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Synthetic Transformation of Abietic Acid II[a]. Oxidation of Diene Adducts

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Summary. The diene adduct of 2-chloroacrylonitrile and abietic acid (**1**) can be converted to tetracyclic ketone **2**. Oxidation of **1** and **2** with ozone, $KMnO_4$, OsO_4, and *tert*-butylchromate are described. Three products have been further oxidized by *Baeyer-Villiger* reactions.

Keywords. Abietic acid; Diene adducts; Ozonization; *Baeyer-Villiger* reaction; Oxidation.

Synthetische Umwandlung des Abietinsäuregerüstes, 2. Mitt. Oxidation von Dien-Addukten

Zusammenfassung. *Diels-Alder*-Addition von 2-Chloracrylnitril an Abietinsäure führt zum entsprechendem Chlornitril **1**, das in weiterer Folge in das tetracyclische Keton **2** umgewandelt werden kann. Es werden Oxidationen von **1** und **2** mit Ozon, $KMnO_4$, OsO_4 und *tert*-Butylchromat sowie *Baeyer-Villiger*-Oxidationen von drei Reaktionsprodukten beschrieben.

Introduction

Abietic acid is a cheap and easily available enantiomerically pure starting material which can be used for stereoselective syntheses of terpene derivatives. We have studied synthetic transformations of its carbon skeleton. In a previous communication on *Diels-Alder* addition of 2-chloroacrylonitrile to abietic acid we have described the synthesis of **1** and **2** [1]. This paper reports the results of oxidative transformations of these compounds.

Oxidation with ozone

1 is inert against ozone at −70°C; however, at −30°C to +10°C a slow conversion can be observed. At room temperature, adduct **1** is transformed completely and gives alcohol **3** in 56% yield. **3** shows a broad OH-absorption at 2429 cm^{-1} in the IR spectrum. In the proton NMR spectrum, two singulets instead of dublets for the diastereotopic methyl groups of the isopropyl residue can be detected indicating

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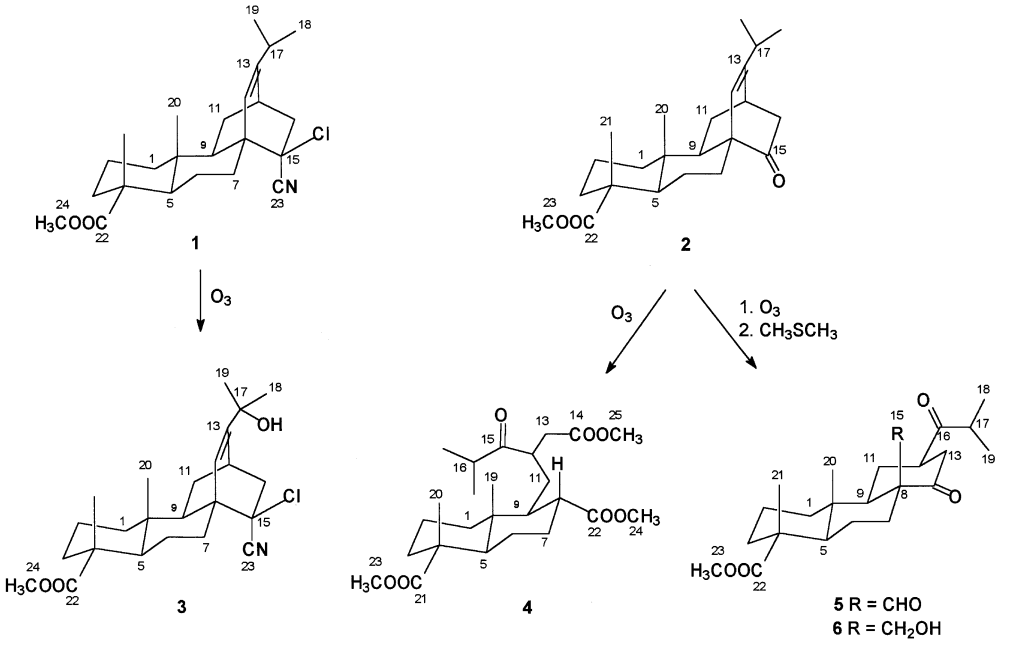


Scheme 1

oxidation at C-17. The structure of **3** was further confirmed by its mass spectrum which showed the M^+ peak at $m/z = 419$. A prominent peak at $m/z = 332$ is the result of a *retro-Diels-Alder* fragmentation $(M - CH_2 = C(Cl)CN]^+$. It seems that the double bond is not accessible for ozone due to steric hindrance by the *endo* chlorine substituent. Instead, oxidation of the tertiary carbon of the isopropyl group takes place. Reactions of this type are well known [2–4]; as mechanism, an oxygen insertion into the tertiary CH-bond has been proposed [5, 6].

Reaction of ozone with compound **2** at $-70°C$ in ethyl acetate and subsequent oxidative workup of the crude ozonide and esterification with diazomethane afforded ketodiester **4** (55%). The proton NMR of **4** shows three methyl sigulets at $\delta = 3.68$, 3.61, and 3.60 ppm; their unambiguous assignment was established by a COLOC experiment. The configuration of C-8 was determined by NOE experiments: correlation signals between H-8 and H-6_{ax} and H-8 and the methyl protons at C-19 can be observed. This proves that H-8 occupies the axial position. The signal of H-8 is a triplet of doublets, indicating two large axial-axial couplings ($J = 12.0$ Hz) which further proves axial arrangement and therefore *R* configuration of C-8. The base peak in the El MS at $m/z = 158$ is the result of a *McLafferty* rearrangement during which the C-11–C-12 bond is cleaved. No experiments have been carried out to investigate the mechanism of this oxidation.

Reduction of the crude ozonide from ozonolysis of **2** in ethyl acetate with dimethylsulfide [7] in AcOEt gives aldehyde **5** in nearly quantitative yield. The aldehyde proton at C-15 is observed as singulet at $\delta = 9.99$ ppm in the ^1H NMR spectrum and shows NOESY correlations with CH_3-20, H-11_{ax}, H-13_{ax}, H-7_{eq}, and H-6_{ax}, proving axial position of the aldehyde group. Using lithium *tris*-((3-ethyl-3-pentyl)-oxo)-aluminum hydride (*LTEPA*), diketoaldehyde **5** was chemoselectively

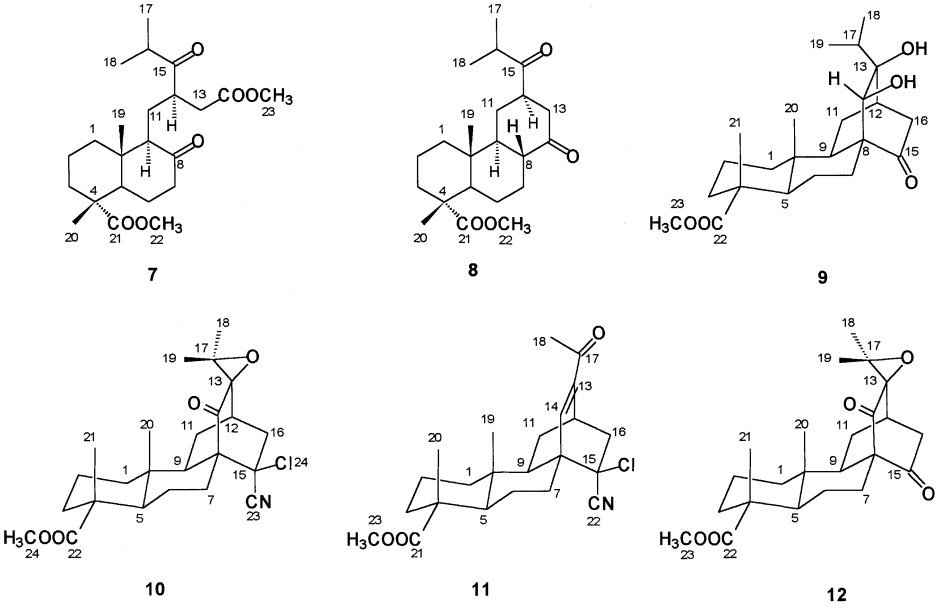
reduced, giving diketoalcohol **6** in 91% yield. In the IR spectrum, the broad OH-stretching vibration appears at 3450 cm^{-1}. The ^1H NMR spectrum shows an AB system for the diastereotopic protons H-15 ($^2J = 11.3$ Hz) at 4.10 and 3.86 ppm. *Jones* oxidation [8, 9] of **5** yields, after esterification with diazomethane, compound **7** and by-product **8**. The configuration of C-8 in **8** was derived by NMR experiments. The signal of H-9 has two large axial-axial couplings with H-11_{ax} and H-8. H-8 also exhibits NOE correlations to methyl group 19. The intermediate during this oxidation is probably the corresponding β-oxo-carboxylic acid which decarboxylates to **8**. This diketone is further oxidized to **7**. Even the use of smoother oxidation reagents like Ag_2O in EtOH [10–12] or pyridinium chlorochromate in *DMF* [13, 14] gave the overoxidized product **7** as the main component.

Oxidation with OsO_4 and $KMnO_4$

1 is inert against OsO_4 and $KMnO_4$ even if used together with dibenzo[18]-crown-6 in benzene [15] or coated silica [16]. **2**, however, can be oxidized in 89% yield by OsO_4 in ^{t}BuOH to *cis*-diol **9**. The ^{13}C NMR spectrum shows two signals at $\delta = 73.8$ and 72.0 ppm for the oxygen bearing carbons and no residual resonances due to olefinic carbons. NOESY correlations between H-14 and H-6_{ax}, H-7_{eq}, CH_3-18, CH_3-19, and CH_3-20 prove that the hydroxy groups are in *endo* position relative to the carbonyl group and that the reagent has approached the molecule form the less hindered side.

