64. Stereoselective Partial Synthesis of (+)-Pisiferic Acid

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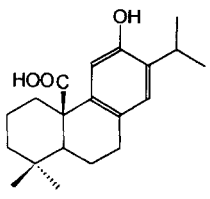
(13.I.95)

(+)-Pisiferic acid (**1**), an antibiotic active against *Gram*-negative and *Gram*-positive bacteria, was synthesized starting from dehydroabietic acid (**2**) or abietic acid (**26**). The terpene ring system was functionalized and a *Barton* reaction used to oxidize Me(20). The intermediates of this photochemical reaction were isolated and characterized.

1. Introduction. – (+)-Pisiferic acid (12-hydroxyabieta-8,11,13-trien-20-oic acid; **1**) was first isolated by *Yatagai et al.* [1–4] from the needles of *Chamaecyparis pisifera* S. *et* Z. (Cupressaceae) [5], which is a common conifer in Japan. Acid **1** and its derivatives show antibiotic activity against a broad variety of bacteria (*i.e. Staphylococcus aureus*, *Bacillus subtilis*, *Proteus vulgaris*). For this reason, they are widely used in Japan in dermatotherapy. Antifungal activity against *Pyricularia oryzae* (which causes rice mildew) was recently observed [6] [7], and it was shown that **1** acts as a cytotoxin against HeLa cells [8]. Because of these biological activities, several synthetic approaches towards **1** or related



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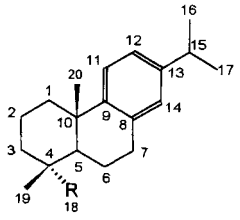
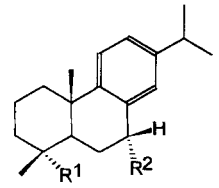
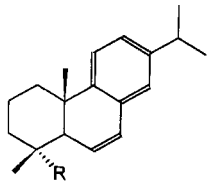


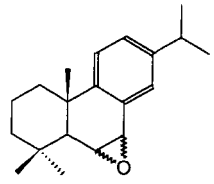
2 R = COOH
3 R = COOMe
4 R = CH_2OH
5 R = CH_2OTos
6 R = Me



7 R^1 = Me, R^2 = AcO
8 R^1 = COOMe, R^2 = AcO
10 R^1 = COOMe, R^2 = MeO



9 R = Me
11 R = COOMe



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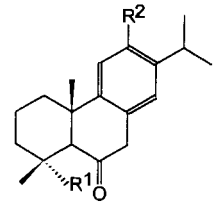


13 R^1 = Me, R^2 = H
15 R^1 = COOMe, R^2 = H
34 R^1 = Me, R^2 = MeO

compounds were reported in the literature [9–13]. *Matsumoto et al.* [14] described a synthesis of (+)-pisiferal (=12-hydroxyabieta-8,11,13-trien-20-al) and (+)-pisiferol using abieta-8,11,13-trien-6-one (**13**) as starting material. The key step was the transannular oxidation of the angular Me group with lead(IV) acetate, to yield the corresponding furan. In the course of our work on synthesis of biologically active natural compounds, we used higher terpenes as chiral starting materials for stereoselective syntheses. We tried to develop a photochemical route for the oxidation of the axial Me group in dehydroabietic acid (= abieta-8,11,13-trien-18-oic acid; **2**) or related compounds.

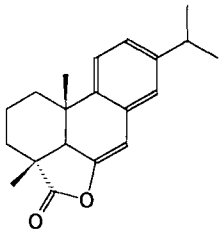
2. Preparative Results. – 2.1. *Starting from Dehydroabietic Acid.* Methyl dehydroabietate (**3**) was converted to the corresponding alcohol **4** by treatment with $LiAlH_4$ or with sodium dihydridobis(2-methoxyethoxy)aluminate in THF. Alcohol **4** was tosylated in pyridine to **5** and further reduced to **6**, using the method described by *Fujimoto* and *Tatsuno* [15]. Instead of the solvent used by these authors (HMPA), we used DMF and obtained **6** from **3** in an overall yield of 62%.

Regio- and stereoselective acetoxylation of the benzylic position with $Pb(OAc)_4$ in AcOH at 100° gave only 30% of **7** [16]. However, *Franzens* and *Edens* showed that homolysis of the PbO bond in lead(IV) tetracarboxylates can be induced by irradiation [17]. Thus, we obtained 74% of **7** from **6** and $Pb(OAc)_4$ using a Hg medium-pressure lamp at room temperature. The ^{1}H-NMR spectrum of **7** showed that the AcO group was introduced in 7α-position (*m* of H–C(7) with only small coupling constants (< 4 Hz)). Similarly, **3** gave **8** (same yield). Acid-catalyzed β-elimination (EtOH/10% HCl) converted **7** quantitatively into **9**. In the β-elimination of **8** (MeOH/10% HCl), a by-product **10** was obtained besides **11**.

Epoxidation of a benzylic double bond and consecutive acid-catalyzed rearrangement to a carbonyl function has been often described [14] [18] [19]. Treatment of **9** with dry 3-chloroperbenzoic acid in CH_2Cl_2 gave a mixture of the diastereoisomeric epoxides **12** which were not isolated but treated directly with toluene-4-sulfonic acid in benzene to yield **13**. Attempts to convert **11** to the corresponding ketone **15** failed, instead we obtained lactone **14**. Lactonization between OH functions in position 6 and the carbonyl group was observed before on similar diterpenes [20] [21]. Cleavage of the lactone by acid or base and immediate esterification with diazomethane gave keto ester **15**.

The reduction of **13** with $LiAlH_4$ was highly stereoselective and produced the alcohol **16** in high yield. Its diastereoisomer with an equatorial OH function was obtained only to 3%. The axial OH function of **16** could now be used to functionalize the angular Me group at position 10 by transannular oxidation *via* a *Barton* reaction. Treatment of **16** in dry pyridine with nitrosyl chloride [22] afforded **17** in nearly quantitative yield.

2.1.1. *The* Barton *Reaction.* Irradiation of nitrite **17** under Ar and in benzene at room temperature with a high-pressure Hg lamp using a *Solidex* glass filter gave a yellow suspension. Primary product was a white insoluble substance, presumably the dimer **17'** (NMR, UV, and MS). It was shown earlier that nitroso compounds form stable dimers [23–26]. After treatment with boiling i-PrOH under Ar, a mixture of the four products, **13** (9%), **16** (7%), **18** (10%), and **19** (65%), was obtained, which could be separated by column chromatography. Compound **19** was presumably formed from an oxime intermediate (see *Scheme*).To gain more structural information, we acetylated **19** with Ac_2O [26] to the crystalline acetate **20**. From the crystal structure, we obtained the (*R*)-configuration of the C-atom bearing the nitrogen.



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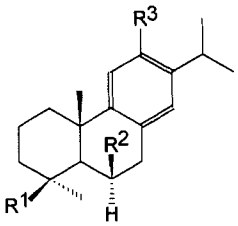
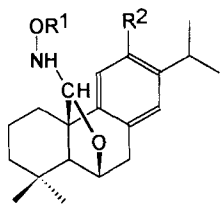
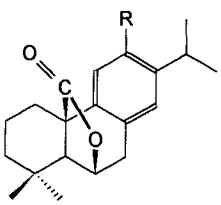


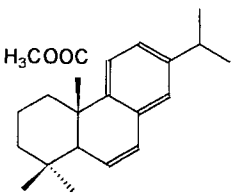
16 R^1 = Me, R^2 = OH, R^3 = H
17 R^1 = Me, R^2 = ONO, R^3 = H
18 R^1 = CH=NOH, R^2 = OH, R^3 = H
35 R^1 = Me, R^2 = ONO, R^3 = MeO
37 R^1 = CH=NOH, R^2 = OH, R^3 = MeO
38 R^1 = Me, R^2 = OH, R^3 = MeO



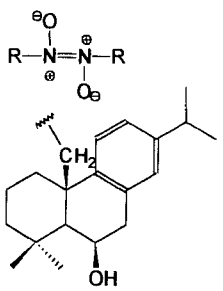
19 R^1 = H, R^2 = H
20 R^1 = Ac, R^2 = H
36 R^1 = H, R^2 = Me



21 R = H
39 R = MeO
40 R = OH



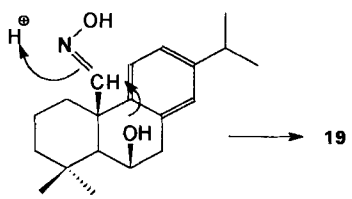
22



R- =

17'

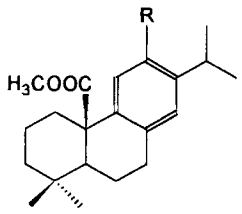
Scheme



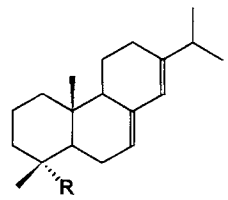
19

The structure of **18** is established by IR and NMR spectra. One observes two O–H valence vibrations and the δ(C) of the oxime C-atom (C(19)) at 157.4 ppm. In the ^{1}H-NMR spectrum, two signals are characteristic for the structure, the OH signal of the oxime at 10.44 ppm and the OH signal of the alcohol at 6.45 ppm. ^{15}N-Enriched (^{15}N)-**18** shows ^{15}N,^{13}C-couplings to C(19) and C(4) and a ^{15}N,^{1}H-coupling to the oxime OH. The NMR spectra of **19** exhibit two exchangeable protons. In ^{15}N-enriched (^{15}N)-**19**, one of these protons is coupled to the N-atom ($^1J(^1H,^1N)$ = 68.0 Hz). Coupling of the N-atom is also observed in the ^{13}C-NMR spectra to C(9) and C(10). Compound **20** has a sharp NH valence vibration, and in the MS one finds AcOH elimination from M^+. An X-ray crystal-structure analysis of **20** (see *Exper. Part*) confirms our results.

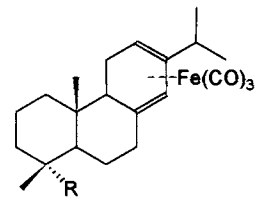
Oxidation of **19** with pyridinium dichromate (PDC) gave in high yield the corresponding lactone **21**. Cleavage of the lactone ring with KOH followed by elimination led to a mixture of two isomeric olefins which, after hydrogenation, can give a mixture of configurational isomers [14]. Thus, instead of KOH, we used lithium methanethiolate as nucleophile [27][28]. During the nucleophilic cleavage of the C(6)–O bond, methanethiol was eliminated [29], and only single isomer, **22**, was obtained, after isolation and esterification with diazomethane. NMR Measurements showed that the double bond was in benzylic position. Hydrogenation over Pd/C [30] converted **22** in high yield into **23**.



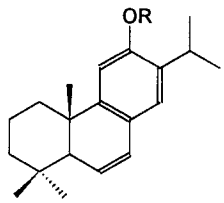
23 R = H
24 R = Ac
25 R = AcO



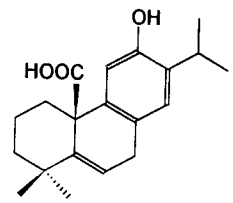
26 R = COOH
27 R = COOMe



28 R = COOMe
29 R = CH_2OH
30 R = CH_2OTos
31 R = Me



32 R = H
33 R = Me



41

Regioselective functionalization of dehydroabietic acid by *Friedel-Crafts* acylation was described in the literature [31] [32]. Thus, compound **24** was obtained from **23** and converted by *Baeyer-Villiger* oxidation [33] to (+)-methyl 12-*O*-acetylpisiferate (**25**), which was quantitatively hydrolyzed to the target **1** using lithium methanethiolate.

2.2. *Starting from Abietic Acid.* Abietic acid (**26**) is a chiral starting material, which is easy available and has often been used before in terpene or steroid synthesis [33–35]. It was converted *via* **27** and the ironcarbonyl complexes **28** and **29** to the compounds **30** and **31** and into dehydroferruginol **32** [35]. This compound is oxygen-sensitive and was methylated with diazomethane in the presence of silica to **33**.

Introduction of the carbonyl group in position 6 of **33** *via* epoxidation and acid rearrangement to **34** and reduction with $LiAlH_4$ to the corresponding alcohol **38** was achieved as described before (*Formulae* above). Photolysis of nitrite **35** in benzene, however, did not lead to a dimer as before (*cf.* **17'**). After treatment of the reaction mixture with i-PrOH and chromatographic separation, 40% of hydroxylamine **36**, 30% of oxime **37**, 10% of alcohol **38**, and 10% of ketone **34** were obtained. In contrast to the photolysis of **17**, the one of **35** produced, more oxime, *i.e.*, **37**. This might be due to the electronic effect of the MeO group. Oxidation of **36** with PDC in DMF to lactone **39** (77%) was completed within 10 min. Cleavage of the lactone ring with lithium methanethiolate as described before was not possible. Even at higher temperatures, the lactone ring of **39** survived, while the MeO group was cleaved. We, therefore, used $AlBr_3$/tetrahydrothiophene to polarize the alkoxy C-atom (C(6)) of **39** and hence to open the lactone [36]. After 2 h, a red mixture was obtained from which we could isolate **40** in high yield, and after 24 h, compound **1** was the main product (82%), besides 10% of olefin **41**. The structure of **41** was confirmed by a COSY spectrum, showing a coupling of the olefinic H–C(6) to H_{ax}–C(7) and H_{eq}–C(7). All physical and spectroscopic data of **1**,

obtained in both synthetic routes, were identical and in good agreement with the data published for (+)-pisiferic acid.

Experimental Part

General. Hydrogenation: *Parr* instrument model *3911*. Photochemical reactions: *Heraeus TQ 150* 150 W or *TQ 150 Z3* 150 W; photoreactor *13/21 H. Mangels/Destillationstechnik*. TLC (Thin-layer chromatography): *Merck 60 F_{256} or Macherey-Nagel Polygram Sil G/UV$_{254}$ or Alugram Sil G/UV$_{254}$*. Prep. TLC: *Chromatotron 8924, Harrison Research*. Column chromatography (CC): silica gel *60* (*Merck*); aluminium oxide (basic, *5016 A* (*Fluka*); *Celite 545* (*Fluka*). Melting points: *SM-LUX* hot-stage apparatus *Leitz* or *Büchi* apparatus designed by Dr. *Tottoli*; corrected. Polarimetric measurements: *Perkin-Elmer 241*. UV: *Perkin-Elmer Lambda 17*; MeOH solns.; λ_{max} (log ε) in nm. IR: *Perkin-Elmer-1R 883*; in cm^{-1}. NMR: *Bruker AC 200* (^1H: 200 MHz; ^{13}C: 50.3 MHz) or *Bruker AMX 500* (^1H: 500 MHz; ^{13}C: 125 MHz); for ^{15}N shifts, nitromethane was used as external standard; no susceptibility corrections were made; for unambiguous assignment, H,H- and H,C-COSY and sometimes NOE measurements were used; trivial atom numbering. Elemental analyses were performed by Mag. *Theiner* (Laboratorium für Mikroanalyse, Institut für Physikalische Chemie, Universität Wien). X-Ray diffraction: *Philips-PW-1100* diffractometer with graphite monochromator, MoK_α (λ = 0.71069 Å); we are grateful to Mrs. *D. Högerle* (Universität Ulm). We are grateful to Dr. *E. Prantz, Krems-Chemie*, Krems/Donau, Austria, for providing us with starting material *Sacotan 90*®.

