Diterpenoid Total Synthesis, XXXII[‡] Synthesis and Absolute Configuration of (−)-Phytocassane D, a Diterpene Phytoalexin Isolated from the Rice Plant, *Oryza sativa*

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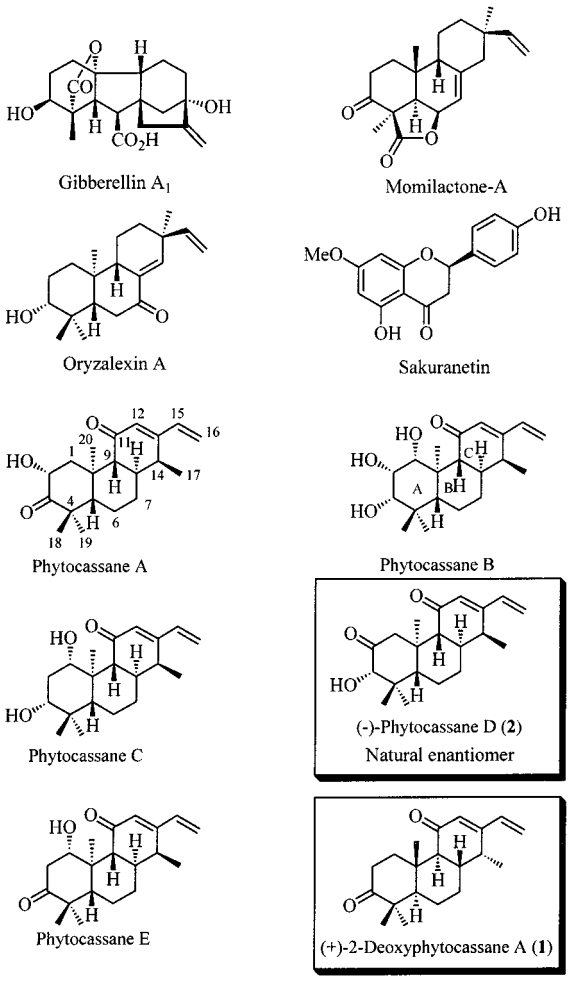
To determine the absolute configuration of the phytocassane group of phytoalexins, the naturally occurring (–)-phytocassane D was synthesized from the (*R*)-Wieland–Miescher ketone, in an approach based on the preliminary model synthesis of the unnatural (+)-2-deoxyphytocassane A. By comparison of their CD spectra with those of synthetic phytocassanes of known absolute configuration, phytocassanes A–E were shown to possess the *ent*-cassane skeleton.

Introduction

The rice plant (*Oryza sativa*) is the major agricultural crop of Japan. Chemical studies of it have contributed enormously to the discovery of new bioregulators. For example, the gibberellin plant hormones were isolated in 1938 as a result of Yabuta and Sumiki's work on rice bakanae disease, caused by the fungus *Gibberella fujikuroi*.[1] It is now established that gibberellin A_1 (Scheme 1) is the major growth hormone in the rice plant.[2]

Recently, self-defense mechanisms of the rice plant against pathogenic microorganisms have been investigated extensively, and several new phytoalexins were isolated and identified. Phytoalexins are antimicrobial secondary metabolites, normally absent in the healthy plant but biosynthesized de novo when the plant is infected by a pathogen.[3] Momilactones A−C[4−6] and oryzalexins A−F and S[7,8] are diterpene phytoalexins, while sakuranetin[9] is a rice plant flavonoid phytoalexin. In 1995, and also in 1997, Koga and his co-workers reported phytocassanes A−E as new diterpene phytoalexins produced by rice plant infected with such disastrous fungi as *Magnaporthe grisea* (old name: *Pyricularia oryzae*), *Rhizoctonia solani*, and *Phytopathora infesta*.[10,11] Their cassane diterpene structures were proposed (Scheme 1) on the basis of extensive spectroscopic analysis.[10,11] Their absolute configurations, however, remained unknown, even after circular dichroism (CD) measurements. (The structures in Scheme 1 represent their correct absolute configuration as established in the present work.)



Scheme 1. Structures of bioactive compounds in the rice plant; the numbering system depicted in the structure of phytocassane A is used throughout the text

We became interested in clarifying the absolute configuration of phytocassanes, because we were curious to know whether they, like gibberellins and oryzalexins, belong to the *ent*-diterpene series. In the case of oryzalexins, Mori and Waku synthesized both enantiomers of oryzalexin A in