Oxidation with tert-butylchromate

A well known reagent for the oxidation of allylic positions is *tert*-butylchromate [17–21]. Oxidation of **1** with this reagent gave epoxyketone **10** in 74% yield. The



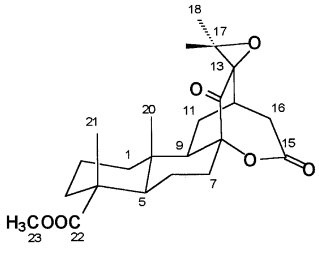
Scheme 2

^{13}C NMR spectrum shows a carbonyl resonance at 205.8 ppm and two epoxy carbons at $\delta = 67.7$ and 67.1 ppm. From an NOE experiment in which the resonance of CH_3-20 was irradiated and the intensity of CH_3-19 was enhanced we conclude the configuration of C-13 to be *R*. By-product **11** is obtained in 21% yield. An α,β-unsaturated carbonyl group is indicated in the IR spectrum by a peak at 1674 cm^{-1}, and the proton NMR spectrum shows no isopropyl methyl resonances. The MS gives a molecular mass of 403 and shows a peak at $m/z =$ 316 which is the result of a *retro-Diels-Alder* fragmentation. The ^{13}C carbonyl resonance has long range correlations to the olefinic proton and to CH_3-18.

Oxidation of **2** with *tert*-butylchromate leads to epoxydiketon **12** in 83% yield. The methyl groups attached to the oxiran ring appear at $\delta = 1.49$ and 1.48 ppm in ^{1}H NMR spectrum. The resonance of CH_3-18 shows NOE correlations to H-12, whereas CH_3-19 is correlated to CH_3-20. From this we determined *R* configuration for C-13. An unambiguous assignment of the ketocarbonyl resonances was obtained from CH-long range correlations: the resonance of C-15 shows small couplings to the protons at C-16.

The keto functions in **10** and **12** can be used for ring opening reaction by *Baeyer-Villiger* oxidation. **10** did not undergo any reaction with *m*-chloroperbenzoic acid (*mCPBA*) [22] even in the presence of trifluoroacetic acid (*TFA*) [23]. Epoxydiketon **12**, however, was quantitative and regioselective oxidized to lactone **13**.

The position of the lactone bond was determined by a CH-correlation spectrum which was optimized for 7 Hz couplings. The ketocarbonyl C-14 ($\delta = 199.9$ ppm) has correlations to the protons in positions 7 and to H-9; the lacton carbonyl ($\delta = 169.8$ ppm) shows correlations to the protons at C-16. Alkoxy C-8 has cross peaks to the protons in position 9, 7, and 11. Cleavage of the oxiran ring in **10** with



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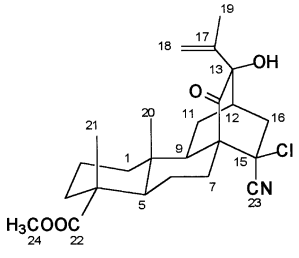

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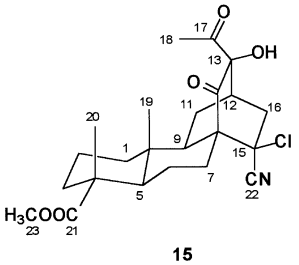

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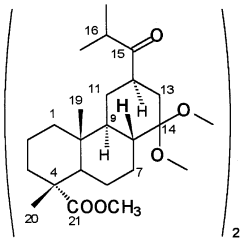

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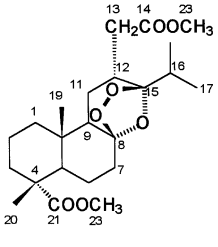

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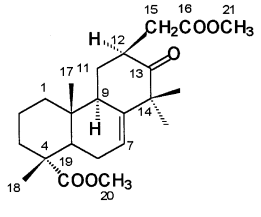

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Scheme 3

acid led to compound **14** in 77% yield. The ^{13}C NMR spectrum of **14** shows two olefinic carbons ($\delta = 141.4$ and 118.3 ppm). Additional information was obtained by a DEPT experiment which shows that the high field resonance has triplet multiplicity. In a COLOC spectrum, correlations between the hydroxyl bearing C-13 and H-16α and H-19 were observed. The signals of both olefinic protons overlap in the ^1H NMR spectrum generating a multiplet at $\delta = 5.15$ ppm. Irradiation of this resonance in an NOE difference experiment gave signal enhancements at H-12, H-19, and CH_3-20. This proves that C-18 and C-20 are close in space and therefore C-13 has *R* configuration.

Acidic treatment of **12** under the same conditions led to a complex mixture of products.

Ozonolysis of the double bond of **14** gave the hydroxydiketone **15** in moderate yield (45%). *R* configuration of C-13 in this compound is proven by a NOESY correlation between 13-OH and H-16β.

Baeyer-Villiger oxidation of **7** and **8**

Bis-(trimethylsilyl)-peroxide oxidizes selectively carbonyl groups in the presence of olefinic double bonds [24–26]. Oxidation of **7** with this reagent in the presence of trimethylsilyltrifluoromethane sulfonate gave the tetracyclic peroxide **17** in 77% yield. The carbon resonances of C-8 and C-15 are in the characteristic region for acetals. From COLOC-correlations with H-11β, H-12, both H-13, and the isopropyl protons the resonance at $\delta = 111.0$ ppm was assigned to C-15. The resonance at $\delta = 109.4$ ppm gives correlations with H-9, H-11β, and both protons in position 7 and therefore corresponds to C-8. The ^1H NMR resonances of H-11β and CH_3-19 are both shifted to higher frequency indicating a β-peroxo bridge. From *Dreiding* models one can see that only in this case both groups can be influenced by the deshielding effect of a close C–O bond. Analogous peroxides have been obtained before in low yield from cyclohexanone derivatives and hydrogen peroxide [27–32]. In an attempt to optimize the conditions of the reaction of **7** with *bis*-(trimethylsilyl)-peroxide we have used twice the amount of trimethylsilyltrifluoromethane sulfonate. In this case, **18** was obtained in 61% yield. Its structure was derived from COSY, COLOC, and NOESY experiments: C,H-(7 Hz) correlations were observed between C-13 and H-11_{eq}, H-12, H-15, and the protons of the methyl groups attached to C-14 and between C-14 and the olefinic H-7. The position of the double bond was derived from COSY cross peaks connecting H-7 to H-9 and the protons at position 6 as well as the homoallyl connectivity between H-9 and the protons at C-6. The ^1H resonance of H-11_{ax} is a *pseudo*-quartet showing three large couplings. This indicates that the proton at C-12 is in α-position and the configuration of C-12 has been inverted during the reaction. In a NOESY experiment one can find a correlation between H-9 and H-12. This proves that both protons are on the same side of the ring system and therefore the configuration of C-12 is S.

Reaction of **8** with *bis*-(trimethylsilyl)-peroxide and a catalytic amount of trimethylsilyltrifluoromethane sulfonate gave dimer **16** in quantitative yield. From FD-MS, a molecular weight of 756 was derived; in the ^{13}C NMR spectrum, however, only 22 carbon resonances were observed, indicating that the molecule

has a C_2-axis; consequently, no optical activity was observed. The signal of C-14 is shifted in the acetal region to $\delta = 109.6$ ppm [33]. The proton resonance of H-13_{eq} appears at unusual high frequency ($\delta = 3.61$ ppm), showing that it is close to the 1,2,4,5-tetroxan ring system.

Experimental

General

Preparative thin layer chromatography: Chromatotron 8924 Harrison Research, 1 mm Kieselgel 60 PF_{254} (Merck) with gypsum; column chromatography (CC): Kieselgel 60 (Merck) (70–230 mesh), pore-diameter 60 Å; thin-layer chromatography (TLC): TLC sheets, ALUGRAM®; SIL G/UV_{254} (Machery-Nagel) and TLC sheets, POLYGRAM®, SIL G/UV_{254} (Machery-Nagel); solvents frequently used: cyclohexane (CH) and AcOEt; the substances were detected in UV light at 254 nm and by spraying with molybdatophoshoric acid or methanol/sulfuric acid (9:1) and subsequent heating with a hot gun. Melting points: melting point apparatus SM-LUX (Leitz), uncorrected; optical rotation: polarimeter 241 MC (Perkin Elmer); IR spectra; Spectrometer 883 (PERKIN-ELMER); UV/Vis: Lambda 17 UV/Vis-spectrometer (Perkin Elmer); NMR spectra: Bruker AC 200 and AMX 500 (300 K), 5 mm tubes, solvent resonance as internal standard. Before NOE experiments were performed, dissolved oxygen was removed by bubbling Ar through the solutions. ^{1}H and ^{13}C resonances were assigned using ^{1}H, ^{1}H and ^{1}H,^{13}C correlation spectra (sometimes optimized for small CH-couplings) and are numbered as given in the formulas. MS: Varian MAT 711 spectrometer; 70 eV electron impact and field desorption. Elementary analyses: Laboratory for Microanalysis, Institute of Physical Chemistry of the University of Vienna and Sektion Analytik, University of Ulm. Ozone generator: GSG 010.2 SORBIOS (0.4 bar, 100 V, 30 l/h).

Methyl-(4α, 15β)-15-chloro-15-cyano-13-(1-methylethyl)-17,19-dinoratis-13-en-4-carboxylate (**1**) and Methyl-(4α)-13-(1-methylethyl)-15-oxo-17,19-dinoratis-13-en-4-carboxylate (**2**) were prepared according to Ref. [1].

Methyl-(4α, 15β)-15-chloro-15-cyano-13-(1-hydroxy-1-methylethyl)-17,19-dinoratis-13-en-4-carboxylate (**3**)

A solution of 400 mg (1 mmol) **1** in 40 ml abs. AcOEt was treated with ozone at room temperature. Excess of ozone was removed by bubbling oxygen through the mixture. After evaporation of the solvent, the residue was purified by CC over silica (CH/AcOEt = 2:1).