Dehydroabietic Acid (**2**). Acid **2** and its ester **3** were obtained from *Sacotan 90*® as described in [37] [38], and **4**–**6** as described in [39–43].

(4aS,9R,10aS)-1,2,3,4,4a,9,10,10a-Octahydro-1,1,4a-trimethyl-7-(1-methylethyl)phenanthren-9-yl Acetate (**7**). A suspension of 13.4 g (50 mmol) of **6** and 40.4 g (91 mmol) of $Pb(OAc)_4$ in 130 ml of AcOH was degassed and saturated with Ar in an ultrasonic bath. After irradiation for 24 h with a 150-W medium-pressure Hg lamp, the mixture was diluted with H_2O (500 ml) and extracted with Et_2O twice. The combined org. soln. was washed successively with aq. $NaHCO_3$ soln. and brine and evaporated. The oily residue was purified by CC (silica gel, cyclohexane/AcOEt 9:1): 12.1 g (74%) of **7**. White crystals. M.p. 126–128° (MeOH; [44]: 127–128°). R_f 0.54 (cyclohexane/AcOEt 9:1). $[\alpha]_D$ = 37.9 (c = 0.4, $CHCl_3$, 25°). UV (MeO): 207 (3.71), 224 (3.90), 275 (2.73). IR (KBr): 3053*m*, 2956*s*, 2924*vs*, 1766*m*, 1727*vs*, 1685*m*, 1655*w*, 1497*m*, 1373*s*, 1246*vs*, 825*m*. ^1H-NMR ($CDCl_3$): 0.92 (*s*, Me–C(4)); 0.93 (*s*, Me–C(4)); 1.15 (*s*, Me–C(10)); 1.22 (*d*, J = 6.9, Me–C(15)); 1.23 (*d*, J = 6.9, Me–C(15)); 1.23 (*m*, H_{ax}–C(3)); 1.44 (*m*, H_{ax}–C(1)); 1.51 (*m*, H_{eq}–C(3)); 1.63 (*m*, H_{eq}–C(2)); 2.00 (*m*, H_{eq}–C(6)); 2.05 (*s*, Ac); 2.28 (*m*, H_{eq}–C(1)); 2.85 (*sept.*, J = 6.9, H–C(15)); 5.99 (*m*, H_{eq}–C(7)); 7.04 (*d*, J = 1.8, H–C(14)); 7.14 (*dd*, J = 8.2, 1.8, H–C(12)); 7.22 (*d*, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.2 (*t*, C(2)); 21.4 (*q*, *Me*CO); 21.5 (*q*, C(19)); 23.8 (*q*, C(20)); 23.9 (*q*, C(16) or C(17)); 24.0 (*q*, C(17) or C(16)); 26.1 (*t*, C(6)); 32.8 (*s*, C(4)); 32.9 (*q*, C(18)); 33.4 (*d*, C(15)); 37.8 (*s*, C(10)); 38.4 (*t*, C(1)); 41.4 (*t*, C(3)); 45.3 (*d*, C(5)); 71.1 (*d*, C(7)); 124.6 (*d*, C(11)); 127.0 (*d*, C(12)); 128.2 (*d*, C(14)); 131.9 (*s*, C(8)); 146.3 (*s*, C(9)); 148.4 (*s*, C(13)); 170.7 (*s*, *Me*CO). EI-MS: 328 (15, M^+), 286 (19), 255 (100), 253 (34), 243 (12), 225 (6), 211 (17), 197 (13), 183 (26), 141 (25), 43 (39), 41 (38). Anal. calc. for $C_{22}H_{32}O_2$ (328.5): C 80.44, H 9.82; found: C 81.03, H 9.95.

Methyl (1R,4aS,9R,10aR)-9-Acetoxy-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)phenanthrene-1-carboxylate (**8**). A suspension of 19.6 g (62 mmol) of **3** and 48.6 g (110 mmol) of $Pb(OAc)_4$ in 150 ml of dry AcOH was degassed and saturated with Ar in an ultrasonic bath and irradiated with a 150-W medium-pressure Hg lamp during 24 h. Workup as described before yielded colorless crystals (17.2 g, 74%). M.p. 173–175° (MeOH). R_f = 0.53 (cyclohexane/AcOH 2:1). $[\alpha]_D$ = 29.1 (c = 0.4, $CHCl_3$, 20°). UV (MeOH): 205 (3.77), 223 (3.87), 270 (2.64), 276 (2.49). IR (KBr): 2960*m*, 1730*vs*, 1480*w*, 1435*w*, 1370*w*, 1245*s*, 1180*m*, 1130*m*. ^1H-NMR ($CDCl_3$): 1.10 (*s*, Me–C(10)); 1.16 (*d*, J = 7.0, 2 Me–C(15)); 1.19 (s, Me–C(4)); 1.45 (*m*, H_{ax}–C(1)); 1.51 (*m*, H_{ax}–C(3)); 1.56 (*m*, H_{eq}–C(6)); 1.59 (*m*, H_{eq}–C(3)); 1.65 (*m*, H–C(2)); 1.72 (*m*, H–C(2)); 1.99 (*m*, H_{ax}–C(6)); 2.01 (*s*, *Me*CO); 2.23 (*m*, H_{eq}–C(1)); 2.51 (*dd*, J = 14.3, 2.5, H_{ax}–C(5)); 2.75 (*sept.*, J = 7.0, H–C(15)); 3.56 (*s*, COOMe); 5.83 (*m*, H_{eq}–C(7)); 6.98 (*s*, H–C(14)); 7.10 (*d*, J = 8.2, H–C(12)); 7.16 (*d*, J = 8.2, H–C(11)). ^{13}C-NMR ($CDCl_3$): 16.3 (*q*, C(19)); 18.4 (*t*, C(2)); 21.4 (*q*, *Me*CO); 23.7 (*q*, C(16) or C(17)); 23.9 (*q*, C(17) or C(16)); 24.2 (*q*, C(20)); 28.1 (*t*, C(6)); 33.4 (*d*, C(15)); 36.2 (*t*, C(3)); 37.2 (*s*, C(10)); 37.4 (*t*, C(1)); 40.2 (*d*, C(5)); 47.1 (*s*, C(4)); 51.7 (*q*, COO*Me*); 70.7 (*d*, C(7)); 124.3 (*d*, C(11)); 127.1 (*d*, C(12)); 128.2 (*d*, C(14)); 131.7 (*s*, C(8)); 146.5 (*s*, C(13)); 147.5 (*s*, C(9)); 170.6 (*s*, *Me*CO); 178.3 (*s*, C(18)). EI-MS: 372 (21, M^+), 330 (36), 312 (66), 297 (8), 287 (14), 270 (43), 253 (29), 237 (100), 195 (28), 43 (22). Anal. calc. for $C_{23}H_{32}O_4$ (372.5): C 74.10, H 8.66; found: C 74.35, H 8.62.

(4aS,10aS)-1,2,3,4,4a,10a-Hexahydro-1,1,4a-trimethyl-7-(1-methylethyl)phenanthrene (**9**). A soln. of 29.7 g (93 mmol) of **7** and 20 ml of 10% HCl soln. in 200 ml of EtOH was heated under reflux for 3 h. Then 400 ml of H_2O

were added, and the mixture was extracted with Et_2O. The Et_2O phases were washed with $NaHCO_3$ soln. and 1M urea. Evaporation and CC (silica gel, cyclohexane/AcOEt 14:1) gave 22.8 g (92%) of **9**. Colorless oil. R_f 0.7 (cyclohexane/AcOEt 14:1). $[\alpha]_D = -124.5$ ($c = 1.5$, $CHCl_3$, 18°). UV (MeOH): 226 (3.99), 264 (3.89). IR (neat): 3034*m*, 2954*vs*, 2866*vs*, 1487*m*, 1459*s*, 1390*s*, 1371*s*, 1084*m*, 889*m*, 823*s*. ^{1}H-NMR ($CDCl_3$): 0.97 (*s*, Me–C(4)); 1.05 (*s*, Me–C(10)); 1.06 (*s*, Me–C(4)); 1.22 (*m*, H_{ax}–C(3)); 1.24 (*d*, $J = 6.9$, Me–C(15)); 1.25 (*d*, $J = 6.9$, Me–C(15)); 1.54 (*m*, H_{eq}–C(3)); 1.62 (*m*, H_{ax}–C(1)); 1.69 (*m*, H_{eq}–C(2)); 1.80 (*m*, H_{ax}–C(2)); 2.12 (*m*, H_{ax}–C(5)); 2.18 (*m*, H_{eq}–C(1)); 2.85 (*sept.*, $J = 6.9$, H–C(15)); 6.00 (*dd*, $J = 9.6$, 2.6, H–C(6)); 6.53 (*dd*, $J = 9.6$, 3.1, H–C(7)); 6.91 (*s*, H–C(14)); 7.07 (*dd*, $J = 7.9$, 1.5, H–C(12)); 7.12 (*d*, $J = 7.9$, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.1 (*t*, C(2)); 20.4 (*q*, C(20)); 22.6 (*q*, C(19)); 23.9 (*q*, C(16), C(17)); 32.6 (*q*, C(18)); 32.9 (*s*, C(4)); 33.6 (*d*, C(15)); 36.1 (*t*, C(1)); 37.7 (*s*, C(10)); 41.2 (*t*, C(3)); 51.3 (*d*, C(5)); 121.8 (*d*, C(11)); 124.5 (*d*, C(14)); 125.6 (*s*, C(12)); 127.9 (*d*, C(7)); 130.2 (*d*, C(6)); 132.8 (*s*, C(8)); 145.9 (*s*, C(9)); 146.1 (*s*, C(13)). EI-MS: 268 (100, M^+), 253 (46), 225 (17), 211 (31), 197 (69), 183 (73), 169 (42), 141 (53), 41 (24). Anal. calc. for $C_{20}H_{28}$ (268.4): C 89.49, H 10.51; found: C 89.38, H 10.62.

*Methyl (1*R*,4a*S*,9*R*,10a*R*)-1,2,3,4,4a,9,10,10a-Octahydro-9-methoxy-1,4a-dimethyl-7-(1-methylethyl)phenanthrene-1-carboxylate* (**10**) *and Methyl (1*R*,4a*S*,10a*R*)-1,2,3,4,4a,10a-Hexahydro-1,4a-dimethyl-7-(1-methylethyl)phenanthrene-1-carboxylate* (**11**). To a soln. of 15.0 g (40 mmol) of **8** in 150 ml of MeOH, 10 ml of 10% HCl soln. was added, and the mixture was heated 3 h under reflux. After dilution with H_2O (200 ml), extraction with Et_2O, neutralization of the combined Et_2O phases with $NaHCO_3$ and urea soln., and evaporation of the org. phase, an oily residue was obtained. CC (silica gel, cyclohexane/AcOH 9:1) gave 8.2 g (65%) of **11**, and 2.5 g (18%) of **10**.

10: Rhombic crystals. M.p. 96–98° (MeOH). R_f 0.19 (cyclohexane/AcOEt 9:1). $[\alpha]_D = +15.5$ ($c = 0.5$, $CHCl_3$, 18°). UV (MeOH): 202 (3.49), 223 (3.50), 257 (2.87). IR (KBr): 3048*m*, 3007*s*, 2985*s*, 2944*vs*, 1724*vs*, 1679*m*, 1494*s*, 1459*vs*, 1249*vs*, 846*m*, 629*m*. ^{1}H-NMR ($CDCl_3$): 1.10 (*s*, Me–C(10)); 1.17 (*d*, $J = 7.0$, 2Me–C(15)); 1.22 (*s*, Me–C(4)); 1.52 (*m*, H_{ax}–C(3)); 1.62 (*m*, H–C(2)); 1.64 (*m*, H–C(2)); 1.65 (*m*, H_{ax}–C(1)); 1.70 (*m*, H–C(6)); 1.72 (*m*, H–C(6)); 1.74 (*m*, H_{eq}–C(3)); 2.20 (*m*, H_{eq}–C(1)); 2.43 (*dd*, $J = 11.4$, 2.2, H_{ax}–C(5)); 2.78 (*sept.*, $J = 7.0$, H–C(15)); 3.34 (*s*, MeO); 3.63 (*s*, COOMe); 4.18 (*m*, H_{eq}–C(7)); 7.05 (*s*, H–C(14)); 7.07 (*m*, H–C(12)); 7.11 (*m*, H–C(11)). ^{13}C-NMR ($CDCl_3$): 16.6 (*q*, C(19)); 18.5 (*t*, C(2)); 23.7 (*q*, C(16) or C(17)); 23.9 (*q*, C(17) or C(16)); 24.2 (*q*, C(20)); 24.9 (*t*, C(6)); 33.4 (*d*, C(15)); 35.8 (*t*, C(3)); 37.3 (*s*, C(10)); 37.6 (*t*, C(1)); 39.8 (*d*, C(5)); 47.4 (*s*, C(4)); 51.8 (*q*, COO*Me*); 56.1 (*q*, MeO); 76.8 (*d*, C(7)); 123.9 (*d*, C(11)); 126.4 (*d*, C(12)); 128.5 (*d*, C(14)); 133.9 (*s*, C(8)); 146.0 (*s*, C(13)); 146.8 (*s*, C(9)); 178.7 (*s*, C(18)). EI-MS: 344 (22, M^+), 313 (16), 312 (24), 301 (18), 253 (28), 237 (100), 195 (22), 176 (39), 155 (13), 133 (14), 43 (17). Anal. calc. for $C_{22}H_{32}O_3$ (344.5): C 76.71, H 9.36; found: C 76.78, H 9.31.