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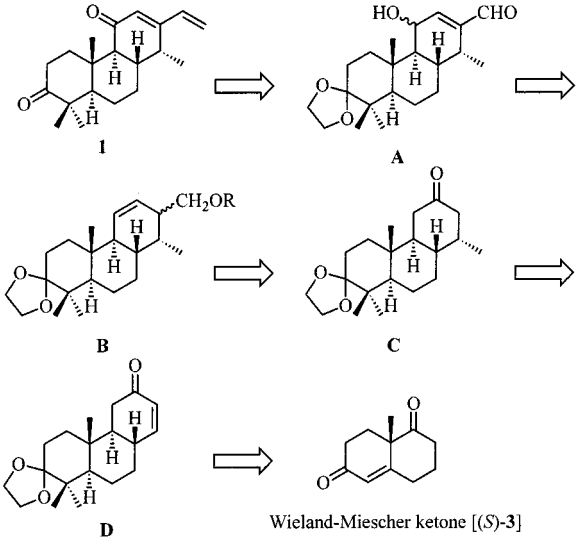
1985, and confirmed their *ent*-isopimarane stereochemistry.[12] Accordingly, as reported in a preliminary communication,[13] we synthesized (+)-2-deoxyphytocassane A (**1**) with cassane stereochemistry, and recorded its CD spectrum to find that **1** was of the opposite absolute configuration to the naturally occurring phytocassanes. This paper describes the details of the synthesis of **1**, and also the first synthesis of (−)-phytocassane D (**2**), one of the naturally occurring phytocassanes. The synthesis of the natural product **2** itself, from the (*R*)-Wieland−Miescher ketone, firmly established its absolute configuration as of the *ent*-cassane type.

Results and Discussion

Synthesis of (+)-2-Deoxyphytocassane A (1)

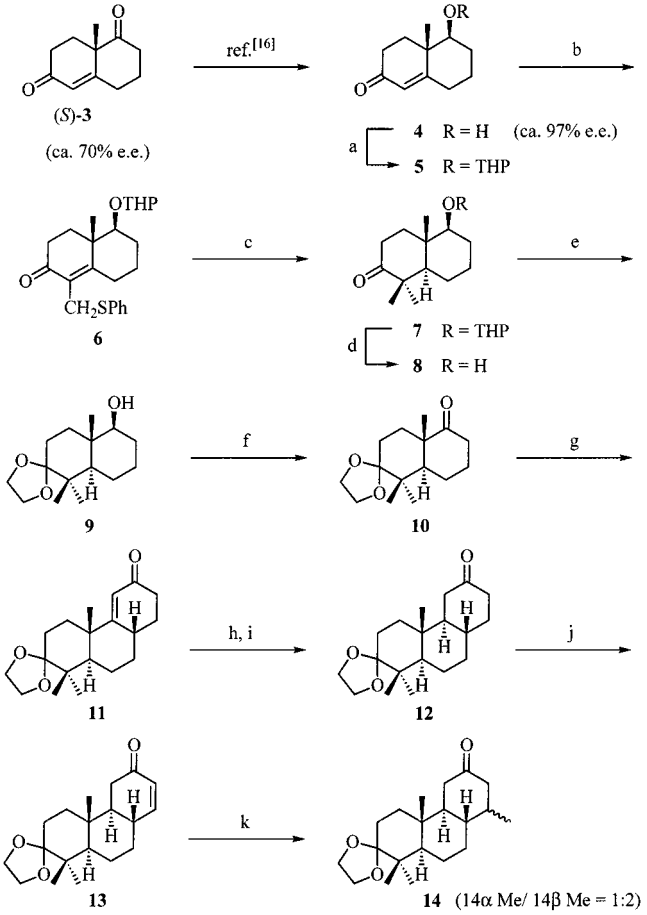
As our first target we chose 2-deoxyphytocassane A (**1**) with the normal cassane stereochemistry, since there was an urgent need to establish the absolute configuration of phytocassanes before planning the synthesis of one of the naturally occurring members of that series. Abolition of the hydroxy group at C-2 of phytocassane A would make the synthesis of **1** shorter and easier than that of the parent compound.



Scheme 2. Retrosynthetic analysis of 2-deoxyphytocassane A

Our retrosynthetic analysis is shown in Scheme 2. The conjugated dienone system around ring C would be constructed by modifying **A**, which could be obtained from **C** via **B**.