Yield: 235 mg **3** (56%); white crystals; m.p.: 77°C; $R_f = 0.31$ (CH/AcOEt = 2:1); $[\alpha]_D^{20} = +20.6$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 3479$ (s), 2934 (s), 2237 (w), 1727 (vs), 1446 (m), 1259 (s), 732 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 203 (3.854) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.59$ (s, 3H, 20-H), 1.02 (m, 1H, 1-H_{ax}), 1.10 (s, 3H, 21-H), 1.15 (m, 1H, 11-Hβ), 1.18 (m, 1H, 6-H_{eq}), 1.30 (s_{br}, 6H, 18-H and 19-H), 1.3–1.5 (m, 2H, 2-H), 1.37 (m, 1H, 1-H_{eq}), 1.45 (m, 1H, 3-H_{eq}), 1.47 (m, 1H, 6-H_{ax}), 1.62 (m, 1H, 11-Hα), 1.72 (m, 1H, 3-H_{ax}), 1.72 (m, 1H, 5-H), 1.74 (m, 1H, 7-H_{ax}), 1.78 (m, 1H, 9-H), 2.01 (dt, $J = 14.7$ Hz, $J = 3.2$ Hz, $J_{11\beta,16\beta} = 3.2$ Hz, 1H, 16-Hβ), 2.27 (m, 1H, 7-H_{eq}), 2.60 (dd, $J = 14.7$ Hz, $J = 2.2$ Hz, 1H, 16-Hα), 2.82 (s_{br}, 1H, 12-H), 3.65 (s, 3H, 24-H), 5.56 (s_{br}, 1H, 14-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.0$ (q, C-20), 16.8 (q, C-21), 17.0 (t, C-2), 21.4 (t, C-6), 27.2 (t, C-11), 27.7 (q, C-18/C-19), 27.9 (q, C-19/C-18), 30.7 (d, C-12), 32.5 (t, C-7), 36.3 (t, C-3), 37.1 (t, C-1), 37.9 (s, C-10), 46.2 (s, C-8), 47.0 (s, C-4), 47.5 (t, C-16), 48.7 (d, C-5), 49.6 (d, C-9), 52.0 (q, C-24), 64.9 (s, C-15), 71.9 (s, C-17), 120.2 (s, C-23), 121.9 (d, C-14), 149.6 (s, C-13), 178.8 (s, C-22) ppm; MS (70 eV): m/z (%) = 421 (7) [$(M+2)^+$], 419 (18) [M^+], 332 (91), 254 (100), 132 (41), 121 (52), 59 (48); $C_{24}H_{34}ClNO_3$ (420.0); calc.: C 68.64, H 8.16, N 3.33; found: C 68.56, H 8.23, N 3.29.

Dimethyl-(1R-(1α,4aα,5β(2R),6α,8aα))-5-(3-methoxycarbonyl-2-(2-methyl-1-oxoethyl)-propyl)-1,4a-dimethyl-perhydro-1,6-naphthalene-dicarboxylate* (**4**)

Ozone was bubbled through a solution of 250 mg (0.7 mmol) **2** in 30 ml dry AcOEt at −70°C until the blue colour became persistent. After removing the excess of ozone by blowing oxygen through the mixture at −70°C it was allowed to reach room temperature, and the solvent was evaporated. The residue was dissolved in 1 ml MeOH, 2 ml HCOOH (98%), and 0.5 ml H_2O_2 (30%) and heated under reflux for 2 h. After cooling, ice water was added, and the product was extracted three times with Et_2O. The organic phases were washed twice with 1% aqueous Kl, with 10% $Na_2S_2O_3$ solution, with 5% NaOH, and with H_2O, and dried over Na_2SO_4. After evaporation the residue was purified by CC over silica (CH/AcOEt = 5:1).

Yield: 174 mg **4** (55%); colourless oil; $R_f = 0.32$ (CH/AcOEt = 5:1), 0.57 (CH/AcOEt = 1:1); $[\alpha]_D^{20} = +44.6$ ($c = 0.1$, $CHCl_3$); IR (neat): $\nu = 2949$ (s), 1731 (vs), 1436 (m), 1250 (s), 1168 (m) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 203 (3.326) nm; ^1H NMR ($CDCl_3$): $\delta = 0.81$ (s, 3H, 19-H), 0.85 (ddd, $J = 14.8$ Hz, $J = 6.2$ Hz, $J = 5.7$ Hz, 1H, 11-H), 0.94 (m, 1H, 1-H_{ax}), 1.08 (d, $J = 6.9$ Hz, 3H, 17-H/18-H), 1.09 (d, $J = 6.9$ Hz, 3H, 18-H/17-H), 1.12 (s, 3H, 20-H), 1.25 (ddd, $J = 11.4$ Hz, $J = 5.2$ Hz, $J = 3.4$ Hz; 1H, 9-H), 1.36 (qd, $3\times J = 12.8$–13.3 Hz, $J = 4.0$ Hz, 1H, 6-H_{ax}), 1.52 (m, 1H, 3-H_{eq}), 1.5–1.8 (m, 2H, 2-H), 1.57 (m, 1H, 7-H_{ax}), 1.67 (m, 1H, 3-H_{ax}), 1.74 (m, 1H, 1-H_{eq}), 1.75 (m, 1H, 5-H), 1.78 (m, 1H, 11-H), 1.80 (m, 1H, 7-H_{eq}), 2.29 (td, $2\times J = 12.0$ Hz, $J = 4.1$ Hz, 1H, 8-H), 2.32 (dd, $J = 16.1$ Hz, $J = 5.4$ Hz, 1H, 13-H), 2.46 (dd, $J = 16.1$ Hz, $J = 8.4$ Hz, 1H, 13-H), 2.74 (sept, $J = 6.9$ Hz, 1H, 16-H), 3.00 (m, 1H, 12-H), 3.60 (s, 3H, 25-H), 3.61 (s, 3H, 23-H), 3.68 (s, 3H, 24-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (q, C-19), 16.7 (q, C-20), 17.78 (q, C-17/C-18), 17.82 (t, C-2), 18.5 (q, C-18/C-17), 23.3 (t, C-6), 30.3 (t, C-7), 31.4 (t, C-11), 36.5 (t, C-13), 36.8 (t, C-3), 37.8 (s, C-10), 37.9 (t, C-1), 41.0 (d, C-16), 45.5 (d, C-12), 47.2 (d, C-8), 47.5 (s, C-4), 48.9 (d, C-5), 50.0 (d, C-9), 51.5 (q, C-25), 51.6 (q, C-24), 51.9 (q, C-23), 172.5 (s, C-14), 176.4 (s, C-22), 178.8 (s, C-21), 216.2 (s, C-15) ppm; MS (70 eV): *m/z* (%) = 452 (16) [M^+], 409 (28), 381 (13), 321 (36), 289 (31), 235 (31), 158 (100), 71 (24), 43 (76); $C_{25}H_{40}O_7$ (452.6); calc.: C 66.35, H 8.91; found: C 66.26, H 8.97.

Methyl-(1R-(1α,4aβ,4bα,6β,8aβ,10aα))-8a-formyl-1,4a-dimethyl-6-(2-methyl-1-oxopropyl)-8-oxo-perhydro-1-phenanthrene-carboxylate (**5**)

Ozone was bubbled through a solution of 2.9 g (8.1 mmol) **2** in 120 ml dry AcOEt at −70°C until the blue colour became persistent. The excess of ozone was removed by oxygen at this temperature, and 10 ml dimethylsulfide were added. This mixture was allowed to reach room temperature and was stirred for 24 h. The residue obtained after evaporation was dissolved in 300 ml Et_2O, washed with brine, and dried over Na_2SO_4. The crude product was obtained after evaporation of the solvent and purified by CC over silica CH/AcOEt (3:1).

Yield: 3.0 g **5** (95%); white crystals (from CH); m.p.: 170–172°C; $R_f = 0.34$ (CH/AcOEt = 3:1), 0.20 (CH/AcOEt = 6:1); $[\alpha]_D^{20} = +128.1$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 2948$ (s), 1731 (vs), 1712 (vs), 1697 (vs), 1469 (m), 1446 (m), 1244 (s) cm^{-1}; UV (MeOH) λ_{max} ($lg\varepsilon$) = 203 (3.128), 316 (1.968) nm; ^1H NMR ($CDCl_3$): $\delta = 0.84$ (s, 3H, 20-H), 1.02 (m, 1H, 1-H_{ax}), 1.08 (d, $J = 6.9$ Hz, 3H, 18-H/19-H), 1.09 (d, $J = 6.9$ Hz, 3H, 19-H/18-H), 1.11 (s, 3H, 21-H), 1.23 (m, 1H, 6-H_{eq}), 1.46 (m, $3\times J = 12.4$–13.7 Hz, $J = 3.3$ Hz, 1H, 6-H_{ax}), 1.5–1.7 (m, 2H, 2-H), 1.54 (m, 1H, 3-H_{eq}), 1.60 (m, 1H, 9-H), 1.61 (m, 1H, 7-H_{ax}), 1.68 (m, 1H, 3-H_{ax}), 1.71 (m, 1H, 1-H_{eq}), 1.72 (m, 1H, 5-H), 1.92 (m, 1H, 11-H_{eq}), 2.15 (q, $3\times J = 13.2$ Hz, 1H, 11-H_{ax}), 2.37 (dt, $J = 14.2$ Hz, $2\times J = 3.2$ Hz, 1H, 7-H_{eq}), 2.45 (ddd, $J = 14.1$ Hz, $J = 4.2$ Hz, $J_{11eq,13eq} = 1.8$ Hz, 1H, 13-H_{eq}), 2.73 (sept, $J = 6.9$ Hz, 1H, 17-H), 2.82 (dd, $J = 14.1$ Hz, $J = 13.1$ Hz, 1H, 13-H_{ax}), 2.95 (tt, $2\times J = 12.0$–13.0 Hz, $2\times J = 4.0$–4.2 Hz, 1H, 12-H), 3.63 (s, 3H, 23-H), 9.99 (s, 1H, 15-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.3$ (q, C-21), 16.6 (q, C-20), 17.8 (t, C-2), 18.1 (q, C-18/C-19), 18.4 (q, C-19/C-18), 21.0 (t, C-6), 22.5 (t, C-11), 28.9 (t, C-7), 36.6 (t, C-3), 38.1 (t, C-1), 38.5 (s, C-10), 39.4 (d, C-17), 42.1 (t, C-13), 47.4 (s, C-4), 48.2