11: Colorless oil. R_f 0.44 (cyclohexane/AcOEt 9:1). $[\alpha]_D = -20.1$ ($c = 0.3$, $CHCl_3$, 18°). UV (MeOH): 220 (3.97), 263 (3.52). IR (neat): 2953*vs*, 2868*s*, 1728*vs*, 1606*w*, 1459*m*, 1248*s*, 1225*m*, 1127*m*, 824*w*. ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, Me–C(10)); 1.17 (*d*, $J = 7.0$, 2Me–C(15)); 1.22 (*s*, Me–C(4)); 1.58 (*m*, H_{ax}–C(3)); 1.61 (*m*, H_{ax}–C(1)); 1.68 (*m*, H–C(2)); 1.69 (*m*, H–C(2)); 1.76 (*m*, H_{eq}–C(3)); 2.12 (*m*, H_{eq}–C(1)); 2.78 (*sept.*, $J = 7.0$, H–C(15)); 2.85 (*m*, H_{ax}–C(5)); 3.56 (*s*, COOMe); 5.64 (*dd*, $J = 9.6$, 2.6, H–C(6)); 6.43 (*dd*, $J = 9.6$, 3.0, H–C(7)); 6.82 (*s*, H–C(14)); 6.98 (*s*, H–C(11), H–C(12)). ^{13}C-NMR ($CDCl_3$): 17.9 (*q*, C(19)); 18.4 (*t*, C(2)); 20.8 (*q*, C(20)); 24.8 (*q*, C(16), C(17)); 33.6 (*d*, C(15)); 35.3 (*t*, C(1)); 35.6 (*t*, C(3)); 37.1 (*s*, C(10)); 46.4 (*s*, C(4)); 46.6 (*d*, C(5)); 52.0 (*q*, COO*Me*); 121.6 (*d*, C(11)); 124.6 (*d*, C(14)); 125.7 (*d*, C(12)); 128.3 (*d*, C(7)); 129.8 (*d*, C(6)); 132.6 (*s*, C(8)); 145.1 (*s*, C(9)); 146.3 (*s*, C(13)); 178.5 (*s*, C(18)). EI-MS: 312 (79, M^+), 297 (9), 253 (12), 237 (100), 209 (11), 197 (53), 179 (12), 167 (17), 155 (17), 141 (18), 43 (16). Anal. calc. for $C_{21}H_{28}O_2$ (312.5): C 80.73, H 9.03; found: C 80.53, H 9.11.

*(4b*S*,8a*S*)-4b,6,7,8,8a,10-Hexahydro-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9(5*H*)-one* (**13**). To a soln. of 6.0 g (22 mmol) of **9** in 150 ml of dry CH_2Cl_2 cooled in an ice bath, 6.3 g (31 mmol) of dry *ca.* 85% 3-chloroperbenzoic acid were added slowly. After 1 h stirring at 0° and 5 h stirring at r.t. in the dark, 300 ml of Et_2O were added, and the mixture was washed 2 × with 60 ml of sat. KI soln., 2× with 2N $Na_2S_2O_3$, and with 100 ml of $NaHCO_3$ soln. The aq. phases were extracted with 100 ml of Et_2O and the combined org. solns. washed with brine, dried (Na_2SO_4), and evaporated: 6.0 g of colorless oil (**12**) which was used without further purification. The oil and 500 mg (2.7 mmol) of TsOH·H_2O were dissolved in 200 ml of benzene, stirred, and heated (80°) under Ar for 2 h. The dark mixture was then cooled to r.t., 300 ml of Et_2O were added, and the org. phase was washed with brine, $NaHCO_3$ soln., and H_2O. After evaporation, a brown residue was obtained which was purified by CC (silica gel, cyclohexane/toluene 1:1): 5.2 g (82%) of **13**. Colorless oil. R_f 0.25 (cyclohexane/toluene 1:1), 0.40 (cyclohexane/AcOEt 14:1). $[\alpha]_D = +186.1$ ($c = 0.8$, $CHCl_3$, 18°). UV (MeOH): 224 (3.40), 273 (3.22), 298 (2.80). IR (neat): 2956*vs*, 2929*vs*, 1745*m*, 1692*s*, 1611*w*, 1563*m*, 1462*m*, 823*m*, 611*w*. ^{1}H-NMR ($CDCl_3$): 1.03 (*s*, Me–C(4)); 1.08 (*s*, Me–C(10)); 1.17 (*m*, H_{ax}–C(3)); 1.18 (*d*, $J = 7.0$, 2 Me–C(15)); 1.20 (*s*, Me–C(4)); 1.38 (*m*, H_{eq}–C(3)); 1.55 (*m*, H_{ax}–C(1)); 1.63 (*m*, H–C(2)); 2.25 (*m*, H_{eq}–C(1)); 2.35 (*s*, H_{ax}–C(5)); 2.80 (*sept.*, $J = 7.0$, H–C(15)); 3.55 (*m*,

2 H–C(7)); 6.84 (*s*, H–C(14)); 7.04 (*d*, *J* = 8.1, H–C(12)); 7.18 (*d*, *J* = 8.1, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.7 (*t*, C(2)); 21.5 (*q*, C(19)); 23.9 (*q*, C(16) or C(17)); 24.0 (*q*, C(17) or C(16)); 24.6 (*q*, C(20)); 32.6 (*s*, C(4)); 33.0 (*q*, C(18)); 33.5 (*d*, C(15)); 38.6 (*t*, C(1)); 40.2 (*s*, C(10)); 42.9 (*t*, C(3)); 45.2 (*t*, C(7)); 62.6 (*d*, C(5)); 123.5 (*d*, C(12)); 124.9 (*d*, C(11)); 126.3 (*d*, C(14)); 132.2 (*s*, C(8)); 146.4 (*s*, C(9)); 146.9 (*s*, C(13)); 209.8 (*s*, C(6)). EI-MS: 284 (61, M^+), 269 (100), 251 (9), 241 (19), 227 (47), 213 (13), 199 (54), 157 (24), 69 (25), 55 (13), 41 (21). Anal. calc. for $C_{20}H_{28}O$ (284.4): C 84.45, H 9.92; found: C 84.51, H 9.90.

*(3a*R*,10b*S*,10c*R*)-2,3,3a,4,10b,10c-Hexahydro-3a,10b-dimethyl-8-(1-methylethyl)-1*H*-phenanthro[10,1-*bc*]-furan-4-one* (**14**). A soln. of 3.1 g (10 mmol) of **11** in abs. CH_2Cl_2 was oxidized as described before with 2.8 g (14 mmol) of dry *ca.* 85% 3-chloroperbenzoic acid (for 10 h): 2.9 g of colorless oil. The crude product and 1.9 g (10 mmol) of TsOH · H_2O in 100 ml of dry benzene were stirred for 48 h under Ar at r.t. After dilution with 20 ml of Et_2O, washing with brine, $NaHCO_3$ soln., and H_2O evaporation yielded an oil which was chromatographed (silica gel, cyclohexane/AcOEt 14:1): 1.88 g (64%) of **14**. Crystals. M.p. 111–113° (MeOH). R_f 0.39 (cyclohexane/AcOEt 9:1), 0.28 (cyclohexane/AcOEt 14:1). $[\alpha]_D$ = –78.2 (*c* = 0.4, $CHCl_3$, 20°). UV (MeOH): 230 (4.16), 269 (3.73), 292 (3.51). IR (KBr): 3069*w*, 2955*m*, 2869*w*, 1813*s*, 1729*vs*, 1692*s*, 1459*m*, 1295*m*, 1259*s*, 1195*m*, 1077*m*, 725*m*. ^{1}H-NMR ($CDCl_3$): 1.18 (*d*, *J* = 7.0, 2 Me–C(15)); 1.24 (*m*, H_{ax}–C(3)); 1.42 (*s*, Me–C(4)); 1.48 (*m*, H_{ax}–C(1)); 1.50 (*s*, Me–C(4)); 1.55 (*m*, H–C(2)); 1.62 (*m*, H_{eq}–C(3)); 1.70 (*m*, H–C(2)); 1.75 (*m*, H_{eq}–C(1)); 2.68 (*s*, H_{ax}–C(5)); 2.78 (*sept.*, *J* = 7.0, H–C(15)); 6.01 (*m*, H–C(7)); 6.81 (*s*, H–C(14)); 6.92 (*dd*, *J* = 8.2, 1.8, H–C(12)); 7.13 (*d*, *J* = 8.2, H–C(11)). ^{13}C-NMR ($CDCl_3$): 17.5 (*t*, C(2)); 21.5 (*q*, C(19)); 23.7 (*q*, C(16), C(17)); 23.9 (*q*, C(20)); 32.1 (*t*, C(1)); 33.4 (*d*, C(15)); 35.8 (*s*, C(10)); 36.8 (*t*, C(3)); 41.7 (*s*, C(4)); 48.8 (*d*, C(5)); 101.9 (*d*, C(7)); 124.1 (*d*, C(11)); 124.6 (*d*, C(12)); 125.1 (*d*, C(14)); 131.3 (*s*, C(8)); 138.3 (*s*, C(6)); 147.3 (*s*, C(9)); 150.1 (*s*, C(13)); 179.2 (*s*, C(18)). EI-MS: 296 (100, M^+), 268 (5), 253 (12), 240 (18), 225 (53), 211 (19), 197 (27), 183 (22), 155 (12), 41 (15). Anal. calc. for $C_{20}H_{24}O_2$ (296.4): C 81.04, H 8.16; found: C 81.09, H 8.15.

*Methyl (1*R*,4a*S*,10a*R*)-1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-10-oxophenanthrene-1-carboxylate* (**15**). At 50°, 200 mg (0.67 mmol) of **14** in 30 ml of MeOH and 5 ml of 2N H_2SO_4 were stirred during 5 h. Then 100 ml of H_2O were added. This mixture was extracted with Et_2O. The combined org. phase was washed with 2N H_2SO_4 and brine, dried (Na_2SO_4), and treated with an Et_2O soln. of diazomethane. Evaporation and CC (silica gel, cyclohexane/AcOEt 9:1) gave 188 mg (85%) of **15**. R_f 0.11 (cyclohexane/AcOEt 9:1), 0.35 (toluene/AcOEt 9:1). $[\alpha]_D$ = +113.9 (*c* = 0.3, $CHCl_3$, 20°; [45]: [α] = +100 (*c* = 0.16)). UV (MeOH): 202 (3.63), 220 (3.79), 275 (2.82). IR (neat): 2957*s*, 2934*vs*, 2827*m*, 1805*w*, 1774*w*, 1738*vs*, 1615*m*, 1462*s*, 1218*s*, 1143*m*, 825*m*. ^{1}H-NMR ($CDCl_3$): 1.03 (*s*, Me–C(10)); 1.08 (*m*, H_{ax}–C(3)); 1.14 (*d*, *J* = 6.9, 2 Me–C(15)); 1.19 (*s*, Me–C(4)); 1.29 (*m*, H_{ax}–C(1)); 1.48 (*m*, H_{eq}–C(2)); 1.98 (*m*, H_{ax}–C(2)); 2.01 (*m*, H_{eq}–C(3)); 2.10 (*s*, H_{ax}–C(5)); 2.44 (*m*, H_{eq}–C(1)); 2.84 (*sept.*, *J* = 6.9, H–C(15)); 2.90 (*s*, COOMe); 3.53 (*m*, 2 H–C(7)); 6.84 (*s*, H–C(14)); 7.00 (*dd*, *J* = 8.1, 1.8, H–C(12)); 7.14 (*d*, *J* = 8.1, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.3 (*t*, C(2)); 23.8 (*q*, C(16) or C(17)); 24.0 (*q*, C(17) or C(16)); 28.6 (*q*, C(19)); 32.0 (*q*, C(20)); 33.6 (*d*, C(15)); 35.5 (*t*, C(1)); 36.8 (*s*, C(10)); 38.3 (*t*, C(3)); 44.2 (*t*, C(7)); 45.1 (*s*, C(4)); 51.0 (*q*, COO*Me*); 64.4 (*d*, C(5)); 124.9 (*d*, C(12)); 125.0 (*d*, C(11)); 126.3 (*d*, C(14)); 134.2 (*s*, C(8)); 136.2 (*s*, C(9)); 147.0 (*s*, C(13)); 174.6 (*s*, C(18)); 210.6 (*s*, C(6)). EI-MS: 328 (41, M^+), 296 (100), 253 (18), 240 (13), 225 (20), 213 (20), 200 (16), 141 (12), 43 (18), 41 (17). Anal. calc. for $C_{21}H_{28}O_3$ (328.5): C 76.78, H 8.59; found: C 76.52, H 8.58.

*(4b*S*,8a*S*,9*R*)-4b,5,6,7,8,8a,9,10-Octahydro-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9-ol* (**16**) *and Its (4b*S*,8a*S*,9*S*)-Diastereoisomer*. To a cooled suspension of 1.7 g (45 mmol) of $LiAlH_4$ in 150 ml of dry THF, a soln. of 12.0 g (22 mmol) of **13** was added dropwise. The mixture was stirred at r.t. for 4 h, THF/H_2O 9:1 was slowly added, and the mixture concentrated. Then 200 ml of 2N H_2SO_4 were added and the mixture was 3 × extracted with 200 ml of Et_2O. Usual workup and CC (silica gel, cyclohexane/AcOEt 14:1) gave 10.6 g (87%) of **16** and 360 mg (3.0%) of the (9*S*)-diastereoisomer.

16: White crystals. M.p. 114° (MeOH; [14]: 100–101°). R_f 0.28 (cyclohexane/AcOEt 14:1), 0.42 (cyclohexane/AcOEt 9:1). $[\alpha]_D$ = +46.0 (*c* = 0.4, $CHCl_3$, 20°). UV (MeOH): 221 (3.56), 266 (2.79), 274 (2.80). ^{1}H-NMR ($CDCl_3$): 1.02 (*s*, Me–C(4)); 1.22 (*d J* = 7.0, 2 Me–C(15)); 1.23 (*m*, H_{ax}–C(3)); 1.28 (*s*, Me–C(10)); 1.39 (*m*, H_{ax}–C(1)); 1.41 (*s*, H_{ax}–C(5)); 1.49 (*m*, H_{eq}–C(3)); 1.56 (*s*, Me–C(10)); 1.60 (*m*, H_{eq}–C(2)); 1.82 (*m*, H_{ax}–C(2)); 2.18 (*m*, H_{eq}–C(1)); 2.82 (*sept.*, *J* = 7.0, H–C(15)); 2.88 (*dd*, *J* = 17.7, 1.8, H_{eq}–C(7)); 3.15 (*dd*, *J* = 17.7, 4.5, H_{ax}–C(7)); 4.61 (*m*, H_{eq}–C(6)); 6.79 (*s*, H–C(14)); 6.95 (*dd*, *J* = 8.1, 2.0, H–C(12)); 7.14 (*d*, *J* = 8.1, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.5 (*t*, C(2)); 23.6 (*q*, *Me*–C(4)); 23.7 (*q*, *Me*–C(15)); 23.8 (*q*, *Me*–C(15)); 26.9 (*q*, C(20)); 33.3 (*d*, C(15)); 33.6 (*q*, C(19)); 34.0 (*s*, C(4)); 37.2 (*s*, C(10)); 41.3 (*t*, C(7)); 42.0 (*t*, C(1)); 43.0 (*t*, C(3)); 53.1 (*d*, C(5)); 65.9 (*d*, C(6)); 124.4 (*d*, C(12)); 124.9 (*d*, C(11)); 127.3 (*d*, C(14)); 130.9 (*s*, C(8)); 145.6 (*s*, C(9)); 146.0 (*s*, C(13)). EI-MS: 286 (24, M^+), 271 (16), 253 (100), 211 (14), 197 (6), 183 (17), 159 (12), 141 (15), 69 (19), 41 (18). Anal. calc. for $C_{20}H_{30}O$ (286.5): C 83.86, H 10.56; found: C 84.06, H 10.60.

