOAc, 5:1). – ^{1}H NMR: δ 1.38 (m, H-1ax), 1.53 (m, H-1eq), 1.16 (m, H-2ax), 1.82 (m, H-2eq), 1.56 (m, H-3ax), 1.73 (m, H-3eq), 5.95 (s, H-6), 2.10 (ddd, *J* = 12.2, 12.2, 4.0, H-8ax), 1.44 (m, H-9ax), 1.14 (m, H-11ax), 1.80 (m, H-11eq), 0.88 (m, H-12ax), 1.71 (m, H-12eq), 1.06 (m, H-13), 0.78 (ddd, *J* = 11.9, 11.9, 11.9, H-14ax), 2.35 (m, H-14eq), 1.44 (m, H-15), 0.85 (d, *J* = 6.8, 3H-16, 3H-17), 1.12 (s, 3H-18*), 1.18 (s, 3H-19*), 1.16 (s, 3H-20). – ^{13}C NMR: δ See Tab. 1. – MS: *m/z* (%): 288.2453 (calc. for $C_{20}H_{32}O$ 288.2453) (100) [M$^+$], 273 (50), 245 (60), 217 (50), 203 (55).

Compounds 13–16

These were synthesized in the same way as (±)-**8** - (±)-**11** starting from cholest-4-en-3-one (**12**)

4,4-Dimethylcholest-5-en-3-one (**13**)

Yield (75%). R_f = 0.75 (cyclohexane/EtOAc, 5:1). *m. p.* 177–178 C. $[\alpha]_D^{22}$ = +1° (c = 1.22, $CHCl_3$) [12] *m. p.* 176–177°C. $[\alpha]_D^{20}$ = + 1° (c = 2.07, $CHCl_3$]. – ^{1}H NMR: δ 5.42 (m, H-6), 0.65 (s, 3H-18), 0.82 (s, 3H-19), 0.88 (d, *J* = 6.5, 3H-21), 0.83 (d, *J* = 6.7, 3H-26, 3H-27), 1.20 (s, 3H-28, 3H-29). – ^{13}C NMR: δ 32.1 (C-1), 33.7 (C-2), 216.8 (C-3), 48.6 (C-4), 149.8 (C-5), 119.9 (C-6), 31.7 (C-7), 31.2 (C-8), 48.9 (C-9), 37.0 (C-10), 21.3 (C-11), 39.7 (C-12), 42.4 (C-13), 56.1 (C-14), 24.2 (C-15), 28.2 (C-16), 56.8 (C-17), 11.9 (C-18), 19.3 (C-19), 35.8 (C-20), 18.7 (C-21), 36.2 (C-22), 23.8 (C-23), 39.5 (C-24), 28.0 (C-25), 22.5 (C-26*), 22.8 (C-27*), 30.2 (C-28†), 27.2 (C-29†). – MS: *m/z*(%) 412 (40) [M$^+$], 123 (100).

4,4-Dimethyl-3-tosylhydrazonocholest-5-ene (**14**)

Yield 95%. R_f = 0.68 (cyclohexane/EtOAc, 4:1). *m. p.* 179–181°C. – ^{1}H NMR: δ 5.48 (m, H-6), 0.55 (s, 3H-18), 0.60 (s, 3H-19), 0.85 (d, *J* = 6.2, 3H-21), 0.81 (d, *J* = 6.5, 3H-26, 3H-27), 1.04 (s, 3H-28*), 1.27 (s, 3H-29*), 7.23 (d, *J* = 8.0, H-2', H-6'), 7.80 (d, *J* = 8.0, H-3', H-5'), 2.36 (s, 3H-7'). – ^{13}C NMR: δ 30.3 (C-1), 21.5 (C-2), 165.4 (C-3), 42.3 (C-4), 149.4 (C-5), 119.2 (C-6), 31.6 (C-7), 31.0 (C-8), 48.6 (C-9), 36.7 (C-10), 21.2 (C-11), 39.7 (C-12), 42.6 (C-13), 56.1 (C-14), 24.1 (C-15), 28.2 (C-16), 56.4 (C-17), 11.9 (C-18), 18.4 (C-19), 35.7 (C-20), 18.6 (C-21), 36.1 (C-22), 23.8 (C-23), 39.4 (C-24), 27.9 (C-25), 22.5 (C-26*), 22.8 (C-27*), 33.7 (C-28†), 28.5 (C-29†), 143.7 (C-1'), 129.2 (C-2', C-6'), 128.1 (C-3', C-5'), 135.4 (C-4'), 21.5 (C-7'). – MS: *m/z*(%) 425 (50), 396 (100), 381 (80), 149 (40).

4,4-Dimethylcholest-5-ene (**15**)

Yield 80%. R_f = 0.83 (cyclohexane). *m. p.* 65–67 °C. $[\alpha]_D^{22}$ = – 56° (c = 0.86, $CHCl_3$) [13] *m. p.* 64–66 °C). $[\alpha]_D^{20}$ = –57° (c = 1.0, $CHCl_3$)]. – ^{1}H NMR: δ 5.45 (m, H-6), 0.65 (s, 3H-18), 1.07 (s, 3H-19), 0.90 (d, *J* = 6.5, 3H-21), 0.85 (d, *J* = 6.6, 3H-26, 3H-27), 1.04 (s, 3H-28*), 1.10 (s, 3H-29*). – ^{13}C NMR: δ 42.2 (C-1), 39.2 (C-2), 18.8 (C-3), 35.6 (C-4), 150.7 (C-5), 118.2 (C-6), 32.5 (C-7), 31.2 (C-8), 51.1 (C-9), 37.1 (C-10), 20.7 (C-11), 40.0 (C-12), 42.2 (C-13), 56.2 (C-14), 24.2 (C-15), 28.3 (C-16), 57.5 (C-17), 11.9 (C-18), 21.5 (C-19), 35.9 (C-20), 18.7 (C-21), 36.3 (C-22), 23.9 (C-23), 39.6 (C-24), 28.0 (C-25), 22.6 (C-26*), 22.8 (C-27*), 32.9 (C-28†), 31.0 (C-29†). – MS: *m/z*(%) 398 (100) [M$^+$], 383 (20), 315 (20).

4,4-Dimethylcholest-5-en-7-one (**16**)

Yield 80%. R_f = 0.64 (cyclohexane/EtOAc, 7:1). *m. p.* 77–78 °C [11] *m. p.* 81–82 °C. $[\alpha]_D^{22}$ = – 77° (c = 0.25, $CHCl_3$). – ^{1}H NMR: δ 5.83 (s, H-6), 0.65 (s, 3H-18), 1.20 (s, 3H-19), 0.88 (d, *J* = 6.5, 3H-21), 0.83 (d, *J* = 6.6, 3H-26, 3H-27), 1.10 (s, 3H-28*), 1.15 (s, 3H-29*). – ^{13}C NMR: δ 20.9 (C-11), 38.8 (C-12), 43.3 (C-13), 50.9 (C-14), 26.4 (C-15), 28.6 (C-16), 55.0 (C-17), 11.9 (C-18), 35.6 (C-20), 18.8 (C-21), 36.2 (C-22), 23.9 (C-23), 39.5 (C-24), 28.0 (C-25), 22.5 (C-26*), 22.8 (C-27*) and Tab. 1. –MS: *m/z*(%) 412.3705 (calc. for $C_{29}H_{48}O$ 412.3705) (100) [M$^+$], 397 (20), 204 (20), 189 (40).

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