(d, C-12), 49.6 (d, C-5), 51.9 (q, C-23), 59.9 (d, C-9), 66.7 (s, C-8), 178.5 (s, C-22), 199.5 (d, C-15), 204.1 (s, C-14), 213.2 (s, C-16) ppm; MS (70 eV): *m/z* (%) = 390 (7) [M^+], 362 (34), 251 (78), 191 (100), 123 (66), 71 (44), 43 (96); $C_{23}H_{34}O_5$ (390.5); calc.: C 70.74, H 8.78; found: C 70.65, H 8.76.

Methyl-(1R-(1α,4aβ,4bα,6β,8aβ,10aα))-8a-hydroxymethyl-1,4a-dimethyl-6-(2-methyl-1-oxopropyl)-8-oxo-perhydro-1-phenanthren-carboxylate (**6**)

To a solution of 1.0 g (2.6 mmol) **5** in dry *THF* at −70°C under Ar, 5.5 ml (2.7 mmol) of a 0.5 *M* solution of lithium-*tris*-((3-ethyl-3-pentyl)-oxo-)-aluminum hydride in *THF* were added dropwise within 2 h. This mixture was stirred for 4 h at −70°C; then a saturated aqueous solution of K-Na-tartrate was added. After addition of water and CH_2Cl_2 this mixture was continuously extracted for 12 h with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporation yielded the crude product which was recrystallised from CH/AcOEt (6:1).

Yield: 930 mg **6** (91%); white crystals; m.p.: 198–199°C; $R_f = 0.33$ (CH_2Cl_2/MeOH = 98:2); $[\alpha]_D^{20} = +80.8$ ($c = 0.1$, $CHCl_3$); IR (KBr) $\nu = 3450$ (s), 2931 (m), 1726 (vs), 1710 (s), 1697 (vs), 1460 (m), 1251 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 203 (3.276), 284 (2.426) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.80$ (s, 3H, 20-H), 0.92 (m, 1H, 1-H_{ax}), 1.04 (d, $J = 6.8$ Hz, 3H, 18-H/19-H), 1.05 (d, $J = 6.9$ Hz, 3H, 19-H/18-H), 1.08 (m, 1H, 6-H_{eq}), 1.09 (s, 3H, 21-H), 1.30 (m, 1H, 9-H), 1.35–1.7 (m, 2H, 2-H), 1.42 (m, 1H, 3-H_{eq}), 1.48 (m, 1H, 6-H_{ax}), 1.55–1.9 (m, 2H, 11-H), 1.58 (m, 1H, 7-H_{ax}), 1.61 (m, 1H, 5-H), 1.64 (m, 1H, 1-H_{eq}), 1.71 (m, 1H, 3-H_{ax}), 1.89 (m, 1H, 7-H_{eq}), 2.26 (m, 1H, 13-H_{eq}), 2.68 (sept, $J = 6.8$ Hz, 1H, 17-H), 2.74 (m, 1H, 13-H_{ax}), 2.84 (m, 1H, 12-H), 3.59 (s, 3H, 23-H), 3.86 (d, $J = 11.3$ Hz, 1H, 15-H), 4.10 (d, $J = 11.3$ Hz, 1H, 15-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.2$ (q, C-21), 16.4 (q, C-20), 17.8 (t, C-2), 18.0 (q, C-18/C-19), 18.2 (q, C-19/C-18), 20.6 (t, C-6), 22.6 (t, C-11), 28.5 (t, C-7), 36.2 (t, C-3), 37.8 (s, C-10), 38.7 (t, C-1), 39.7 (d, C-17), 40.4 (t, C-13), 47.5 (s, C-4), 48.4 (d, C-12), 50.3 (d, C-5), 51.9 (q, C-23), 55.5 (s, C-8), 57.2 (d, C-9), 61.8 (t, C-15), 178.8 (s, C-22), 211.9 (s, C-14), 214.5 (s, C-16) ppm; MS (70 eV): *m/z* (%) = 392 (7) [M^+], 362 (30), 319 (14), 303 (22), 181 (51), 121 (82), 71 (61), 43 (100); $C_{23}H_{36}O_5$ (392.5); calc.: C 70.38, H 9.24; found: C 70.40, H 9.22.

Methyl-(1R-(1α,4aβ,5β(2R),8aα))-5-(3-methoxycarbonyl-2-(2-methyl-1-oxoethyl)-propyl)-1,4a-dimethyl-6-oxo-perhydro-1-naphthalene-carboxylate* (**7**) and *Methyl-(1R-(1α,4aβ,4bα,6β,8aβ,10aα))-1,4a-dimethyl-6-(2-methyl-1-oxopropyl)-8-oxo-perhydro-1-phenanthrene carboxylate* (**8**)

To a solution of 3.4 g (8.7 mmol) **5** in 180 ml acetone, 20 ml *Jones* reagent (7 g CrO_3 dissolved in 50 ml H_2O, cooled with ice, 6 ml H_2SO_4 added) were added dropwise during 48 h at RT. The excess of reagent was destroyed with *i*-propanol, the mixture was filtered, and the solvent removed *in vacuo*. To the residue 40 ml 5% NaOH were added, and the mixture was extracted three times with Et_2O. The combined organic phases were washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave the crude product which was purified by CC (silica, CH/AcOEt (4:1)) to afford 690 mg (22%) **8** (white crystals).

The aqueous phase was acidified with 2 *N* H_2SO_4 and then extracted three times with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated. The crude product was purified by CC over silica with CH/AcOEt (3:1) to afford 2.6 g (74%) **7** (colourless oil).

7: $R_f = 0.29$ (CH/AcOEt = 3:1); $[\alpha]_D^{20} = -29.6$ ($c = 0.2$, $CHCl_3$); IR (neat): $\nu = 2949$ (s), 1713 (vs), 1436 (m), 1248 (s), 1169 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 202 (3.428), 274 (2.408) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.64$ (s, 3H, 19-H), 0.97 (s, 3H, 17-H/18-H), 1.03 (s, 3H, 18-H/17-H), 1.22 (td, $2\times J = 12.7$–13.0, $J = 4.0$ Hz, 1H, 1-H_{ax}), 1.4–1.6 (m, 2H, 2-H), 1.49 (m, 1H, 11-H), 1.52 (m, 1H, 6-H_{eq}), 1.58 (m, 1H, 3-H_{eq}), 1.63 (m, 1H, 6-H_{ax}), 1.71 (m, 1H, 3-H_{ax}), 1.72 (m, 1H, 1-H_{eq}), 1.85 (ddd, $J = 13.6$ Hz, $J = 10.0$ Hz, $J = 4.3$ Hz, 1H, 11-H), 2.03 (d, $J = 9.8$ Hz, 1H, 9-H), 2.2–2.3 (m, 2H, 7-H),

2.25 (m, 1H, 5-H), 2.25 (m, 1H, 13-H), 2.59 (dd, $J = 16.0$ Hz, $J = 8.1$ Hz, 1H, 13-H), 2.67 (sept, $J = 6.9$ Hz, 1H, 16-H), 3.08 (m, 1H, 12-H), 3.59 (s, 3H, 23-H), 3.63 (s, 3H, 22-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.7$ (q, C-19), 16.5 (q, C-20), 17.7 (t, C-2), 17.9 (q, C-17/C-18), 18.1 (q, C-18/C-17), 23.4 (t, C-11), 25.8 (t, C-6), 36.8 (t, C-13), 36.9 (t, C-3), 37.9 (t, C-1), 40.2 (d, C-16), 41.8 (s, C-10), 41.9 (t, C-7), 44.3 (d, C-12), 47.3 (s, C-4), 48.5 (d, C-5), 51.5 (q, C-23), 52.0 (q, C-22), 61.2 (d, C-9), 172.1 (s, C-14), 178.5 (s, C-21), 210.3 (s, C-8), 216.1 (s, C-15) ppm; MS (FD): *m/z* (%) = 408 (100) [M^+]; MS (70 eV): *m/z* (%) = 408 (31) [M^+], 365 (39), 337 (8), 317 (62), 305 (76), 223 (62), 158 (68), 121 (84), 71 (48), 43 (100); $C_{23}H_{36}O_6$ (408.5); calc.: C 67.62, H 8.88; found: C 67.59, H 8.87.