*(9*S*)-Diastereoisomer*: Colorless oil. R_f 0.18 (cyclohexane/AcOEt 14:1), 0.25 (cyclohexane/AcOEt 9:1). $[\alpha]_D$ = +27.8 (*c* = 0.3, $CHCl_3$, 20°). UV (MeOH): 223 (3.55), 263 (2.74), 274 (2.81). IR (neat): 3438*s*, 2957*vs*,

2926*vs*, 2868*s*, 1496*m*, 1461*m*, 1379*m*, 1298*m*, 1039*m*, 822*m*. ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, Me–C(4)); 1.04 (*s*, Me–C(4)); 1.10 (*s*, Me–C(10)); 1.17 (*d*, *J* = 7.0, 2 Me–C(15)); 1.21 (*m*, H_{ax}–C(3)); 1.38 (*m*, H_{ax}–C(1)); 1.45 (*d*, *J* = 14.5, H_{ax}–C(5)); 1.49 (*m*, H_{eq}–C(3)); 1.52 (*m*, H_{eq}–C(2)); 1.68 (*m*, H_{ax}–C(2)); 2.10 (*m*, H_{eq}–C(1)); 2.68 (*dd*, *J* = 17.6, 2.8, H_{eq}–C(7)); 2.77 (*sept.*, *J* = 7.0, H–C(15)); 6.95 (*dd*, *J* = 17.6, 7.1, H_{ax}–C(7)); 4.25 (*m*, H_{ax}–C(6)); 6.89 (*s*, H–C(14)); 6.95 (*dd*, *J* = 8.2, 2.0, H–C(12)); 7.05 (*d*, *J* = 8.2, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.0 (*t*, C(2)); 22.4 (*q*, C(19)); 24.0 (*q*, C(16), C(17)); 29.2 (*q*, C(20)); 33.5 (*d*, C(15)); 34.1 (*s*, C(4)); 34.7 (*q*, C(18)); 38.1 (*s*, C(10)); 39.0 (*t*, C(7)); 39.9 (*t*, C(1)); 42.8 (*t*, C(3)); 58.8 (*d*, C(5)); 68.5 (*d*, C(6)); 122.2 (*d*, C(11)); 124.4 (*d*, C(12)); 126.9 (*d*, C(14)); 133.6 (*s*, C(8)); 146.1 (*s*, C(9)); 147.2 (*s*, C(13)). EI-MS: 286 (17, M^+), 271 (100), 253 (98), 211 (12), 183 (58), 169 (21), 155 (25), 141 (48), 69 (56), 41 (67). Anal. calc. for $C_{20}H_{30}O$ (286.5): C 83.86, H 10.56; found: C 84.24, H 10.56.

*(4b*S*,8a*S*,9*R*)-4b,5,6,7,8,8a,9,10-Octahydro-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9-yl Nitrite* (**17**). Nitrosyl chloride was introduced in an O_2-free soln. of 3.5 g (12 mmol) of **16** in 60 ml of dry pyridine at −30° until a persistent brown color was observed. Immediately, 30 g of ice were added, and the mixture was allowed to reach r.t. and poured on 100 g of ice. The precipitate was filtered off and dried in the dark: 3.8 g (97%) of **17** which were used without further purification. A sample (50 mg) was purified by prep. TLC (*Chromatotron*, cyclohexane/AcOEt 9:1). M.p. 94°. R_f 0.56 (cyclohexane/AcOEt 9:1), 0.41 (cyclohexane/AcOEt 14:1). $[\alpha]_D$ = −33.9 (*c* = 0.3, $CHCl_3$, 25°). UV (MeOH): 222 (3.68), 358 (1.93). IR (KBr): 3017*w*, 2959*m*, 2934*m*, 2889*w*, 1633*vs*, 1381*w*, 1367*w*, 829*w*, 798*w*, 775*m*, 759*m*, 621*m*. ^{1}H-NMR ($CDCl_3$): 1.29 (*s*, Me–C(4)); 1.38 (*s*, Me–C(4)); 1.51 (*d*, *J* = 7.0, 2 Me–C(15)); 1.57 (*m*, H_{ax}–C(3)); 1.70 (*s*, Me–C(10)); 1.73 (*m*, H_{ax}–C(1)); 1.79 (*m*, H_{eq}–C(3)); 1.92 (*m*, H_{eq}–C(2)); 2.03 (*s*, H_{ax}–C(5)); 2.08 (*m*, H_{ax}–C(2)); 2.48 (*m*, H_{eq}–C(1)); 3.03 (*sept.*, *J* = 7.0, H–C(15)); 3.21 (*d*, *J* = 17.7, H_{eq}–C(7)); 3.62 (*dd*, *J* = 17.7, 5.6, H_{ax}–C(7)); 6.81 (*m*, H_{eq}–C(6)); 6.78 (*s*, H–C(14)); 6.96 (*dd*, *J* = 8.2, 1.8, H–C(12)); 7.16 (*d*, *J* = 8.2, H–C(11)). ^{13}C-NMR ($CDCl_3$): 19.5 (*t*, C(2)); 23.2 (*q*, C(19)); 24.0 (*q*, C(16), C(17)); 26.9 (*q*, C(20)); 33.4 (*q*, C(18)); 33.5 (*d*, C(15)); 34.2 (*s*, C(4)); 37.6 (*s*, C(10)); 38.7 (*d*, C(7)); 41.7 (*t*, C(1)); 43.4 (*t*, C(3)); 53.7 (*d*, C(5)); 73.7 (*d*, C(6)); 124.8 (*d*, C(12)); 125.1 (*d*, C(11)); 126.9 (*d*, C(14)); 130.2 (*s*, C(8)); 145.9 (*s*, C(9)); 146.0 (*s*, C(13)). EI-MS: 315 (51, M^+), 270 (46), 255 (20), 253 (42), 197 (18), 183 (21), 161 (100), 155 (22), 145 (22), 129 (30), 69 (42), 43 (55), 41 (45). Anal. calc. for $C_{20}H_{29}NO_2$ (315.5): C 76.15, H 9.27, N 4.44; found: C 76.48, H 9.26, N 4.57.

(^{15}N)Nitrite (^{15}N)-**17**. Into a soln. of 400 mg (1.4 mmol) of **16** in 10 ml of AcOH at 50°, 280 mg (3.3 mmol) of $K^{15}NO_3$ were added during 1 min. The mixture was stirred for 40 s, poured in 100 ml of ice water, and extracted twice with 50 ml of Et_2O. The combined Et_2O phase was washed with $NaHCO_3$ soln. and brine, dried (Na_2SO_4), and evaporated, and the residue purified by prep. TLC (*Chromatotron*, cyclohexane/AcOEt 9:1): 332 mg (75%) of (^{15}N)-**17**. Data identical with data of **17**, except for the following: $[\alpha]_D$ = −33.9 (*c* = 0.3, $CHCl_3$, 20°). ^{15}N-NMR ($CDCl_3$, *c* = 0.09M): −28.8 (*s*, 1, ^{15}N). EI-MS: 316 (74, M^+), 271 (13), 270 (50), 255 (29), 253 (19), 197 (17), 189 (36), 183 (17), 161 (100), 155 (20), 129 (30), 69 (33), 43 (50), 41 (36). Anal. calc. for $C_{20}H_{29}{}^{15}NO_2$ (97.4 atom-% ^{15}N; 316.5): C 75.91, H 9.24, ^{15}N 4.74; found: C 75.76, H 9.47, ^{15}N 4.77.

*(1*S*,4a*S*,10*R*,10a*R*)-1,2,3,4,4a,9,10,10a-Octahydro-10-hydroxy-1,4a-dimethyl-7-(1-methylethyl)phenanthren-1-carbaldehyde Oxime* (**18**), *4a,4'a-Azobis{methylenebis[(4a*R*,10*R*,10a*S*)-1,2,3,4,4a,9,10,10a-octahydro-10-hydroxy-1,1-dimethyl-7-(1-methylethyl)phenanthrene]} N,N'-Dioxide* (**17'**), *and N-[(4a*R*,10*R*,10a*S*,12*R*)-1,3,4,9,10,10a-Hexahydro-1,1-dimethyl-7-(1-methylethyl)-2*H*-10,4a-(epoxymethano)phenanthren-12-yl]hydroxylamine* (**19**). A soln. of 2.4 g (7.6 mmol) of **17** in 200 ml of abs. benzene was irradiated under Ar at 18° for 1 h with a 150-W high-pressure Hg lamp (*Solidex* glass filter). The solvent was evaporated and the remaining residue washed with 300 ml of i-PrOH and filtered: 1.58 g (65%) of **17'** (amorph, colorless). A suspension of 1.58 g of **17'** in 400 ml of i-PrOH was stirred under Ar at 80° for 16 h and then evaporated. The resulting oil was purified by CC (silica gel, toluene/AcOEt 1:1) yielding 1.50 g (62%) of **19**. The filtrate (i-PrOH soln.; see **17'**) was heated for 16 h to 80° and evaporated. CC (silica gel, cyclohexane/AcOEt 1:1) gave a polar and a nonpolar mixture. The polar was separated by further CC (silica gel, cyclohexane/AcOEt 9:1) and gave 340 mg (14%) of **18** and 80 mg (4%) of **19**. The nonpolar substances were separated by CC (cyclohexane/AcOEt 13:1) yielding 108 mg (5%) of ketone **13** and 211 mg (8%) alcohol **16**.

18: M.p. 211° (MeOH). R_f 0.31 (cyclohexane/AcOEt 1:1), 0.32 (toluene/AcOEt 9:1). $[\alpha]_D$ = +154.4 (*c* = 0.4, $CHCl_3$, 18°). UV (MeOH): 221 (3.57), 271 (2.82). IR (KBr): 3216*m*, 3129*s*, 2955*s*, 2925*vs*, 2867*s*, 2894*m*, 1499*m*, 1462*m*, 1432*m*, 1380*w*, 984*m*, 864*s*, 825*s*. ^{1}H-NMR ($CDCl_3$): 1.15 (*d*, *J* = 6.9, 2 Me–C(15)); 1.17 (*s*, Me–C(4)); 1.19 (*m*, H_{ax}–C(3)); 1.23 (*s*, Me–C(10)); 1.33 (*m*, H_{ax}–C(1)); 1.55 (*m*, H–C(2)); 1.56 (*m*, H–C(2)); 1.57 (*s*, H_{ax}–C(5)); 1.79 (*m*, H_{eq}–C(3)); 2.08 (*m*, H_{eq}–C(1)); 2.75 (*sept.*, *J* = 6.9, H–C(15)); 2.92 (*d*, *J* = 17.2, H_{eq}–C(7)); 3.04 (*dd*, *J* = 17.2, 4.8, H_{ax}–C(7)); 4.71 (*m*, H_{eq}–C(6)); 6.45 (*s*, OH); 6.82 (*s*, H–C(14)); 6.93 (*dd*, *J* = 8.2, 1.8, H–C(12)); 7.09 (*d*, *J* = 8.2, H–C(11)); 7.37 (*s*, H–C(19)); 10.44 (*s*, NOH). ^{13}C-NMR ($CDCl_3$): 20.0 (*t*, C(2)); 23.7 (*q*, C(16), C(17)); 27.4 (*q*, C(20)); 30.0 (*q*, C(18)); 33.2 (*d*, C(15)); 37.1 (*s*, C(10)); 38.9 (*t*, C(7)); 39.8 (*s*, C(4)); 41.7 (*t*, C(1)); 41.8 (*t*, C(3)); 53.6 (*d*, C(5)); 64.1 (*d*, C(6)); 124.2 (*d*, C(12)); 125.0 (*d*, C(11)); 127.1 (*d*, C(14)); 130.9 (*s*, C(8)); 143.9 (*s*, C(9)); 145.6 (*s*, C(13)); 157.4 (*d*, C(19)). EI-MS: 315 (10, M^+), 280 (13), 266 (25), 265 (100), 254 (11),

239 (23), 223 (7), 195 (15), 43 (19), 41 (14). Anal. calc. for $C_{20}H_{29}NO_2$ (315.5): C 76.15, H 9.27, N 4.44; found: C 76.12, H 9.28, N 4.48.

17′: M.p. 233° (dec.). UV ($BaSO_4$): 221 (0.74), 275 (0.76). IR (KBr): 3335*s*, 3078*m*, 2961*vs*, 2926*vs*, 2871*s*, 1613*w*, 1570*w*, 1499*m*, 1460*s*, 1391*s*, 1226*m*, 1059*m*, 1044*m*, 860*w*, 834*w*, 700*m*. ^{1}H-NMR ($CDCl_3$/0.1% CF_3COOD): 0.69 (*s*, Me–C(4)); 0.90 (*s*, Me–C(4)); 1.04 (*m*, H_{ax}–C(1)); 1.05 (*m*, H_{ax}–C(3)); 1.11 (*d*, *J* = 6.9, Me–C(15)); 1.12 (*d*, *J* = 6.9, Me–C(15)); 1.35 (*m*, H_{eq}–C(3)); 1.40 (*s*, H_{ax}–C(5)); 1.52 (*m*, H_{eq}–C(2)); 1.70 (*m*, H_{ax}–C(2)); 2.73 (*sept.*, H–C(15)); 2.80 (*m*, H_{eq}–C(1)); 2.87 (*d*, *J* = 18.2, H_{eq}–C(7)); 3.10 (*dd*, *J* = 18.2, 5.0, H_{ax}–C(7)); 3.59 (*d*, *J* = 14.2, H–C(20)); 4.42 (*d*, *J* = 14.2, H–C(20)); 4.65 (*m*, H_{eq}–C(6)); 6.76 (*d*, *J* = 8.2, H–C(11)); 6.85 (*s*, H–C(14)); 6.97 (*d*, *J* = 8.2, H–C(12)); 8.27 (*s*, OH). ^{13}C-NMR ($CDCl_3$/0.1% CF_3COOD): 18.6 (*t*, C(2)); 23.6 (*q*, C(16) or C(17)); 23.7 (*q*, C(17) or C(16)); 24.5 (*q*, C(19)); 33.4 (*q*, C(18)); 33.5 (*d*, C(15)); 33.9 (*s*, C(4)); 36.3 (*t*, C(1)); 39.5 (*t*, C(7)); 42.2 (*s*, C(10)); 42.6 (*t*, C(3)); 54.7 (*d*, C(5)); 62.7 (*t*, C(20)); 66.1 (*d*, C(6)); 125.2 (*d*, C(12)); 126.5 (*d*, C(11)); 127.6 (*d*, C(14)); 131.2 (*s*, C(8)); 136.9 (*s*, C(9)); 148.8 (*s*, C(13)). FD-MS (susp. in CH_2Cl_2): 631 (M^+), 597, 315, 297, 285, 271, 254. Anal. calc. for $C_{40}H_{58}N_2O_4$ (631.0): C 76.14, H 9.26, N 4.44; found: C 76.12, H 9.13, N 4.54.