8: M.p.: 113°C; $R_f = 0.39$ (CH/AcOEt = 4:1), $[\alpha]_D^{20} = +50.5$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 2937$ (s), 1731 (vs), 1707 (vs), 1444 (m), 1244 (s), 1172 (m) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 217 (2.477), 295 (1.380) nm; ^{1}H NMR (C_6D_6): $\delta = 0.58$ (s, 3H, 19-H), 0.65 (td, $2\times J = 13.3$ Hz, $J = 4.0$ Hz, 1H, 1-H_{ax}), 0.80 (td, $2\times J = 12.2$ Hz, $J = 2.9$ Hz, 1H, 9-H), 0.87 (d, $J = 6.9$ Hz, 3H, 17-H/18-H), 0.91 (d, $J = 6.9$ Hz, 3H, 18-H/17-H), 1.1–1.3 (m, 2H, 6-H), 1.19 (m, 1H, 11-H_{ax}), 1.20 (s, 3H, 20-H), 1.2–1.4 (m, 2H, 2-H), 1.32 (m, 1, 1-H_{eq}), 1.49 (m, 1H, 3-H_{eq}, 1.54 (m, 1H, 7-H_{ax}), 1.58 (m, 1H, 11-H_{eq}), 1.68 (m, 1H, 5-H), 1.70 (m, 1H, 8-H), 1.74 (td, $2\times J = 13.0$ Hz, $J = 4.4$ Hz, 1H, 3-H_{ax}), 1.95 (m, 1H, 7-H_{eq}), 2.24 (m, 1H, 16-H), 2.26 (m, 1H, 13-H_{ax}), 2.34 (ddd, $J = 13.4$ Hz, $J = 3.7$ Hz, $J_{11eq,13eq} = 2.0$ Hz, 1H, 13-H_{ax}), 2.42 (tt, $2\times J = 12.5$–12.6 Hz, $2\times J = 3.4$–3.6 Hz, 1H, 12-H), 3.36 (s, 3H, 22-H) ppm; ^{13}C NMR (C_6D_6): $\delta = 13.9$ (q, C-19), 17.0 (q, C-20), 18.1 (q, C-17/C-18), 18.29 (q, C-18/C-17), 18.34 (t, C-2), 23.4 (t, C-6), 26.5 (t, C-7), 27.2 (t, C-11), 36.9 (s, C-10), 37.2 (t, C-3), 38.2 (t, C-1), 39.5 (d, C-16), 43.2 (t, C-13), 47.6 (s, C-4), 47.7 (d, C-12), 48.7 (d, C-8), 49.0 (d, C-5), 51.5 (q, C-22), 55.1 (d, C-9), 178.3 (s, C-21), 209.2 (s, C-14), 212.6 (s, C-15) ppm; MS (70 eV): *m/z* (%) = 362 (50) [M^+], 319 (41), 303 (48), 291 (22), 259 (46), 231 (36), 181 (54), 123 (70), 71 (60), 43 (100); $C_{22}H_{34}O_4$ (362.5); calc.: C 72.89, H 9.45; found: C 72.80, H 9.45.

Methyl-(4α,13S,14R)-13,14-dihydroxy-13-(1-methylethyl)-15-oxo-17,19-dinoratisan-4-carboxylate (**9**)

A mixture of 480 mg (4.3 mmol) trimethylamine-N-oxide dihydrate, 0.3 ml pyridine, 2 ml H_2O, 10 ml *tert*-butanol, and 1.0 g (2.8 mmol) **2** under Ar was heated to 100°C. During 4 days, 64 mg (0.25 mmol) OsO_4 dissolved in 3 ml *tert*-butanol were added in small portions. After cooling to RT, 15 ml 20% $Na_2S_2O_5$ solution were added and the solvent was evaporated. The residue was mixed with H_2O and Et_2O and extracted continuously with Et_2O during 12 h. The organic phase was dried over Na_2SO_4, the solvent evaporated, and the residue crystallized from CH/AcOEt (3:1).

Yield: 945 mg **9** (86%); colourless crystals ($CHCl_3$); m.p.: 219°C; $R_f = 0.15$ (CH/AcOEt = 2:1); $[\alpha]_D^{20} = +37.0$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 3515$ (m), 3403 (s), 2950 (s), 1729 (vs), 1712 (vs), 1469 (m), 1246 (s) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 201 (3.119), 265 (1.913) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.94$ (m, 1H, 1-H_{ax}), 0.95 (d, $J = 6.8$ Hz, 6H, 18-H u. 19-H), 1.03 (s, 3H, 20-H), 1.09 (m, 1H, 6-H_{eq}), 1.16 (s, 3H, 21-H), 1.41 (m, 1H, 6-H_{ax}), 1.45–1.6 (m, 2H, 2-H), 1.49 (m, 1H, 9-H), 1.54 (m, 1H, 3-H_{eq}), 1.56 (m, 1H, 11-Hβ), 1.58 (m, 1H, 1-H_{eq}), 1.63 (m, 1H, 5-H), 1.67 (m, 1H, 7-H_{ax}), 1.67 (m, 1H, 11-Hα), 1.68 (m, 1H, 3-H_{ax}), 2.00 (m, 1H, 7-H_{eq}), 2.03 (m, 1H, 16-Hα), 2.05 (m, 1H, 17-H), 2.42 (s_{br}, 1H, 12-H), 2.51 (d, $J = 7.0$ Hz, 1H, 14-OH), 2.55 (s_{br}, 1H, 13-OH), 2.73 (ddd, $J = 18.6$ Hz, $J = 3.7$ Hz, $J_{11\beta,16\beta} = 2.7$ Hz, 1H, 16-Hβ), 3.62 (s, 3H, 23-H), 3.97 (d, $J = 7.0$ Hz, 1H, 14-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.0$ (q, C-18/C-19), 16.2 (q, C-20), 16.4 (q, C-19/C-18), 16.8 (q, C-21), 17.3 (t, C-2), 20.6 (t, C-6), 21.6 (t, C-11), 24.4 (t, C-7), 33.4 (d, C-17), 34.3 (d, C-12), 36.4 (t, C-3), 37.9 (s, C-10), 38.6 (t, C-16), 38.9 (t, C-1), 47.08 (d, C-9), 47.12 (s, C-4), 49.3 (d, C-5), 52.0 (t, C-23), 52.5 (s, C-8), 72.0 (d, C-14), 73.8 (s, C-13), 178.9 (s, C-22), 214.8 (s, C-15) ppm; MS (FD): *m/z* (%) = 393 (100) [$(M+1)^+$], 374 (51), 331 (95); MS (70 eV): *m/z* (%) = 374 (1), 349 (4), 331 (100), 181 (21), 121 (42), 43 (22); $C_{23}H_{36}O_5$ (392.5); calc.: C 70.38, H 9.24; found: C 70.29, H 9.25.

Methyl-(4α,8α,12α,14R,16α)-14-chloro-14-cyano-16,17-epoxy-17,17-dimethyl-15-oxo-19-noratisan-4-carboxylate (**10**) and *Methyl-(4α,15β)-13-acetyl-15-chloro-15-cyano-17,19-dinoratis-13-en-4-carboxylate* (**11**)

tert-Butylchromate solution: 6.8 g CrO_3 were dissolved in a mixture of 60 ml dry *THF*, 20 ml *tert*-butanol, 10 ml acetic acid, and 3 ml acetic anhydride. 65 ml of this solution and 2.0 g (5.0 mmol) **1** in 40 ml abs. CCl_4 were refluxed under Ar for 24 h. An additional portion of 20 ml *tert*-butylchromate solution was added, and refluxing was continued for 24 h. After cooling to RT, 100 ml ice water and 200 ml $CHCl_3$ were added, and the aqueous layer was extracted three times with $CHCl_3$. The combined organic phases were washed with H_2O, 5% NaOH, and H_2O, dried over Na_2SO_4, and evaporated. The components of the crude product were separated by CC over silica with CH/AcOEt (4:1). Yield: 1.6 g (74%) **10** (white crystals) and 420 mg **11** (21%).

10: M.p.: 172–173°C; $R_f = 0.21$ (CH/AcOEt = 4:1), 0.28 (CH/AcOEt = 3:1); $[\alpha]_D^{20} = -82.1$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 2934$ (s), 2237 (w), 1732 (vs), 1447 (m), 1256 (s), 1179 (s) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 204 (3.763), 316 (1.781) nm; ^1H NMR ($CDCl_3$): $\delta = 0.60$ (s, 3H, 20-H), 1.05 (m, 1H, 1-H_{ax}), 1.07 (s, 3H, 21-H), 1.15 (m, 1H, 6-H_{eq}), 1.32 (m, 1H, 7-H_{ax}), 1.33 (m, 1H, 6-H_{ax}), 1.40 (s, 3H, 18-H), 1.4–1.6 (m, 2H, 2-H), 1.45 (s, 3H, 19-H), 1.49 (m, 1H, 3-H_{eq}), 1.59 (m, 1H, 1-H_{eq}), 1.73 (m, 1H, 5-H), 1.75 (m, 1H, 3-H_{ax}), 1.75 (m, 1H, 11-Hβ), 1.95 (td, $2\times J = 11.0$–14.0 Hz, $J = 3.0$ Hz, 1H, 11-Hα), 2.08 (m, 1H, 12-H), 2.12 (m, 1H, 9-H), 2.61 (m, 1H, 7-H_{eq}), 2.66 (dt, $J = 16.0$ Hz, $J = 2.5$ Hz, $J_{11\beta,16\beta} = 2.5$ Hz, 1H, 16-Hβ), 2.87 (dd, $J = 16.0$ Hz, $J = 3.1$ Hz, 1H, 16-Hα), 3.64 (s, 3H, 24-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (q, C-20), 16.6 (q, C-21), 17.3 (t, C-2), 18.7 (q, C-18/C-19), 20.9 (q, C-19/C-18), 21.0 (t, C-6), 23.6 (t, C-11), 27.1 (t, C-7), 32.5 (d, C-12), 36.2 (t, C-3), 37.1 (t, C-1), 37.9 (s, C-10), 42.9 (t, C-16), 46.9 (s, C-4), 48.5 (d, C-9), 48.7 (d, C-5), 52.0 (q, C-24), 55.6 (q, C-8), 62.7 (s, C-15), 67.1 (s, C-13), 67.7 (s, C-17), 118.5 (s, C-23), 178.3 (s, C-22), 205.8 (s, C-14) ppm; MS (70 eV): *m/z* (%) = 435 (8) [$(M+2)^+$], 433 (25) [M^+], 346 (100), 217 (35), 165 (81), 55 (28), 41 (42); $C_{24}H_{32}ClNO_4$ (434.0); calc.: C 66.42, H 7.43, N 3.23; found: C 66.50, H 7.42, N 3.31.