19: R_f 0.31 (cyclohexane/AcOEt 1:1), 0.25 (toluene/AcOEt 9:1). $[\alpha]_D = -221.3$ (*c* = 0.8, $CHCl_3$, 20°). UV (MeOH): 216 (3.30), 237 (3.40), 266 (3.10), 293 (3.03). IR (neat): 3350*s*, 2956*vs*, 2868*vs*, 1612*w*, 1496*m*, 1461*m*, 1425*m*, 1074*s*, 945*m*, 824*s*, 678*w*, 652*w*, 613*w*. ^{1}H-NMR ($CDCl_3$): 0.89 (*s*, Me–C(4)); 1.05 (*s*, Me–C(4)); 1.09 (*m*, H_{ax}–C(3)); 1.14 (*d*, *J* = 6.9, 2 Me–C(15)); 1.45 (*m*, H_{eq}–C(3)); 1.58 (*m*, H_{ax}–C(1)); 1.61 (*m*, H_{eq}–C(2)); 1.64 (*m*, H_{ax}–C(2)); 1.65 (*s*, H_{ax}–C(5)); 2.27 (*m*, H_{eq}–C(1)); 2.75 (*sept.*, *J* = 6.9, H–C(15)); 2.92 (*dd*, *J* = 17.2, 2.3, H_{ax}–C(7)); 3.06 (*dd*, *J* = 17.2, 2.2, H_{eq}–C(7)); 4.18 (*d*, *J* = 9.4, NH); 4.41 (*m*, H_{eq}–C(6)); 5.03 (*d*, *J* = 9.4, H–C(20)); 5.61 (*s*, OH); 6.88 (*s*, H–C(14)); 6.91 (*dd*, *J* = 8.1, 1.6, H–C(12)); 6.94 (*d*, *J* = 8.1, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.6 (*t*, C(2)); 23.0 (*q*, C(19)); 23.8 (*q*, C(16) or C(17)); 23.9 (*q*, C(17) or C(16)); 27.7 (*t*, C(1)); 31.2 (*s*, C(4)); 33.3 (*q*, C(18)); 33.6 (*d*, C(15)); 40.0 (*t*, C(3)); 40.8 (*t*, C(7)); 46.0 (*s*, C(10)); 56.5 (*d*, C(5)); 75.9 (*s*, C(6)); 98.1 (*d*, C(20)); 123.9 (*d*, C(11)); 124.8 (*d*, C(12)); 127.5 (*d*, C(14)); 133.7 (s, C(8)); 139.9 (*s*, C(9)); 147.8 (*s*, C(13)). EI-MS: 297 (10), 283 (7), 255 (13), 254 (51), 240 (22), 239 (100), 211 (10), 183 (21), 155 (17), 141 (24), 43 (24). FD-MS: 315 (M^+), 297, 283, 270, 254. Anal. calc. for $C_{20}H_{29}NO_2$ (315.5): C 76.15, H 9.27, N 4.44; found: C 75.93, H 9.13, N 4.56.

(15N)Oxime (15N)-**18**, *(15N2)Azobis(methylene)bis(phenanthrene) Dioxide (15N2)*-**17′**, *and (15N)Hydroxylamine (15N)*-**19**. As described before, except that (^{15}N)-**17** was used. Data identical to those of **18**, **17′**, and **19**, except for the MS and microanalyses.

(15N)-**18**: EI-MS: 316 (15, M^+), 283 (21), 280 (14), 265 (24), 264 (100), 255 (13), 239 (53), 233 (7), 195 (14), 43 (20). Anal. calc. for $C_{20}H_{29}{}^{15}NO_2$ (316.5; 97.4 atom-% ^{15}N): C 75.91, H 9.24, ^{15}N 4.74; found: C 75.62, H 9.27, ^{15}N 4.82.

(15N2)-**17′**: FD-MS ($CHCl_3$/2% CF_3COOH): 633, 598, 339, 317, 298, 271, 267, 254. Anal. calc. for $C_{40}H_{58}{}^{15}N_2O_4$ (633.0; 97.4 atom-% ^{15}N): C 75.90, H 9.24, ^{15}N 4.71; found: C 75.47, H 9.44, ^{15}N 4.98.

(15N)-**19**: FD-MS: 316 (M^+), 298, 283. Anal. calc. for $C_{20}H_{29}{}^{15}NO_2$ (316.5; 97.4 atom-% ^{15}N): C 75.91, H 9.24, ^{15}N 4.74; found: C 75.32, H 9.26, ^{15}N 4.82.

O-*Acetyl*-N-*[(4aR,10R,10aS,12R)-1,3,4,9,10,10a-hexahydro-1,1-dimethyl-7-(1-methylethyl)-2H-10,4a-(epoxymethano)phenanthren-12-yl]hydroxylamine* (**20**). Within 20 min, 5 ml of Ac_2O were dropwise added to a soln. of 100 mg (0.32 mmol) of **19** in abs. pyridine. After stirring at r.t. for 12 h, 100 g of ice were added, and the mixture was extracted 3 × with 50 ml of Et_2O. The combined Et_2O phase was washed with $NaHCO_3$ soln. and brine, dried ($NaSO_4$), and evaporated. CC (silica gel, toluene/AcOEt 9:1) yielded 41 mg (36%) of **20**. White crystals. M.p. 115–116° (MeOH). R_f 0.20 (toluene/AcOEt 9:1). $[\alpha]_D = -64.7$ (*c* = 0.2, $CHCl_3$, 20°). UV (MeOH): 219 (3.74), 265 (2.63), 273 (2.60). IR (KBr): 3473*w*, 3236*m*, 2956*vs*, 1746*s*, 1429*s*, 1369*s*, 1234*vs*, 1107*m*, 823*s*, 794*m*, 756*s*, 612*m*. ^{1}H-NMR ($CDCl_3$): 0.95 (*s*, Me–C(4)); 1.10 (*s*, Me–C(4)); 1.18 (*m*, H_{ax}–C(3)); 1.22 (*d*, *J* = 6.9, 2 Me–C(15)); 1.52 (*m*, H_{eq}–C(3)); 1.70 (*m*, H_{ax}–C(1)); 1.71 (*m*, H–C(2)); 1.73 (*m*, H–C(2)); 1.74 (*s*, H_{ax}–C(5)); 1.98 (*s*, Ac); 2.44 (*m*, H_{eq}–C(1)); 2.85 (*sept.*, *J* = 6.9, H–C(15)); 3.00 (*dd*, *J* = 17.1, 2.3, H_{ax}–C(7)); 3.13 (*dd*, *J* = 17.1, 1.7, H_{eq}–C(7)); 4.45 (*m*, H_{eq}–C(6)); 5.18 (*d*, *J* = 10.8, H–C(20)); 6.98 (*s*, H–C(14)); 7.03 (*dd*, *J* = 8.1, 1.3, H–C(12)); 7.10 (*d*, *J* = 8.1, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.5 (*t*, C(2)); 19.2 (*q*, *Me*CO); 23.0 (*q*, C(19)); 23.8 (*q*, C(16) or C(17)); 23.9 (*q*, C(17) or C(16)); 27.6 (*t*, C(1)); 31.2 (*s*, C(4)); 33.2 (*q*, C(18)); 33.6 (*d*, C(15)); 39.5 (*t*, C(3)); 40.4 (*t*, C(7)); 46.3 (*s*, C(5)); 56.3 (*d*, C(5)); 76.4 (*d*, C(6)); 95.3 (*d*, C(20)); 124.0 (*d*, C(12)); 125.0 (*d*, C(11)); 127.4 (*d*, C(14)); 133.5 (*s*, C(8)); 139.2 (*s*, C(9)); 147.9 (*s*, C(13)); 170.0 (*s*, *Me*CO). EI-MS: 357 (4, M^+), 297 (3), 255 (17), 254 (79), 240 (21), 239 (100), 183 (12), 141 (16), 69 (8), 55 (79), 41 (11). Anal. calc. for $C_{22}H_{31}NO_3$ (357.5): C 73.92, H 8.74, N 3.78; found: C 73.24, H 8.92, N 3.78.

Crystallographic Data of **20**: space group hexagonal, $P6_5$; unit cell dimensions: $a = b = 18.315$ Å, $c = 11.911$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 3535.4$ Å^3; measured reflections 2215, used reflections 1040; $R = 0.099$, $R_w = 0.103$.

Bond length ([Å] (standard deviation)): C(1)–C(2) 1.500(18), C(1)–C(10) 1.522(16), C(2)–C(3) 1.561(19), C(3)–C(4) 1.549(18), C(4)–C(19) 1.530(18), C(4)–C(18) 1.590(20), C(4)–C(5) 1.511 (17), C(5)–C(10) 1.532(16), C(5)–C(6) 1.562(17), C(6)–O(1) 1.472(15), C(6)–C(7) 1.556(17), C(7)–C(8) 1.512(17), C(8)–C(9) 1.404(17), C(8)–C(14) 1.425(18), C(9)–C(10) 1.533(16), C(9)–C(11) 1.421(17), C(10)–C(20) 1.475(16), C(11)–C(12) 1.393(18), C(12)–C(13) 1.414(19), C(13)–C(14) 1.362(18), C(13)–C(15) 1.493(20), C(15)–C(16) 1.475(26), C(15)–C(17) 1.498(24), C(20)–O(1) 1.363(14), C(20)–N 1.237(16), N–O(2) 1.455(12), C(21)–O(2) 1.349(13), C(21)–O(3) 1.196(17), C(21)–C(22) 1.441(18). Some bond angles ([°] (standard deviation)): C(2)–C(1)–C(10) 112.4(8), C(1)–C(2)–C(3) 110.6(10), C(2)–C(3)–C(4) 110.5(9), C(3)–C(4)–C(18) 108.8(10), C(3)–C(4)–C(19) 109.6(10), C(3)–C(4)–C(5) 109.8(8), C(19)–C(4)–C(18) 105.8(9), C(19)–C(4)–C(5) 115.7(10), C(18)–C(4)–C(5) 106.8(10), C(4)–C(5)–C(10) 116.9(9), C(4)–C(5)–C(6) 115.3(8), C(10)–C(5)–C(6) 98.2(8), C(5)–C(6)–C(7) 111.0(8), C(5)–C(10)–C(1) 114.4(9), C(5)–C(6)–O(1) 102.6(8), O(1)–C(6)–C(7) 108.8(8), C(6)–O(1)–C(20) 108.0(7), C(6)–C(7)–C(8) 110.4(8), C(7)–C(8)–C(9) 121.3(10), C(7)–C(8)–C(14) 118.4(9), C(9)–C(8)–C(14) 120.3(9), C(8)–C(9)–C(10) 120.4(9), C(8)–C(9)–C(11) 117.4(10), C(10)–C(9)–C(11) 122.0(9), C(9)–C(10)–C(20) 104.3(8), C(9)–C(11)–C(12) 121.4(10), C(11)–C(12)–C(13) 120.1(10), C(9)–C(10)–C(5) 108.6(8), C(12)–C(13)–C(14) 119.2(10), C(12)–C(13)–C(15) 121.5(10), C(13)–C(14)–C(8) 121.4(10), C(15)–C(16)–C(17) 116.2(13), C(13)–C(15)–C(16) 111.5(13), C(13)–C(15)–C(17) 113.3(13), C(14)–C(13)–C(15) 119.3(10), C(10)–C(20)–O(1) 110.7(8), C(1)–C(10)–C(9) 112.4(8), C(5)–C(10)–C(20) 100.8(7), C(10)–C(20)–N 125.0(9), C(20)–N–O(2) 109.7(8), C(21)–O(2)–N 114.4(6), C(22)–C(21)–O(2) 110.8(9), C(22)–C(21)–O(3) 126.1(11), C(20)–C(10)–C(1) 115.3(9).

(4aR,10R,10aS)-1,3,4,9,10,10a-Hexahydro-1,1-dimethyl-7-(1-methylethyl)-2H-10,4a-(epoxymethano)-phenanthren-12-one (**21**). To a cooled soln. of 1.9 g (5.1 mmol) of PDC in 4 ml of abs. DMF was added a soln. of 400 mg (1.27 mmol) of **19** during 1 min. After 10 min stirring at r.t., 50 ml of ice water were added. The mixture was extracted 3 × with 50 ml of Et_2O, the combined Et_2O phase washed with 2N H_2SO_4, $NaHCO_3$ soln. and brine and evaporated, and the residue purified by CC (silica gel): 285 mg (75%) of **21**. Colorless crystals. M.p. 124–125° (MeOH). R_f 0.56 (toluene/AcOEt 9:1). $[\alpha]_D = +46.2$ ($c = 0.7$, $CHCl_3$, 18°). UV (MeOH): 236 (3.50), 274 (2.74). IR (KBr): 2962*s*, 2929*s*, 2868*s*, 1767*vs*, 1593*m*, 1460*m*, 1000*m*, 885*m*, 793*w*, 731*w*. ^{1}H-NMR ($CDCl_3$): 0.95 (*s*, Me–C(4)); 0.99 (*s*, Me–C(4)); 1.18 (*m*, H_{ax}–C(3)); 1.20 (*d*, $J = 6.9$, 2 Me–C(15)); 1.46 (*m*, H_{eq}–C(3)); 1.63 (*m*, H–C(2)); 1.65 (*m*, H_{ax}–C(1)); 1.66 (*m*, H–C(2)); 1.91 (*s*, H_{ax}–C(5)); 2.73 (*m*, H_{eq}–C(1)); 2.83 (*sept.*, $J = 6.9$, H–C(15)); 3.11 (*dd*, $J = 17.5$, 1.8, H_{ax}–C(7)); 4.81 (*m*, H_{eq}–C(6)); 6.97 (*s*, H–C(14)); 7.06 (*dd*, $J = 8.2$, 1.8, H–C(12)); 7.17 (*d*, $J = 8.2$, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.4 (*t*, C(2)); 21.8 (*q*, C(19)); 23.7 (*q*, C(16), C(17)); 26.3 (*t*, C(1)); 31.1 (*s*, C(4)); 31.5 (*q*, C(18)); 33.5 (*d*, C(15)); 35.5 (*t*, C(7)); 38.4 (*t*, C(3)); 45.6 (*s*, C(10)); 53.7 (*d*, C(5)); 75.3 (*d*, C(6)); 124.0 (*d*, C(11)); 124.8 (*d*, C(12)); 127.4 (*d*, C(14)); 132.0 (*s*, C(8)); 137.2 (*s*, C(9)); 148.5 (*s*, C(13)); 177.9 (*s*, C(20)). EI-MS: 298 (23, M^+), 283 (7), 254 (53), 239 (100), 183 (18), 155 (26), 141 (31), 129 (13), 43 (17), 41 (16). Anal. calc. for $C_{20}H_{26}O_2$ (298.4): C 80.50, H 8.78; found: C 80.64, H 8.68.

Methyl (4aR,10aS)-1,3,4,10a-Tetrahydro-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2H)-carboxylate (**22**). To the colorless soln. of 560 mg (10.4 mmol) of LiSMe [27] [28] in 10 ml of HMPA (hexamethylphosphoric triamide; freshly distilled over CaH) under Ar, 620 mg (2.1 mmol) of **21** were added. The mixture was stirred for 5 h at 60°, then 70 ml of 2N H_2SO_4 were added. The mixture was extracted 3 × with 80 ml of Et_2O and the combined Et_2O phase washed with 2N H_2SO_4 and brine and combined with a diazomethane soln. Evaporation and purification by CC (silica gel, cyclohexane/AcOEt 9:1) gave 522 mg (80%) of **22**. Colorless crystals. M.p. 74–76°. R_f 0.44 (cyclohexane/AcOEt 9:1). $[\alpha]_D = +28.5$ ($c = 0.3$, $CHCl_3$, 20°). UV (MeOH): 217 (4.20), 235 (4.28), 275 (3.74). IR (KBr): 3044*w*, 3007*w*, 2955*s*, 2866*s*, 2807*w*, 1711*vs*, 1671*w*, 1291*s*, 1195*s*, 987*m*, 902*m*, 705*m*. ^{1}H-NMR ($CDCl_3$): 0.83 (*s*, Me–C(4)); 0.96 (*s*, Me–C(4)); 1.14 (*d*, $J = 6.9$, Me–C(15)); 1.15 (*d*, Me–C(15)); 1.20 (*m*, H_{ax}–C(3)); 1.37 (*m*, H_{ax}–C(1)); 1.42 (*m*, H_{eq}–C(3)); 1.62 (*m*, H_{eq}–C(2)); 1.65 (*m*, H_{ax}–C(2)); 2.44 (*m*, H_{ax}–C(1)); 2.76 (*sept.*, $J = 6.9$, H–C(15)); 2.93 (*m*, H_{eq}–C(1)); 3.39 (*s*, COOMe); 6.06 (*dd*, $J = 9.7$, 2.7, H–C(6)); 6.35 (*dd*, $J = 9.7$, 3.2, H–C(7)); 6.83 (*s*, H–C(14)); 6.93 (*dd*, $J = 8.1$, 1.9, H–C(12)); 7.15 (*d*, $J = 8.1$, H–C(11)). ^{13}C-NMR ($CDCl_3$): 20.2 (*t*, C(2)); 21.9 (*q*, C(19)); 23.7 (*q*, C(16) or C(17)); 23.8 (*q*, C(17) or C(16)); 31.5 (*q*, C(18)); 33.3 (*s*, C(4)); 33.5 (*d*, C(15)); 34.4 (*t*, C(1)); 41.1 (*t*, C(3)); 47.7 (*s*, C(10)); 50.9 (*d*, C(5)); 51.2 (*q*, COO*Me*); 124.6 (*d*, C(11)); 124.9 (*d*, C(14)); 125.2 (*d*, C(12)); 126.5 (*d*, C(7)); 129.5 (*d*, C(6)); 134.3 (*s*, C(8)); 136.4 (*s*, C(9)); 147.8 (*s*, C(13)); 174.4 (*s*, C(20)). EI-MS: 312 (37, M^+), 254 (22), 253 (100), 237 (14), 211 (52), 183 (95), 141 (62), 55 (15), 43 (18), 41 (16). Anal. calc. for $C_{21}H_{28}O_2$ (312.5): C 80.73, H 9.03; found: C 80.36, H 9.00.

Methyl (4aR,10aS)-1,3,4,9,10,10a-Hexahydro-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2H)-carboxylate (**23**). A soln. of 410 mg (1.31 mmol) of **22** in 100 ml of abs. EtOH and 60 mg of 5% Pd/C were hydrogenated for 12 h at r.t. in a *Parr* apparatus (420 kPa H_2 pressure). The catalyst was removed by filtration, 40 mg of PtO_2 were added, and hydrogenation was continued for 12 h. After filtration and evaporation, the residue was chromatographed (silica gel, toluene), yielding a colorless oil which crystallized slowly: 390 mg (94%) of **23**. M.p.

46–48° (MeOH/Et_2O). R_f 0.56 (toluene), 0.29 (cyclohexane/AcOEt 30:1). $[\alpha]_D$ = +186.5 (*c* = 0.3, $CHCl_3$, 20°). UV (MeOH): 213 (3.99), 236 (3.83), 275 (2.59). IR (KBr): 2958*vs*, 2870*s*, 2843*s*, 1721*vs*, 1693*w*, 1611*m*, 1217*s*, 1165*s*, 1131*s*, 986*m*, 983*m*, 790*m*. ^{1}H-NMR ($CDCl_3$): 0.71 (*s*, Me–C(4)); 0.89 (*s*, Me–C(4)); 1.14 (*d*, *J* = 6.9, 2 Me–C(15)); 1.15 (*m*, H_{ax}–C(1)); 1.16 (*m*, H_{ax}–C(3)); 1.38 (*m*, H_{eq}–C(3)); 1.43 (*dd*, *J* = 13.0, 3.1, H_{ax}–C(5)); 1.54 (*m*, H_{eq}–C(2)); 1.83 (*m*, H_{eq}–C(6)); 1.88 (*m*, H_{ax}–C(2)); 2.42 (*m*, H_{ax}–C(6)); 2.74 (*sept.*, *J* = 6.9, H–C(15)); 2.80 (*m*, H_{ax}–C(7)); 2.89 (*m*, H_{eq}–C(7)); 2.90 (*m*, H_{eq}–C(1)); 3.57 (*s*, COOMe); 6.86 (*s*, H–C(14)); 6.87 (*d*, *J* = 8.0, H–C(12)); 7.14 (*d*, *J* = 8.0, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.7 (*t*, C(6)); 20.2 (*q*, C(19)); 20.5 (*q*, C(19)); 20.5 (*t*, C(2)); 23.8 (*q*, C(16) or C(17)); 23.9 (*q*, C(17) or C(16)); 30.1 (*t*, C(7)); 32.1 (*q*, C(18)); 33.5 (*d*, C(15)); 33.9 (*s*, C(4)); 37.0 (*t*, C(1)); 42.0 (*t*, C(3)); 47.8 (*s*, C(10)); 51.4 (*q*, COOMe); 52.4 (*d*, C(5)); 123.8 (*d*, C(12)); 125.6 (*d*, C(11)); 127.5 (*d*, C(14)); 136.8 (*s*, C(8)); 138.1 (*s*, C(9)); 146.9 (*s*, C(13)); 176.0 (*s*, C(20)). EI-MS: 314 (16, M^+), 255 (100), 254 (15), 185 (19), 173 (28), 69 (25), 43 (18), 41 (16). Anal. calc. for $C_{21}H_{30}O_2$ (314.5): C 80.14, H 9.62; found: C 79.62, H 9.65.

*Methyl (4a*R*,10a*S*)-6-Acetyl-1,3,4,9,10,10a-hexahydro-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2*H*)-carboxylate* (**24**). To a soln. of 560 mg (1.78 mmol) of **23** and 0.38 ml (5.37 mmol) of AcCl in 20 ml of abs. CH_2Cl_2 at 0° were added 700 mg (5.25 mmol) of $AlCl_3$. The mixture was stirred at 0° for 0.5 h and at r.t. for 14 h. Then 100 ml of ice-cooled 2N H_2SO_4 were added. Extraction with 3 portions of 80 ml of Et_2O, usual workup and CC (silica gel, cyclohexane/AcOEt 9:1) yielded 542 mg (85%) of **24**. Colorless crystals. M.p. 113–114° (MeOH). R_f 0.36 (cyclohexane/AcOEt 9:1), 0.30 (toluene/AcOEt 9:1). $[\alpha]_D$ = +123.9 (*c* = 0.4, $CHCl_3$, 20°). UV (MeOH): 224 (4.13), 254 (3.85), 300 (3.08). IR (KBr): 2950*s*, 2871*s*, 1721*vs*, 1685*vs*, 1605*w*, 1553*w*, 1459*m*, 1262*s*, 1226*s*, 1139*m*, 984*s*. ^{1}H-NMR ($CDCl_3$): 0.89 (*s*, Me–C(4)); 0.96 (*s*, Me–C(4)); 1.17 (*d*, *J* = 6.9, Me–C(15)); 1.20 (*d*, Me–C(15)); 1.25 (*m*, H_{ax}–C(1), H_{ax}–C(3)); 1.47 (*m*, H_{eq}–C(3)); 1.49 (*dd*, *J* = 12.9, 3.1, H_{ax}–C(5)); 1.63 (*m*, H_{eq}–C(2)); 1.92 (*m*, H_{eq}–C(6)); 1.95 (*m*, H_{ax}–C(2)); 2.47 (*m*, H_{ax}–C(6)); 2.49 (*s*, Ac); 2.87 (*m*, H–C(7)); 2.97 (*m*, H–C(7)); 2.99 (*m*, H_{eq}–C(1)); 3.48 (*sept.*, *J* = 6.9, H–C(15)); 3.56 (*s*, COOMe); 7.01 (*s*, H–C(14)); 7.45 (*s*, H–C(11)). ^{13}C-NMR ($CDCl_3$): 18.3 (*t*, C(6)); 19.9 (*q*, C(19)); 20.1 (*t*, C(2)); 23.7 (*q*, C(16) or C(17)); 24.1 (*q*, C(17) or C(16)); 28.5 (*d*, C(15)); 29.9 (*t*, C(7)); 30.2 (*q*, *Me*CO); 31.8 (*q*, C(18)); 33.8 (*s*, C(4)); 36.7 (*t*, C(1)); 41.6 (*t*, C(3)); 47.3 (*s*, C(10)); 51.5 (*q*, COO*Me*); 51.9 (*d*, C(5)); 127.5 (*d*, C(11)); 125.7 (*d*, C(14)); 135.9 (*s*, C(12)); 137.6 (*s*, C(9)); 140.7 (*s*, C(8)); 146.1 (*s*, C(13)); 175.5 (*s*, C(20)); 202.7 (*s*, Me*C*O). EI-MS: 356 (87, M^+), 341 (6), 298 (26), 297 (100), 281 (7), 255 (12), 229 (40), 215 (48), 201 (36), 69 (31), 43 (98), 41 (34). Anal. calc. for $C_{23}H_{32}O_3$ (356.5): C 77.49, H 9.05; found: C 77.59, H 8.98.

*Methyl (4a*R*,10a*S*)-6-Acetoxy-1,3,4,9,10,10a-hexahydro-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2*H*)-carboxylate* (**25**). A soln. of 320 mg (0.90 mmol) of **24**, 270 mg (1.83 mmol) of dry 85% 3-chloroperbenzoic acid, and 3.5 mg of TsOH in abs. 1,2-dichloroethane was stirred under Ar at 85° for 6 h. The cooled mixture was diluted with 100 ml of Et_2O and washed with sat. aq. solns. of NaI, $Na_2S_2O_3$, and $NaHCO_3$ and 1M urea. The aq. phases were again extracted with 50 ml of Et_2O and the combined Et_2O phases dried and evaporated. The residue was chromatographed (silica gel, cyclohexane/AcOEt 9:1): 275 mg (82%) of **25**. Colorless crystals. M.p. 112° (MeOH). R_f 0.36 (cyclohexane/AcOEt 9:1), 0.30 (toluene/AcOEt 9:1). $[\alpha]_D$ = +145.5 (*c* = 0.6, $CHCl_3$, 20°). UV (MeOH): 212 (3.85), 234 (3.28), 265 (3.16), 279 (3.16). IR (KBr): 2957*s*, 2905*s*, 2871*m*, 1763*vs*, 1717*vs*, 1492*m*, 1459*m*, 1213*s*, 1198*s*, 986*m*, 844*w*, 608*w*. ^{1}H-NMR ($CDCl_3$): 0.78 (*s*, Me–C(4)); 0.96 (*s*, Me–C(4)); 1.16 (*d*, *J* = 7.3, Me–C(15)); 1.17 (*d*, *J* = 7.3, Me–C(15)); 1.25 (*m*, H_{ax}–C(1)); 1.26 (*m*, H_{ax}–C(3)); 1.44 (*m*, H_{eq}–C(3)); 1.49 (*dd*, *J* = 12.9, 2.9, H_{ax}–C(5)); 1.92 (*m*, H_{eq}–C(2)); 1.89 (*m*, H_{eq}–C(6)); 1.92 (*m*, H_{ax}–C(2)); 2.25 (*s*, AcO); 2.48 (*m*, H_{ax}–C(6)); 2.86 (*m*, H_{ax}–C(7)); 2.88 (*m*, H_{eq}–C(1)); 2.89 (*sept.*, *J* = 7.3, H–C(15)); 2.96 (*m*, H_{eq}–C(7)); 3.53 (*s*, COOMe); 6.89 (*s*, H–C(11)); 6.89 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.4 (*t*, C(6)); 19.9 (*q*, *Me*–C(4)); 20.1 (*t*, C(2)); 20.6 (*q*, *Me*COO); 22.6 (*q*, C(16) or C(17)); 22.7 (*q*, C(17) or C(16)); 26.9 (*d*, C(15)); 29.3 (*t*, C(7)); 31.8 (*q*, C(18)); 33.6 (*s*, C(4)); 36.6 (*t*, C(1)); 41.5 (*t*, C(3)); 47.4 (*s*, C(10)); 51.4 (*q*, COO*Me*); 51.6 (*d*, C(5)); 119.1 (*d*, C(11)); 127.3 (*d*, C(14)); 134.7 (*s*, C(8)); 138.7 (*s*, C(9)); 145.7 (*s*, C(12)); 168.4 (*s*, Me*C*OO); 175.4 (*s*, C(20)). EI-MS: 372 (43, M^+), 330 (73), 314 (22), 313 (97), 272 (21), 271 (100), 270 (56), 175 (25), 69 (44), 43 (46). Anal. calc. for $C_{23}H_{32}O_4$ (372.5): C 74.16, H 8.66; found: C 74.18, H 8.69.