11: M.p.: 212°C; $R_f = 0.28$ (CH/AcOEt = 9:1), 0.42 (CH/AcOEt = 3:1); $[\alpha]_D^{20} = 8.4$ ($c = 0.2$, $CHCl_3$); IR (KBr): $\nu = 2942$ (s), 2236 (w), 1713 (vs), 1674 (vs), 1387 (m), 1263 (s), 1184 (m) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 233 (4.103) nm; ^1H NMR ($CDCl_3$): $\delta = 0.49$ (s, 3H, 19-H), 0.98 (m, 1H, 1-H_{ax}), 1.11 (s, 3H, 20-H), 1.13 (m, 1H, 11-Hβ), 1.30 (m, 1H, 6-H_{eq}), 1.3–1.5 (m, 2H, 2-H), 1.36 (m, 1H, 1-H_{eq}), 1.48 (m, 1H, 3-H_{eq}), 1.53 (m, 1H, 6-H_{ax}), 1.62 (m, 1H, 11-Hα), 1.71 (m, 1H, 3-H_{ax}), 1.78 (m, 1H, 5-H), 1.82 (m, 1H, 7-H_{ax}), 1.90 (m, 1H, 9-H), 1.92 (dt, $J = 14.9$ Hz, $J = 3.2$ Hz, $J_{11\beta,16\beta} = 3.2$ Hz, 1H, 16-Hβ), 2.30 (dt, $J = 13.4$ Hz, $2\times J = 2.9$–3.5 Hz, 1H, 7-H_{eq}), 2.30 (s, 3H, 18-H), 2.50 (dd, $J = 14.9$ Hz, $J = 2.2$ Hz, 1H, 16-Hα), 3.40 (m, 1H, 12-H), 3.64 (s, 3H, 23-H), 6.68 (s_{br}, 1H, 14-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.1$ (q, C-19), 16.7 (q, C-20), 17.0 (t, C-2), 21.3 (t, C-6), 24.9 (q, C-18), 26.4 (t, C-11), 27.2 (d, C-12), 31.9 (t, C-7), 36.3 (t, C-3), 37.7 (t, C-1), 37.9 (s, C-10), 46.4 (t, C-16), 46.9 (s, C-4), 47.6 (s, C-8), 48.5 (d, C-5), 50.1 (d, C-9), 52.0 (q, C-23), 64.3 (s, C-15), 119.4 (s, C-22), 142.4 (d, C-14), 144.0 (s, C-13), 178.5 (s, C-21), 194.3 (s, C-17) ppm; MS (70 eV): *m/z* (%) = 405 (15) [$(M+2)^+$], 403 (44) [M^+], 388 (6), 344 (7), 316 (37), 256 (31), 181 (24), 123 (40), 43 (100); $C_{23}H_{30}ClNO_3$ (403.9); calc.: C 68.39, H 7.49, N 3.47; found: C 68.44, H 7.43, N 3.51.

Methyl-(4α,8α,12α,16α)-16,17-epoxy-17,17-dimethyl-14,15-dioxo-19-noratisan-4-carboxylate (**12**)

The same procedure as described for **10** and **11** has been used. Typical quantities: 1.9 g (5.3 mmol) **2** in 40 ml abs. *THF*, 70 ml *tert*-butylchromate solution; CC: silica, CH/AcOEt (3:1).

Yield: 1.7 g **12** (83%); white crystals; m.p.: 142°C; $R_f = 0.38$ (CH/AcOEt = 3:1); $[\alpha]_D^{20} = +24.7$ ($c = 0.5$, $CHCl_3$); IR (KBr): $\nu = 2952$ (s), 1736 (vs), 1720 (vs), 1706 (vs), 1394 (m), 1235 (s), 1106 (m) cm^{-1}; UV (MeOH): λ_{max} ($lg\varepsilon$) = 203 (3.861), 282 (2.520) nm; ^1H NMR ($CDCl_3$): $\delta = 0.67$ (s,

3H, 20-H), 0.95 (m, 1H, 1-H_{ax}), 1.08 (s, 3H, 21-H), 1.11 (m, 1H, 6-H_{eq}), 1.36 (qd, $3\times J = 12.6$–13.6 Hz, $J = 3.9$ Hz, 1H, 6-H_{ax}), 1.45–1.65 (m, 2H, 2-H), 1.48 (s, 3H, 9-H), 1.49 (s, 3H, 18-H), 1.52 (m, 1H, 3-H_{eq}), 1.52 (ddd, $J = 13.2$ Hz, $J = 4.9$ Hz, $J = 3.5$ Hz, 1H, 1-H_{eq}), 1.65 (m, 1H, 3-H_{ax}), 1.66 (m, 1H, 5-H), 1.68 (td, $2\times J = 13.9$–14.1 Hz, $J = 5.1$ Hz, 1H, 7-H_{ax}), 1.79 (dd, $J = 11.5$ Hz, $J = 5.8$ Hz, 1H, 9-H), 1.88 (dddd, $J = 14.4$ Hz, $J = 5.8$ Hz, $J = 3.0$ Hz, $J_{11\beta,16\beta} = 2.5$ Hz, 1H, 11-Hβ), 1.98 (ddd, $J = 14.4$ Hz, $J = 11.5$ Hz, $J = 3.0$ Hz, 1H, 11-Hα), 2.25 (ddd, $J = 14.1$ Hz, $J = 3.8$ Hz, $J = 2.7$ Hz, 1H, 7-H_{eq}), 2.34 (quint, $J = 3.0$ Hz, 1H, 12-H), 2.50 (dd, $J = 19.4$ Hz, $J = 3.0$ Hz, 1H, 16-Hα), 2.55 (ddd, $J = 19.4$ Hz, $J = 3.0$ Hz, $J_{11\beta,16\beta} = 2.5$ Hz, 1H, 16-Hβ), 3.61 (s, 3H, 23-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ (q, C-20), 16.5 (q, C-21), 17.4 (t, C-2), 18.7 (q, C-19), 20.5 (t, C-6), 20.6 (q, C-18), 22.2 (t, C-7), 24.1 (t, C-11), 31.5 (d, C-12), 36.5 (t, C-3), 37.2 (t, C-1), 38.5 (s, C-10), 40.3 (t, C-16), 47.0 (s, C-4), 48.8 (d, C-5), 49.1 (d, C-9), 52.0 (q, C-23), 67.4 (s, C-17), 68.4 (s, C-13), 69.0 (s, C-8), 178.5 (s, C-22), 204.9 (s, C-14), 205.9 (s, C-15) ppm; MS (70 eV): *m/z* (%) = 388 (37) [M^+], 360 (42), 329 (56), 300 (48), 121 (100), 41 (81); $C_{23}H_{32}O_5$ (388.5); calc.: C 71.11, H 8.30; found: C 71.15, H 8.26.

Methyl-(4α,8α,12α,16α)-16,17-epoxy-17,17-dimethyl-14,15-dioxo-14α-homo-14a-oxa-19-noratisan-4-carboxylate (**13**)

A mixture of 240 mg (0.62 mmol) **12**, 600 mg *mCPBA* (93%, dried over P_2O_5) in 7 ml abs. 1,2-dichloroethane, and 140 mg freshly distilled CF_3COOH dissolved in 2 ml abs. 1,2-dichloroethane under Ar was stirred for 22 h at RT and in the absence of light. Then additional 400 mg *mCPBA* in 2 ml 1,2-dichloroethane were added and the mixture was stirred for further 4 days. 100 ml Et_2O were added, and this mixture was washed twice with 1% Kl, three times with 10% $Na_2S_2O_3$, twice with 5% NaOH, and once with brine, and dried over Na_2SO_4. Evaporation and recrystallization from CH/AcOEt (1:1) yielded 235 mg (94%) **13** as white crystals.

M.p.: 171°C; $R_f = 0.27$ (CH_2Cl_2/MeOH = 60:1); $[\alpha]_D^{20} = +5.7$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 2940$ (s), 1729 (vs), 1464 (m), 1241 (s), 1186 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 204 (3.804), 321 (2.104) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.65$ (s, 3H, 20-H), 1.04 (m, 1H, 1-H_{ax}), 1.09 (s, 3H, 21-H), 1.12–1.25 (m, 2H, 6-H), 1.40 (s, 3H, 19-H), 1.47 (s, 3H, 18-H), 1.5–1.6 (m, 2H, 2-H), 1.55 (m, 1H, 3-H_{eq}), 1.57 (m, 1H, 7-H_{ax}), 1.65 (m, 1H, 1-H_{eq}), 1.68 (m, 1H, 3-H_{ax}), 1.88 (dd, $J = 11.4$ Hz, $J = 3.2$ Hz, 1H, 5-H), 2.04 (m, 2H, 11-H), 2.13 (s_{br}, 1H, 12-H), 2.37 (t, $J = 2.37$ Hz, 1H, 9-H), 2.80 (dt, $J = 13.5$ Hz, $2\times J = 3.3$ Hz, 1H, 7-H_{eq}), 2.90 (dd, $J = 19.0$ Hz, $J = 5.2$ Hz, 1H, 16-Hα), 3.01 (d_{br}, $J = 19.0$ Hz, 1H, 16-Hβ), 3.63 (s, 3H, 23-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (q, C-20), 16.8 (q, C-21), 17.2 (t, C-2), 18.8 (q, C-19), 20.7 (q, C-18), 21.4 (t, C-6), 23.8 (t, C-11), 30.1 (d, C-12), 32.0 (t, C-7), 36.4 (t, C-3), 37.3 (t, C-1), 38.68 (t, C-16), 38.70 (s, C-4), 46.9 (s, C-10), 48.4 (d, C-5), 51.2 (d, C-9), 52.0 (q, C-23), 68.3 (s, C-13), 69.5 (s, C-17), 85.0 (s, C-8), 169.8 (s, C-15), 178.3 (s, C-22), 199.9 (s, C-14) ppm; MS (70 eV): *m/z* (%) = 404 (16) [M^+], 376 (69), 360 (48), 251 (55), 223 (88), 121 (100), 41 (95); $C_{23}H_{32}O_6$ (404.5); calc.: C 68.29, H 7.97; found: C 68.11, H 7.92.