*(4a*R*,10a*S*)-1,3,4,9,10,10a-Hexahydro-6-hydroxy-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2*H*)-carboxylic Acid (= (+)-Pisiferic Acid*; **1**). To a soln. of 86 mg (1.60 mmol) of LiSMe in 7 ml of HMPA (distilled over CaH) under Ar, 120 mg (0.32 mmol) of **25** were added and stirred at r.t. for 24 h. After dilution with 60 ml of 2N H_2SO_4 extraction with Et_2O (3 × 50 ml), washing the Et_2O phases with 2N H_2SO_4 and brine, and evaporation, a residue was obtained which was chromatographed (silica gel, cyclohexane/AcOEt 3:1): 95.5 mg (94%) of **1**. Colorless crystals. M.p. 184–186° (MeOH; [46]: 155–159°; [2]: 177°; [17]: 185–186°). $[\alpha]_D$ = +175.5 (*c* = 0.4, MeOH, 20°; [2]: $[\alpha]_D$ = +177.0, *c* = 0.35, MeOH, 20°; [48]: $[\alpha]_D$ = 166.7, *c* = 0.3, 25°). UV (MeOH): 211 (4.03), 231 (3.69), 284 (3.40). IR (KBr): 3400*m*, 2962*vs*, 2900*s*, 2844*m*, 1686*vs*, 1616*m*, 1500*m*, 1256*m*, 890*w*, 760*m*. ^{1}H-NMR ($CDCl_3$): 0.82 (*s*, Me–C(4)), 0.95 (*s*, Me–C(4)); 1.19 (*d*, *J* = 6.9, 2 Me–C(15)); 1.20 (*m*, H_{ax}–C(1)); 1.23

(*m*, H_{ax}–C(3)); 1.45 (*m*, H_{eq}–C(3)); 1.49 (*dd*, *J* = 13.1, 2.6, H_{ax}–C(5)); 1.58 (*m*, H_{eq}–C(2)); 1.88 (*m*, H_{eq}–C(6)); 1.95 (*m*, H_{ax}–C(2)); 2.46 (*m*, H_{ax}–C(6)); 2.78 (*m*, H_{ax}–C(7)); 2.79 (*m*, H_{eq}–C(1)); 2.89 (*m*, H_{eq}–C(7)); 3.10 (*sept.*, *J* = 6.9, H–C(15)); 6.66 (*s*, H–C(11)); 6.87 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.7 (*t*, C(6)); 20.1 (*q*, C(19)); 20.4 (*t*, C(2)); 22.4 (*q*, *Me*–C(15)); 22.6 (*q*, *Me*–C(15)); 26.9 (*d*, C(15)); 29.3 (*t*, C(7)); 32.1 (*q*, C(18)); 34.1 (*s*, C(4)); 36.1 (*t*, C(1)); 41.9 (*t*, C(3)); 47.6 (*s*, C(10)); 52.3 (*d*, C(5)); 112.4 (*d*, C(11)); 127.4 (*d*, C(14)); 129.2 (*s*, C(9)); 133.6 (*s*, C(13)); 138.3 (*s*, C(8)); 150.7 (*s*, C(12)); 181.1 (*s*, C(20)). EI-MS: 316 (79, M^+), 301 (5), 272 (21), 270 (100), 229 (14), 201 (31), 189 (43), 175 (39), 145 (13), 69 (44), 55 (15), 43 (28), 41 (33). Anal. calc. for $C_{20}H_{28}O_3$ (316.4): C 75.91, H 8.92; found: C 75.86, H 8.79.

Abietic Acid (**26**) *and Methyl Abietate* (**27**). They were obtained from *Sacotan 90*® as reported in [48] [49]. Compounds **28**–**32** were obtained according to [35] and **33** from **32** by etherification with diazomethane and in the presence of silica gel.

(4bS,8aS)-4b,6,7,8,8a,10-Hexahydro-3-methoxy-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9(5H)-one (**34**). To a soln. of 2.6 g (8.7 mmol) of **33** in 50 ml of abs. CH_2Cl_2 at 0° were added 2.7 g (13.3 mmol) of dry *ca.* 85% 3-chloroperbenzoic acid. The mixture was stirred in the dark for 1 h and 2 h at r.t. Then 200 ml of Et_2O were added. The org. phase was washed with sat. aq. KI, 2N H_2SO_4, and $NaHCO_3$ solns. and evaporated: 2.7 g of colorless oil. The oil and 510 mg (2.8 mmol) of TsOH in 80 ml of benzene were refluxed under Ar for 2 h. The brown mixture was diluted with 200 ml of Et_2O, washed with brine and $NaHCO_3$ soln., and evaporated. The brown oily residue was chromatographed (silica gel, cyclohexane/toluene 1:1): 2.2 g (82%) of **34**. Colorless oil. R_f 0.38 (cyclohexane/toluene 1:1), 0.54 (cyclohexane/AcOEt 9:1). $[\alpha]_D$ = +96.3 (*c* = 0.3, $CHCl_3$, 18°). UV (MeOH): 214 (3.68), 227 (3.77), 280 (3.50), 314 (2.73). IR (neat): 2929*vs*, 2868*vs*, 1712*s*, 1680*w*, 1500*s*, 1464*m*, 1291*m*, 1209*m*, 1052*m*, 949*w*. ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, Me–C(4)); 1.08 (*d*, *J* = 6.9, Me–C(15)); 1.12 (*s*, Me–C(10)); 1.13 (*m*, H_{ax}–C(3)); 1.16 (*d*, *J* = 6.9, Me–C(15)); 1.22 (*s*, Me–C(4)); 1.48 (*m*, H_{eq}–C(3)); 1.68 (*m*, H–C(2)); 1.75 (*m*, H_{ax}–C(1)); 1.85 (*m*, H–C(2)); 2.24 (*m*, H_{eq}–C(1)); 2.33 (*s*, H_{ax}–C(5)); 3.17 (*sept.*, *J* = 6.9, H–C(15)); 3.55 (*s*, H–C(7)); 3.83 (*s*, MeO); 6.71 (*s*, H–C(11)); 6.85 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.6 (*t*, C(2)); 21.5 (*q*, C(2)); 22.5 (*q*, C(16) or C(17)); 22.7 (*q*, C(17) or C(16)); 24.5 (*q*, C(20)); 26.4 (*d*, C(15)); 32.5 (*s*, C(4)); 32.8 (*q*, C(18)); 38.5 (*t*, C(1)); 40.5 (*s*, C(10)); 42.7 (*t*, C(3)); 44.5 (*t*, C(7)); 55.5 (*q*, MeO); 62.5 (*d*, C(5)); 105.7 (*d*, C(11)); 123.8 (*s*, C(8)); 125.8 (*d*, C(14)); 135.3 (*s*, C(13)); 146.9 (*s*, C(9)); 155.6 (*s*, C(12)); 210.5 (*s*, C(6)). EI-MS: 314 (100, M^+), 300 (16), 299 (74), 271 (36), 257 (31), 229 (28), 187 (18), 128 (15), 69 (26), 55 (17), 43 (21), 41 (40). Anal. calc. for $C_{21}H_{30}O_2$ (314.5): C 80.21, H 9.62; found: C 79.81, H 9.35.

(4bS,8aS,9R)-4b,5,6,7,8,8a,9,10-Octahydro-3-methoxy-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9-ol (**38**). A soln. of 1.5 g (4.8 mmol) of **34** in 30 ml of abs. THF was dropwise added to an ice-cold suspension of 345 mg (9.1 mmol) of $LiAlH_4$ in 50 ml of dry THF. The mixture was stirred for 3 h at r.t. After slow addition of 40 ml of THF/H_2O 9:1 and evaporation to half the volume, 100 ml of 2N H_2SO_4 were added. The mixture was extracted 3 × with 70 ml of Et_2O, the combined Et_2O phase washed with 2N H_2SO_4, $NaHCO_3$ soln., and brine and evaporated, and the residue chromatographed (silica gel, cyclohexane/AcOEt 5:1): 1.3 g (87%) of **38**. Colorless oil. R_f 0.44 (cyclohexane/AcOEt 5:1), 0.17 (cyclohexane/AcOEt 9:1). $[\alpha]_D$ = +58.8 (*c* = 0.2, $CHCl_3$, 18°). UV (MeOH): 223 (3.70), 280 (3.39). IR (neat): 3562*w*, 3449*m*, 2926*m*, 2866*vs*, 2848*vs*, 1663*m*, 1500*s*, 1238*m*, 1223*m*, 1046*s*, 973*m*, 865*m*. ^{1}H-NMR ($CDCl_3$): 0.98 (*s*, Me–C(4)); 1.09 (*d*, *J* = 6.9, Me–C(15)); 1.13 (*d*, *J* = 6.9, Me–C(15)); 1.18 (*m*, H_{ax}–C(3)); 1.23 (*s*, Me–C(4)); 1.34 (*s*, H_{ax}–C(5)); 1.46 (*m*, H_{ax}–C(1)); 1.51 (*s*, Me–C(4)); 1.52 (*m*, H_{eq}–C(3)); 1.55 (*m*, H_{eq}–C(2)); 1.78 (*m*, H_{ax}–C(2)); 2.09 (*m*, H_{eq}–C(1)); 2.77 (*d*, *J* = 17.2, H_{eq}–C(7)); 3.04 (*dd*, *J* = 17.2, 4.3, H_{ax}–C(7)); 3.17 (*sept.*, *J* = 6.9, H–C(15)); 3.80 (*s*, MeO); 4.59 (*m*, H_{eq}–C(6)); 6.70 (*s*, H–C(11)); 6.77 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 19.5 (*t*, C(2)); 22.5 (*q*, *Me*–C(15)); 22.7 (*q*, *Me*–C(15)); 23.6 (*q*, C(19)); 26.3 (*d*, C(15)); 26.8 (*q*, C(20)); 33.6 (*q*, C(18)); 34.0 (*s*, C(4)); 37.5 (*s*, C(10)); 40.7 (*t*, C(7)); 42.0 (*t*, C(1)); 42.9 (*t*, C(3)); 53.1 (*d*, C(5)); 55.4 (*q*, MeO); 66.0 (*d*, C(6)); 106.9 (*d*, C(11)); 122.8 (*s*, C(8)); 126.9 (*d*, C(14)); 135.5 (*s*, C(13)); 146.5 (*s*, C(9)); 155.4 (*s*, C(12)). EI-MS: 316 (100, M^+), 301 (18), 284 (23), 283 (97), 241 (23), 227 (7), 213 (13), 171 (11), 69 (19), 55 (14), 43 (14), 41 (21). Anal. calc. for $C_{21}H_{32}O_2$ (316.5): C 79.70, H 10.19; found: C 80.04, H 10.29.

(4bS,8aS,9R)-4b,5,6,7,8,8a,9,10-Octahydro-3-methoxy-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-9-yl Nitrite (**35**). A soln. of 810 mg (2.56 mmol) of **38** in 20 ml of dry pyridine was degassed in an ultrasonic bath and saturated with Ar. After cooling to −30°, NOCl was introduced until the soln. showed a brown color. At this moment, 10 ml of ice water was added and the cooling bath removed. At r.t., again 10 ml of H_2O were added, and the precipitated nitrite was isolated by filtration and stored in the dark: 869 mg (91%) of **35**. A sample (30 mg) was purified by prep. TLC (*Chromatotron*, cyclohexane/AcOEt 5:1): colorless crystals. M.p. 109°. R_f 0.54 (cyclohexane/AcOEt 5:1), 0.63 (cyclohexane/AcOEt 2:1). $[\alpha]_D$ = −33.3 (*c* = 0.3, $CHCl_3$, 20°). UV (MeOH): 221 (4.07), 278 (3.58), 359 (1.90). IR (KBr): 2958*w*, 2935*vs*, 2910*s*, 2868*m*, 1639*vs*, 1592*s*, 1502*s*, 1057*m*, 778*w*, 748*m*. ^{1}H-NMR ($CDCl_3$): 1.00 (*s*, Me–C(4)); 1.09 (*s*, Me–C(4)); 1.17 (*d*, *J* = 6.9, Me–C(15)); 1.18 (*d*, *J* = 6.9, Me–C(15)); 1.27 (*m*, H_{ax}–C(3)); 1.44 (*s*, Me–C(10)); 1.48 (*m*, H_{ax}–C(1)); 1.49 (*m*, H_{eq}–C(3)); 1.63 (*m*, H_{eq}–C(2)); 1.75 (*s*, H_{ax}–C(5));

1.85 (*m*, H_{ax}–C(2)); 2.18 (*m*, H_{eq}–C(1)); 2.94 (*d*, *J* = 17.7, H_{eq}–C(7)); 3.21 (*sept.*, *J* = 6.9, H–C(15)); 3.36 (*dd*, *J* = 17.7, 5.1, H_{ax}–C(7)); 3.79 (*s*, MeO); 6.37 (*d*, *J* = 5.1 H_{eq}–C(6)); 6.76 (*s*, H–C(11)); 6.79 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 19.5 (*t*, C(2)); 22.6 (*q*, *Me*–C(15)); 22.8 (*q*, *Me*–C(15)); 23.2 (*q*, C(19)); 26.5 (*d*, C(15)); 26.7 (*q*, C(20)); 33.5 (*q*, C(18)); 34.2 (*s*, C(4)); 37.9 (*s*, C(10)); 38.1 (*t*, C(7)); 41.8 (*t*, C(3)); 52.6 (*d*, C(5)); 55.5 (*q*, MeO); 73.8 (*d*, C(6)); 107.0 (*d*, C(11)); 122.1 (*s*, C(3)); 126.5 (*d*, C(14)); 134.9 (*s*, C(13)); 155.7 (*s*, C(12)). EI-MS: 345 (100, M^+), 314 (12), 299 (13), 273 (24), 255 (19), 229 (14), 191 (97), 175 (31), 69 (30), 43 (28), 41 (33). Anal. calc. for $C_{21}H_{31}NO_3$ (345.5): C 73.01, H 9.04, N 4.05; found: C 73.04, H 9.17, N 4.37.

N-[(4aR,10R,10aS,12R)-1,3,4,9,10,10a-Hexahydro-6-methoxy-1,1-dimethyl-7-(1-methylethyl)-2H-10,4a-(epoxymethano)phenanthren-12-yl]hydroxylamin (**36**) *and (1S,4aS,10R,10aR)-1,2,3,4,4a,9,10,10a-Octahydro-10-hydroxy-6-methoxy-1,4a-dimethyl-7-(1-methylethyl)phenanthren-1-carbaldehyde Oxime* (**37**). A soln. of 300 mg (0.87 mmol) of **35** in 200 ml of dry benzene under Ar at 18° was irradiated with a 150-W high-pressure Hg lamp (*Solidex* glass filter). The mixture became yellow-green, and after evaporation, an oil was obtained. This could be separated by CC (silica gel, toluene/AcOEt 3:1) in a polar and a nonpolar fraction. From the nonpolar fraction, we obtained by CC (silica gel, cyclohexane/AcOEt 9:1) 27 mg (10%) of **34** and 26 mg (10%) of **38**. CC (silica gel, toluene/AcOEt 9:2) of the polar fraction gave 119 mg (40%) of **36** and 91 mg (31%) of **37**.

36: Oil, slowly crystallizing. M.p. 188° (MeOH). R_f 0.28 (toluene/AcOEt 3:1), 0.18 (toluene/AcOEt 9:2). $[\alpha]_D$ = −26.2 (*c* = 1.2, $CHCl_3$, 20°). UV (MeOH): 216 (3.72), 237 (3.76), 274 (3.49), 289 (3.47). IR (KBr): 3538*m*, 3435*w*, 2952*vs*, 2867*m*, 1498*m*, 1463*m*, 1238*m*, 1199*m*, 800*m*. ^{1}H-NMR ($CDCl_3$): 0.95 (*s*, Me–C(4)); 1.08 (*s*, Me–C(4)); 1.15 (*m*, H_{ax}–C(3)); 1.17 (*d*, *J* = 6.9, Me–C(15)); 1.18 (*d*, *J* = 6.9, Me–C(15)); 1.52 (*m*, H_{eq}–C(3)); 1.67 (*m*, H–C(2)); 1.68 (*m*, H_{ax}–C(1)); 1.70 (*m*, H–C(2)); 1.82 (*s*, H_{ax}–C(5)); 2.29 (*m*, H_{eq}–C(1)); 2.94 (*dd*, *J* = 16.8, 2.6, H_{ax}–C(7)); 2.98 (*dd*, *J* = 16.8, 2.6, H_{eq}–C(7)); 3.24 (*sept.*, *J* = 6.9, H–C(15)); 3.80 (*s*, MeO); 4.38 (*t*, *J* = 2.6, H_{eq}–C(6)); 5.40 (*d*, *J* = 14.9, H–C(18)); 6.67 (*s*, H–C(11)); 6.96 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.5 (*t*, C(2)); 22.6 (*q*, *Me*–C(15)); 22.8 (*q*, *Me*–C(15)); 23.1 (*q*, C(19)); 26.6 (*d*, C(15)); 27.0 (*t*, C(1)); 31.2 (*s*, C(4)); 33.1 (*q*, C(18)); 39.4 (*t*, C(3)); 39.9 (*t*, C(7)); 48.8 (*s*, C(10)); 55.6 (*q*, MeO); 56.0 (*d*, C(5)); 75.6 (*d*, C(6)); 103.8 (*d*, C(20)); 108.3 (*d*, C(11)); 126.3 (*s*, C(8)); 128.2 (*d*, C(14)); 136.7 (*s*, C(13)); 139.3 (*s*, C(9)); 155.2 (*s*, C(12)). FD-MS: 345 (M^+). Anal. calc. for $C_{21}H_{31}NO_3$ (345.5): C 73.01, H 9.04, N 4.05; found: C 72.96, H 9.02, N 4.17.

37: Colorless crystals. M.p. 78° (MeOH). R_f 0.35 (toluene/AcOEt 3:1), 0.26 (toluene/AcOEt 9:2). $[\alpha]_D$ = +59.5 (*c* = 0.2, $CHCl_3$, 18°). UV (MeOH): 223 (3.77), 278 (3.47). IR (KBr): 3228*m*, 2957*vs*, 2926*vs*, 2865*m*, 1500*s*, 1465*s*, 1222*s*, 1090*s*, 1050*s*, 865*m*, 801*m*. ^{1}H-NMR ($CDCl_3$): 1.10 (*d*, *J* = 6.9, *Me*–C(15)); 1.12 (*d*, *J* = 6.9, *Me*–C(15)); 1.17 (*s*, *Me*–C(4)); 1.20 (*m*, H_{ax}–C(3)); 1.26 (*s*, Me–C(10)); 1.37 (*m*, H_{ax}–C(1)); 1.56 (*s*, H_{ax}–C(5)); 1.59 (*m*, H–C(2)); 1.60 (*m*, H–C(2)); 1.81 (*m*, H_{eq}–C(3)); 2.06 (*m*, H_{eq}–C(1)); 2.87 (*d*, *J* = 17.1, H–C(7)); 2.98 (*dd*, *J* = 17.1, 4.7, H_{ax}–C(7)); 3.14 (*sept.*, *J* = 6.9, H–C(15)); 3.69 (*s*, MeO); 4.71 (*d*, H_{eq}–C(6)); 6.63 (*s*, H–C(11)); 6.77 (*s*, H–C(14)); 7.41 (*s*, H–C(19)). ^{13}C-NMR ($CDCl_3$): 20.3 (*t*, C(2)); 22.6 (*q*, *Me*–C(15)); 22.9 (*q*, *Me*–C(15)); 26.6 (*d*, C(15)); 27.4 (*q*, C(20)); 30.1 (*q*, C(18)); 37.7 (*s*, C(10)); 38.5 (*t*, C(7)); 40.1 (*s*, C(4)); 41.8 (*t*, C(3)); 42.0 (*t*, C(1)); 53.9 (*d*, C(5)); 55.5 (*q*, MeO); 64.5 (*d*, C(6)); 107.3 (*d*, C(11)); 123.2 (*s*, C(8)); 127.0 (*d*, C(14)); 134.9 (*s*, C(13)); 144.8 (*s*, C(9)); 155.5 (*s*, C(12)); 157.8 (*d*, C(19)). EI-MS: 345 (93, M^+), 310 (91), 295 (100), 284 (20), 269 (54), 253 (9), 227 (17), 43 (14). Anal. calc. for $C_{21}H_{31}NO_3$ (345.5): C 73.01, H 9.04, N 4.05; found: C 73.11, H 9.14, N 4.10.

(4aR,10R,10aS)-1,3,4,9,10,10a-Hexahydro-6-methoxy-1,1-dimethyl-7-(1-methylethyl)-2H-10,4a-(epoxymethano)phenanthren-12-one (**39**). To a cooled soln. of 505 mg (1.35 mmol) of PDC in 4 ml of dry DMF was added within 1 min a soln. of 116 mg (0.35 mmol) of **36** in 4 ml of dry DMF. The mixture was stirred for 10 min at r.t. and then diluted with 50 ml of ice water. Extraction with Et_2O (3 × 50 ml), usual workup, and CC (silica gel, toluene/AcOEt 9:1) gave 85 mg (77%) of **39**. Colorless crystals. M.p. 218–220° (MeOH). R_f 0.28 (toluene/AcOEt 9:1), 0.39 (cyclohexane/AcOEt 3:1). $[\alpha]_D$ = +42.9 (*c* = 0.2, $CHCl_3$, 20°). UV (MeOH): 218 (3.40), 233 (2.71), 281 (2.70). IR (KBr): 2957*m*, 2868*s*, 2843*m*, 1764*vs*, 1613*w*, 1497*m*, 1462*m*, 1438*m*, 946*w*, 883*w*, 845*w*. ^{1}H-NMR ($CDCl_3$): 0.94 (*s*, Me–C(4)); 0.98 (*s*, Me–C(4)); 1.13 (*m*, H_{ax}–C(3)); 1.15 (*d*, *J* = 6.9, Me–C(15)); 1.16 (*d*, *J* = 6.9, Me–C(15)); 1.46 (*m*, H_{eq}–C(3)); 1.66 (*m*, H–C(2)); 1.67 (*m*, H_{ax}–C(1)); 1.69 (*m*, H–C(2)); 1.92 (*s*, H_{ax}–C(5)); 3.06 (*dd*, *J* = 17.3, 2.5, H–C(7)); 3.14 (*dd*, *J* = 17.3, 2.5, H–C(7)); 3.24 (*sept.*, *J* = 6.9, H–C(14)); 3.80 (*s*, MeO); 4.81 (*t*, *J* = 2.5, H_{eq}–C(6)); 6.71 (*s*, H–C(11)); 6.91 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.6 (*t*, C(2)); 22.0 (*q*, C(19)); 22.5 (*q*, *Me*–C(15)); 22.7 (*q*, *Me*–C(15)); 26.5 (*d*, C(15)); 26.6 (*t*, C(1)); 31.3 (*s*, C(4)); 31.7 (*q*, C(18)); 35.0 (*t*, C(7)); 38.6 (*t*, C(3)); 46.0 (*s*, C(10)); 54.0 (*d*, C(5)); 55.5 (*q*, MeO); 75.7 (*d*, C(6)); 106.5 (*d*, C(11)); 123.9 (*s*, C(8)); 127.2 (*d*, C(14)); 127.2 (*d*, C(14)); 137.3 (*s*, C(13)); 138.0 (*s*, C(9)); 155.8 (*s*, C(12)); 177.9 (*s*, C(20)). EI-MS: 328 (88, M^+), 284 (42), 269 (100), 213 (34), 199 (7), 185 (16), 171 (23), 159 (10), 43 (15), 41 (17). Anal. calc. for $C_{21}H_{28}O_3$ (328.5): C 76.79, H 8.59; found: C 76.41, H 8.40

(4aR,10R,10aS)-1,3,4,9,10,10a-Hexahydro-6-hydroxy-1,1-dimethyl-7-(1-methylethyl)-2H-10,4a-(epoxymethano)phenanthren-12-one (**40**). At 0°, 144 mg (0.54 mmol) of $AlBr_3$ were added to a soln. of 45 mg (0.14 mmol)

of **39** in 1.5 ml of dry tetrahydrothiophene under Ar. The mixture was stirred for 2 h at r.t. After dilution with 20 ml of 2N H_2SO_4, extraction with Et_2O (3 × 40 ml), usual workup, and evaporation, a crystalline residue was obtained. CC (silica gel, toluene/AcOEt 3:1) yielded 32.5 mg (85%) of **40**. Colorless crystals. M.p. 92–93°. R_f 0.31 (toluene/AcOEt 3:1), 0.41 (toluene/AcOEt 2:1). $[\alpha]_D = +35.9$ ($c = 0.2$, $CHCl_3$, 18°). UV (MeOH): 216 (3.81), 295 (3.22). IR (KBr): 3387*s*, 2961*s*, 2869*m*, 1753*vs*, 1659*m*, 1427*s*, 1261*s*, 1091*s*, 1029*s*, 798*w*, 734*m*, 626*m*. ^{1}H-NMR ($CDCl_3$): 0.93 (*s*, Me–C(4)); 0.98 (*s*, Me–C(4)); 1.14 (*m*, H_{ax}–C(3)); 1.18 (*d*, $J = 6.9$, Me–C(15)); 1.19 (*d*, $J = 6.9$, Me–C(15)); 1.43 (*m*, H_{eq}–C(3)); 1.60 (*m*, H–C(2)); 1.62 (*m*, H_{ax}–C(1)); 1.67 (*m*, H–C(2)); 1.90 (*s*, H_{ax}–C(5)); 2.64 (*m*, H_{eq}–C(1)); 3.04 (*dd*, $J = 17.2, 2.3$, H–C(7)); 3.13 (*sept.*, $J = 6.9$, H–C(15)); 3.15 (*dd*, $J = 17.2, 2.3$, H–C(7)); 4.80 (*t*, $J = 2.3$, H_{eq}–C(6)); 6.64 (*s*, H–C(11)); 6.89 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 18.6 (*t*, C(2)); 21.9 (*q*, C(19)); 22.4 (*q*, *Me*–C(15)); 22.5 (*q*, *Me*–C(15)); 26.5 (*t*, C(1)); 26.9 (*d*, C(15)); 31.3 (*s*, C(4)); 31.7 (*q*, C(18)); 35.0 (*t*, C(7)); 38.7 (*t*, C(2)); 45.8 (*s*, C(10)); 53.9 (*d*, C(5)); 75.8 (*d*, C(6)); 111.3 (*d*, C(11)); 124.0 (*s*, C(8)); 127.6 (*d*, C(14)); 124.8 (*s*, C(13)); 138.2 (*s*, C(9)); 151.8 (*s*, C(12)); 178.0 (*s*, C(20)). EI-MS: 314 (54, M^+), 270 (49), 256 (22), 255 (100), 200 (11), 199 (34), 171 (17), 157 (22), 91 (5), 55 (9), 41 (18). Anal. calc. for $C_{20}H_{26}O_3$ (314.4): C 76.40, H 8.33; found: C 76.06, H 8.26.

(+)-Pisiferic Acid (**1**) *and (4a*R*)-1,3,4,9-Tetrahydro-6-hydroxy-1,1-dimethyl-7-(1-methylethyl)phenanthrene-4a(2*H*)-carboxylic Acid* (**41**). At 0°, 192 mg (0.72 mmol) of $AlBr_3$ were added to a soln. of 60 mg (0.18 mmol) of **39** in 2 ml of dry tetrahydrothiophen under Ar. This mixture was stirred at r.t. for 24 h. Then 40 ml of ice-cooled 2N H_2SO_4 were added. The mixture was extracted 3 times with 40 ml of Et_2O and the combined Et_2O phase washed with 2N H_2SO_4 and brine. Evaporation and CC (silica gel, toluene/AcOEt 3:1) gave 47.1 mg (82%) of **1** and 6.0 mg (10%) of **41**.

1: Colorless crystals. All physical and spectroscopic data identical with the data given above and, within experimental error, with the data from [2] [46] [47].

41: M.p. 144–146°. R_f 0.16 (toluene/AcOEt 3:1), 0.23 (cyclohexane/AcOEt 3:1). $[\alpha]_D = +168.0$ ($c = 0.1$, $CHCl_3$, 20°). UV (MeOH): 216 (3.92), 238 (4.11), 282 (3.56). IR (KBr): 3400*m*, 2959*vs*, 2928*vs*, 2869*m*, 1696*m*, 1629*w*, 1512*m*, 1261*m*, 1233*m*, 1025*m*, 802*m*. ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, Me–C(4)); 1.12 (*s*, Me–C(4)); 1.15 (*d*, $J = 6.9$, Me–C(15)); 1.17 (*d*, $J = 6.9$, Me–C(15)); 1.24 (*m*, H_{ax}–C(3)); 1.34 (*m*, H_{ax}–C(1)); 1.41 (*m*, H_{eq}–C(3)); 1.56 (*m*, H_{eq}–C(2)); 1.95 (*m*, H_{ax}–C(2)); 2.87 (*m*, H_{eq}–C(1)); 3.07 (*sept.*, $J = 6.9$, H–C(15)); 3.34 (*dd*, $J = 21.4, 4.9$, H_{ax}–C(7)); 3.41 (*dd*, $J = 21.4, 2.7$, H_{eq}–C(7)); 5.98 (*dd*, $J = 4.9, 2.7$, H–C(6)); 6.67 (*s*, H–C(11)); 6.85 (*s*, H–C(14)). ^{13}C-NMR ($CDCl_3$): 19.9 (*t*, C(2)); 22.4 (*q*, *Me*–C(15)); 22.6 (*q*, *Me*–C(15)); 27.0 (*q*, C(19)); 27.4 (*d*, C(15)); 29.8 (*t*, C(7)); 31.1 (*q*, C(18)); 36.8 (*s*, C(4)); 37.2 (*t*, C(1)); 40.5 (*t*, C(3)); 48.8 (*s*, C(10)); 112.5 (*d*, C(11)); 120.5 (*d*, C(6)); 125.1 (*s*, C(9)); 126.0 (*s*, C(14)); 134.2 (*s*, C(13)); 136.3 (*s*, C(5)); 141.9 (*s*, C(8)); 151.5 (*s*, C(12)); 177.0 (*s*, C(20)). EI-MS: 314 (59, M^+), 269 (88), 268 (33), 253 (44), 232 (37), 227 (71), 211 (17), 199 (100), 157 (70), 83 (22), 43 (27), 41 (25). Anal. calc. for $C_{20}H_{26}O_3$ (314.4): C 76.40, H 8.33; found: C 75.93, H 8.10.

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