Methyl-(4α,13R,15α)-15-chloro-15-cyano-13-hydroxy-13-(1-methylvinyl)-14-oxo-17,19-dinoratisan-4-carboxylate (**14**)

A solution of 860 mg (1.98 mmol) **10** in 20 ml 90% formic acid and 2 ml 85% H_3PO_4 was heated to 100°C for 15 h. After cooling, 100 ml ice water were added and the mixture was extracted three times with Et_2O. The combined organic phases were washed with 5% NaOH until the aqueous phase remained basic. After washing with brine, the etheral solution was dried over Na_2SO_4 and the solvent was evaporated; CC: silica (CH/AcOEt = 3:1).

Yield: 660 mg **14** (77%); pale yellow crystals; m.p.: 84°C, $R_f = 0.29$ (CH/AcOEt = 3:1); $[\alpha]_D^{20} = -108.6$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 3454$ (s), 2928 (s), 1728 (vs), 1450 (m), 1255 (s), 1031 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 204 (3.419), 291 (1.972) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.57$

(s, 3H, 20-H), 1.02 (m, 1H, 1-H_{ax}), 1.08 (s, 3H, 21-H), 1.20 (m, 2H, 6-H), 1.35–1.55 (m, 2H, 2-H), 1.42 (m, 1H, 7-H_{ax}), 1.49 (m, 1H, 3-H_{eq}), 1.52 (m, 1H, 1-H_{eq}), 1.52 (m, 1H, 11-Hβ), 1.70 (m, 1H, 3-H_{ax}), 1.71 (m, 1H, 5-H), 1.76 (m, 1H, 11-Hα), 1.82 (s, 3H, 19-H), 2.03 (m, 1H, 9-H), 2.47 (s_{br}, 1H, 12-H), 2.63 (dd, $J = 15.5$ Hz, $J = 2.4$ Hz, 1H, 16-Hα), 3.03 (dt, $J = 15.5$ Hz, $J = 3.0$ Hz, $J_{11\beta,16\beta} = 3.0$ Hz, 1H, 16-Hβ), 3.60 (s, 3H, 24-H), 5.15 (m, 2H, 18-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 15.5$ (q, C-20), 16.8 (q, C-21), 17.3 (t, C-2), 18.9 (q, C-19), 21.1 (t, C-6), 22.3 (t, C-11), 27.0 (t, C-7), 33.7 (d, C-12), 36.2 (t, C-3), 37.4 (s, C-10), 37.7 (t, C-1), 39.4 (t, C-16), 46.7 (s, C-4), 47.9 (d, C-5), 49.1 (d, C-9), 52.0 (q, C-24), 54.0 (s, C-8), 64.1 (s, C-15), 76.6 (s, C-13), 118.2 (t, C-18), 119.0 (s, C-23), 141.4 (s, C-17), 178.4 (s, C-22), 209.3 (s, C-14) ppm; MS (FD): $m/z = 433$ (100) [M^+], 405 (11), 369 (12); MS (70 eV): $m/z = 433$ (0.5) [M^+], 405 (3), 369 (100), 121 (53), 69 (59), 41 (55); $C_{24}H_{32}ClNO_4$ (434.0); calc.: C 66.42, H 7.43, N 3.23; found: C 66.41, H 7.43, N 3.25.

Methyl-(4α,13R,15α)-13-acetyl-15-chloro-15-cyano-13-hydroxy-14-oxo-17,19-dinoratisan-4-carboxylate (**15**)

A solution of 310 mg (0.71 mmol) **14** in 70 ml abs. MeOH was treated with ozone at −70°C until it turned blue. The excess of ozone was removed by oxygen at this temperature, and 7 ml $(CH_3)_2S$ were added. This mixture was allowed to reach RT. Evaporation of the solvent and recrystallization from CH/acetone (7:1) gave 130 mg (42%) **15** as white crystals. M.p.: 169–170°C; $R_f = 0.22$ (CH/AcOEt = 3:1), $[\alpha]_D^{20} = -153.7$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 3492$ (s), 2955 (s), 1726 (vs), 1435 (m), 1247 (s), 1181 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 203 (3.279), 331 (1.867) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.50$ (s, 3H, 19-H), 0.99 (td, $2\times J = 12.8$ Hz, $J = 3.7$ Hz, 1H, 1-H_{ax}), 1.10 (s, 3H, 20-H), 1.22 (m, 1H, 6-H_{eq}), 1.35–1.55 (m, 2H, 2-H), 1.40 (qd, $3\times J = 12.5$ Hz, $J = 3.5$ Hz, 1H, 6-H_{ax}), 1.44 (m, 1H, 7-H_{ax}), 1.54 (m, 1H, 3-H_{eq}), 155 (m, 1H, 1-H_{eq}), 1.68 (td, $2\times J = 13.0$ Hz, $J = 4.0$ Hz, 1H, 3-H_{ax}), 1.72 (m, 1H, 5-H), 1.8–2.0 (m, 2H, 11-H), 2.07 (dd, $J = 11.7$ Hz, $J = 7.1$ Hz, 1H, 9-H), 2.37 (s, 3H, 18-H), 2.58 (m, 1H, 7-H_{eq}), 2.60 (s_{br}, 1H, 12-H), 2.70 (dd, $J = 15.7$ Hz, $J = 2.3$ Hz, 1H, 16-Hα), 3.00 (dt, $J = 15.7$ Hz, $J = 2.8$ Hz, $J_{11\beta,16\beta} = 2.8$ Hz, 1H, 16-Hβ), 3.18 (s_{br}, 1H, 13-OH), 3.64 (s, 3H, 23-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.5$ (q, C-19), 16.8 (q, C-20), 17.3 (t, C-2), 21.0 (t, C-6), 22.0 (t, C-11), 24.9 (q, C-18), 27.2 (t, C-7), 32.9 (d, C-12), 36.3 (t, C-3), 37.6 (t, C-1), 37.8 (s, C-10), 40.6 (t, C-16), 46.8 (s, C-4), 48.1 (d, C-5), 49.4 (d, C-9), 52.1 (q, C-23), 54.6 (s, C-8), 63.7 (s, C-15), 80.2 (s, C-13), 118.4 (s, C-22), 178.4 (s, C-21), 201.3 (s, C-17), 209.4 (s, C-14) ppm; MS (70 eV): m/z (%) = 437 (10) [(M+2)]$^+$], 435 (26) [M^+], 393 (82), 306 (63), 43 (100); $C_{23}H_{30}ClNO_5$ (436.0); calc.: C 63.37, H 6.94, N 3.21; found: C 63.12, H 6.94, N 3.15.

Dimethyl-(3R-(1-3″R,4″aS*,4″bR*,8″R*,8″aR*)-3α,4aβ,4bα,8β,8aβ))-4b,4″b,8,8″-tetramethyl-3,3″-di-(2-methyl-1-oxopropyl)-perhydro-dispiro[phenanthreno-1(2H),3′-(1,2,4,5]tetroxan-6′,1″(2″H)-phenanthren)-8,8″-dicarboxylate* (**16**)

Bis-(trimethylsilyl)-peroxide was prepared according to the literature [26, 34]. 16 mg (0.07 mmol) trimethylsilytrifluoromethan sulfonate were dissolved in 3 ml abs. CH_2Cl_2 under extreme dry conditions and cooled to −50°C. At this temperature, 500 mg *bis*-(trimethylsilyl)-peroxide and a cold (−50°C) solution of 200 mg **8** in 1 ml abs. CH_2Cl_2 were added. This mixture was kept for two days at −22°C, and after the first day another portion of 200 mg peroxide and 16 mg trimethylsilyltrifluoromethan sulfonate was added. After pouring onto 20 ml ice cold saturated $NaHCO_3$ solution, extraction with three portions of Et_2O, washing with H_2O, drying of the combined organic phases, evaporation and recrystallization from CH/AcOEt (2:1), 190 mg **16** (91%) were obtained.

M.p.: 223–225°C; $R_f = 0.43$ (CH/AcOEt) = 3:1), 0.62 (CH/AcOEt = 2:1); IR (KBr): $\nu = 2938$ (m), 1727 (vs), 1712 (vs), 1453 (m), 1250 (s), 1145 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 203 (3.896), 264 (2.724) nm; ^{1}H NMR (C_6D_6): $\delta = 0.53$ (s, 3H, 19-H), 0.66 (m, 1H, 1-H_{ax}), 1.07 (d,

$J = 6.9$ Hz, 3H, 17-H/18-H), 1.08 (d, $J = 6.9$ Hz, 3H, 18-H/17-H), 1.1–1.3 (m, 2H, 6-H), 1.14 (s, 3H, 20-H), 1.15–1.3 (m, 2H, 2-H), 1.21 (m, 1H, 11-H_{ax}), 1.32 (m, 1H, 1-H_{eq}), 1.33 (m, 1H, 9-H), 1.47 (d_{br}, $J = 12.7$ Hz, 1H, 3-H_{eq}), 1.58 (m, 1H, 8-H), 1.64 (m, 1H, 7-H_{ax}), 1.64 (m, 1H, 13-H_{ax}), 1.69 (m, 1H, 3-H_{ax}), 1.69 (m, 1H, 11-H_{eq}), 1.78 (dd, $J = 11.7$ Hz, $J = 2.9$ Hz, 1H, 5-H), 2.13 (m, 1H, 7-H_{eq}), 2.57 (sept, $J = 6.9$ Hz, 1H, 17-H), 2.96 (tt, $2\times J = 12.2$–12.5 Hz, $2\times J = 3.0$ Hz, 1H, 12-H), 3.34 (s, 3H, 22-H), 3.61 (d_{br}, $J = 13.5$ Hz, 1H, 13-H_{eq}) ppm; ^{13}C NMR (C_6D_6): $\delta = 13.8$ (q, C-19), 17.0 (q, C-20), 18.2 (t, C-2), 18.3 (q, C-17/C-18), 18.4 (q, C-18/C-17), 23.8 (t, C-6), 25.0 (t, C-7), 27.3 (t, C-11), 33.2 (t, C-13), 36.8 (s, C-10), 37.1 (t, C-3), 38.1 (t, C-1), 40.1 (d, C-16), 43.3 (s, C-8), 43.7 (d, C-12), 47.5 (s, C-4), 49.1 (d, C-5), 49.9 (d, C-9), 51.4 (q, C-22), 109.6 (s, C-14), 178.3 (s, C-21), 214.1 (s, C-15) ppm; MS (FD): *m/z* (%) = 795 (5) [$(M+K)^+$], 779 (30) [$(M+Na)^+$], 394 (25), 378 (8), 362 (100); MS (70 eV); *m/z* (%) = 712 (0.3), 668 (1), 394 (1), 362 (31), 319 (30), 291 (22), 181 (38), 123 (58), 71 (71), 43 (100); $C_{44}H_{68}O_{10}$ (757.0); calc.: C 69.81, H 9.05, O 21.13; found: C 69.68, H 9.14, O 21.09.

(4R-(4α,4aα,6aα,9α,10α,11aα,11bβ))-4-Methoxycarbonyl-10-(methoxycarbonyl-methyl)-4,11b-dimethyl-9-(1-methylethyl)-perhydro-6a,9-epoxy-2H-naphtho[2,1-c][1,2]dioxepin (**17**)

The same procedure has been used as described for **16**. Typical quantities: 200 mg (0.49 mmol) **7** in 1 ml abs. CH_2Cl_2, 220 mg *bis*-(trimethylsilyl)-peroxide, 16 mg (0.07 mmol) trimethylsilyltrifluoromethan sulfonate in 3 ml abs. CH_2Cl_2; reaction time: 7 days (−22°C); CC: silica, CH/AcOEt = 4:1.

Yield: 160 mg **17** (77%); colourless oil; $R_f = 0.45$ (CH/AcOEt = 4:1), 0.60 (CH/AcOEt = 2:1); $[\alpha]_D^{20} = -4.4$ ($c = 0.1$, $CHCl_3$); IR (neat): $\nu = 2948$ (s), 1729 (vs), 1435 (m), 1244 (s), 1164 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε) = 203 (3.059) nm; ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (d, $J = 6.9$ Hz, 3H, 17-H/18-H), 0.95 (d, $J = 6.9$ Hz, 3H, 18-H/17-H), 0.95 (m, 1H, 1-H_{ax}), 0.96 (s, 3H, 19-H), 1.12 (s, 3H, 20-H), 1.21 (m, 1H, 6-H_{eq}), 1.37 (m, 1H, 11-Hα), 1.45 (m, 1H, 6-H_{ax}), 1.45–1.6 (m, 2H, 2-H), 1.57 (m, 1H, 1-H_{eq}), 1.57 (m, 1H, 3-H_{eq}), 1.62 (m, 1H, 9-H), 1.68 (m, 1H, 3-H_{ax}), 1.80 (dd, $J = 12.2$ Hz, $J = 1.9$ Hz, 1H, 5-H), 1.85 (ddd, $J = 13.9$ Hz, $J = 4.2$ Hz, $J = 2.4$ Hz, 1H, 7-H_{eq}), 1.92 (td, $2\times J = 13.8$–13.9 Hz, $J = 5.4$ Hz, 1H, 7-H_{ax}), 2.06 (sept, $J = 6.9$ Hz, 1H, 16-H), 2.61 (td, $2\times J = 12.9$–13.0 Hz, $J = 5.7$ Hz, 1H, 11-Hβ), 2.38 (dd, $J = 15.4$ Hz, $J = 9.9$ Hz, 1H, 13-H), 2.44 (dd, $J = 15.4$ Hz, $J = 4.2$ Hz, 1H, 13-H), 2.58 (m, 1H, 12-H), 3.63 (s, 3H, 23-H), 3.66 (s, 3H, 22-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (q, C-19), 14.9 (q, C-17/C-18), 16.8 (q, C-20), 16.9 (q, C-18/C-17), 17.3 (t, C-2), 21.6 (t, C-11), 22.0 (t, C-6), 29.6 (d, C-16), 32.1 (t, C-7), 34.8 (t, C-13), 35.1 (d, C-12), 36.3 (s, C-10), 36.9 (t, C-3), 37.8 (t, C-1), 47.2 (s, C-4), 49.08 (d, C-5), 49.14 (d, C-9), 51.6 (d, C-22), 51.9 (q, C-23), 109.4 (s, C-8), 111.0 (s, C-15), 172.9 (s, C-14), 178.9 (s, C-21), ppm; MS (FD): *m/z* (%) = 424 (100) [M^+], 337 (11); MS (70 eV): *m/z* (%) = 392 (3), 377 (13), 337 (45), 121 (77), 71 (40), 43 (100); $C_{23}H_{36}O_7$ (424.5); calc.: C 65.07, H 8.55, O 26.38; found: C 65.24, H 8.56, O 26.33.

Methyl-(3S-(3α,4aβ,4bα,8β,8aβ))-3-(methoxycarbonyl-methyl)-1,1,4b,8-tetramethyl-2-oxo-1,2,3,4,4a,4b,5,6,7,8,8a,9-dodecahydro-8-phenanthrencarboxylate (**18**)

The same oxidation procedure as described for **16** has been used. Typical quantities: 300 mg (0.73 mmol) **7** in 1.5 ml abs. CH_2Cl_2, 400 mg *bis*-(trimethysilyl)-peroxide, 50 mg (0.21 mmol) trimethylsilytrifluoromethan sulfonate in 8 ml abs. CH_2Cl_2. Reaction conditions: warming up from −40°C to 0°C within 7 h, stirring at 5°C for 2 h, no further addition of peroxide and trimethylsilytrifluoromethan sulfonate; CC: silica, CH/AcOEt = 9:1.

Yield: 175 mg **18** (61%); white crystals; m.p.: 108–110°C; $R_f = 0.31$ (CH/AcOEt = 5:1), 0.19 (CH/AcOEt = 9:1); $[\alpha]_D^{20} = -75.9$ ($c = 0.1$, $CHCl_3$); IR (KBr): $\nu = 2950$ (s), 1741 (vs), 1727 (vs), 1713 (vs), 1434 (m), 1241 (s), 1150 (m) cm^{-1}; UV (MeOH): λ_{max} (lgε): 204 (3.761), 270 (2.275) nm; ^{1}H NMR (C_6D_6): $\delta = 0.58$ (s, 3H, 17-H), 0.92 (m, 1H, 1-H_{ax}), 0.98 (q, $J = 13.2$ Hz, 1H, 11-H_{ax}),

1.13 (s, 3H, 14-Meα), 1.2–1.4 (m, 2H, 2-H), 1.25 (s, 3H, 18-H), 1.27 (s, 3H, 14-Meβ), 1.53 (m, 1H, 1-H_{eq}), 1.56 (m, 1H, 3-H_{eq}), 1.65 (dt, $J = 12.6$ Hz, $2 \times J = 4.5$ Hz, 1H, 11-H_{eq}), 1.74 (m, 1H, 6-H_{eq}), 1.83 (m, 1H, 3-H_{ax}), 1.88 (m, 1H, 6-H_{ax}), 1.99 (dd, $J = 16.7$ Hz, $J = 5.7$ Hz, 1H, 15-H), 2.06 (dd, $J = 12.2$ Hz, $J = 4.6$ Hz, 1H, 5-H), 2.22 (m, 1H, 9-H), 2,81 (dd, $J = 16.7$ Hz, $J = 7.6$ Hz, 1H, 15-H), 3.08 (m, 1H, 12-H), 3.32 (s, 3H, 20-H), 3.38 (s, 3H, 21-H), 5.46 (m, 1H, 7-H) ppm; ^{13}C NMR (C_6D_6): $\delta = 14.9$ (q, C-17), 17.5 (q, C-18), 18.3 (t, C-2), 22.8 (q, 14-Meβ), 25.7 (t, C-6), 30.4 (q, 14-Meα), 30.9 (t, C-11), 34.9 (t, C-15), 35.3 (s, C-10), 37.3 (t, C-3), 38.9 (t, C-1), 42.3 (d, C-12), 44.7 (d, C-5), 46.5 (s, C-4), 50.1 (d, C-9), 50.4 (s, C-14), 51.1 (q, C-21), 51.5 (q, C-20), 119.8 (d, C-7), 144.3 (s, C-8), 172.5 (s, C-16), 178.1 (s, C-19), 211.8 (s, C-13) ppm; MS (70 eV): m/z (%) = 390 (98) [M^+], 330 (47), 204 (38), 181 (80), 121 (100), 55 (39), 41 (44); $C_{23}H_{34}O_5$ (390.5); calc.: 70.74, H 8.78, O 20.48; found: C 70.58, H 8.70, O 20.42.

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