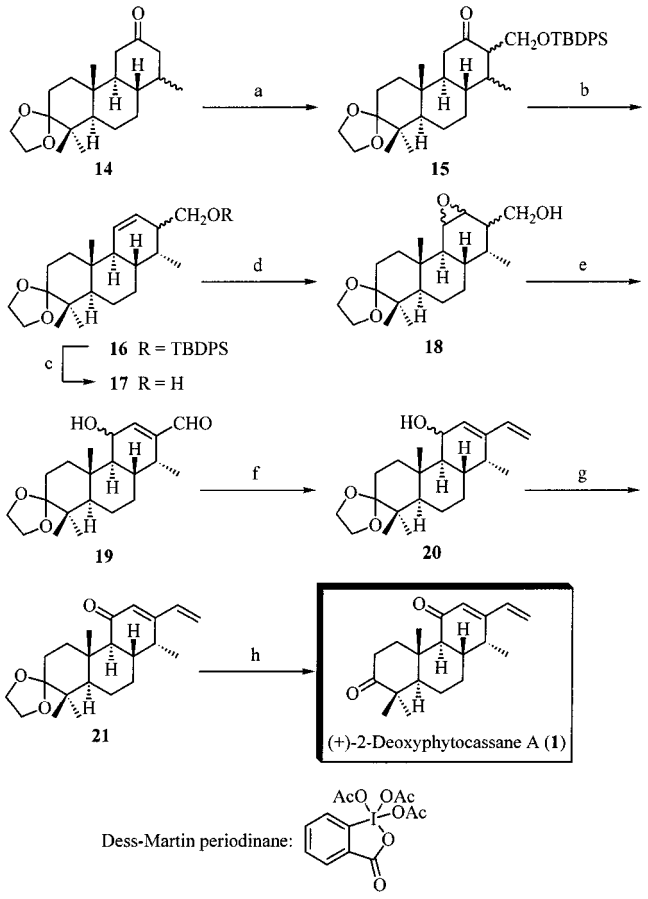
The use of the intermediate **B** would facilitate the introduction of the sterically hindered oxygen function at C-11. Conjugate addition of an organocopper reagent to **D** would generate **C**. A similar transformation had been adopted previously by Spencer et al. in their synthesis of methyl (±)-vinhaticoate, a diterpene with a methyl group at C-14.[14] For the preparation of the tricyclic ketone **D**, the readily available (*S*)-Wieland−Miescher ketone (**3**)[15] was selected as the starting material. The above plan was accomplished as detailed below, and also served as the model in our subsequent work on the synthesis of (−)-phytocassane D (**2**), except that it was necessary to employ (*R*)-**3** as starting material in the latter case.



Scheme 3. Synthesis of tricyclic ketone **14**; reagents: (a) DHP, TsOH, CH_2Cl_2 (91%); (b) PhSH, aq. CH_2O, Et_3N, EtOH (79%); (c) Li, liq. NH_3, H_2O, THF, then MeI, THF (79%); (d) TsOH, MeOH, H_2O (99%); (e) $HO(CH_2)_2OH$, PPTS, C_6H_6 (94%); (f) DMSO, $(COCl)_2$, Et_3N, CH_2Cl_2 (92%); (g) i) NaH, HCO_2Et, THF, PhMe; ii) $MeCOCH{=}CH_2$, Et_3N; iii) NaOMe, MeOH (76%, 3 steps); (h) Li, liq. NH_3, EtOH, THF; (i) PCC, 3-Å MS, CH_2Cl_2 (76%, 2 steps); (j) i) LDA, $PhSSO_2Ph$, THF; ii) Me_2CO_2, CH_2Cl_2; iii) $CaCO_3$, PhMe, heat (83% based on consumed **12**, 3 steps); (k) Me_2CuLi, Et_2O, 0 °C (quant.)

Scheme 3 and Scheme 4 summarize our synthesis of (+)-2-deoxyphytocassane A (**1**). Although purification of the (*S*)-Wieland−Miescher ketone (**3**) by fractional crystallization is a well-known and established process,[15] a more reproducible purification procedure reported by Sugai and co-workers was adopted to give enantiomerically pure **4** by simple yeast reduction of enantiomerically impure **3** with *Torulaspora delbrückii* IFO 10921.[16] Protection of the hydroxy group of **4** as a tetrahydropyranyl (THP) ether afforded **5**.

Introduction of the two methyl groups at C-4 of **5** with concomitant stereoselective reduction of the double bond was executed by the method of Smith and Mewshaw.[17] Hence, the enone **5** was treated with aqueous formaldehyde and thiophenol in the presence of triethylamine in hot ethanol to give phenylthio ether **6**. Reductive methylation of



Scheme 4. Synthesis of (+)-2-deoxyphytocassane A (**1**); reagents: (a) i) NaH, HCO_2Et, MeOH; ii) NaH, $NaAl[O(CH_2)_2OMe]_2H_2$ (Red-Al®), THF; iii) TBDPSCl, imidazole, DMF; (b) i) $TsNHNH_2$, $MgSO_4$, THF; ii) excess LDA, THF, quenched with aq. NH_4Cl then SiO_2 chromatography (8%, based on **14**); (c) TBAF, THF (74%); (d) MCPBA, $NaHCO_3$, $CHCl_3$ (72%); (e) i) Dess−Martin periodinane, CH_2Cl_2; ii) pyrrolidine, Et_2O (85%, 2 steps); (f) $Ph_3P{=}CH_2$, THF (77%); (g) TPAP, 3-Å MS, CH_2Cl_2, MeCN (91%); (h) aq. HCl, THF (64%)

6 with lithium in wet liquid ammonia and methyl iodide furnished ketone **7**. Removal of the THP protecting group of **7** yielded hydroxy ketone **8**, the carbonyl group of which was acetalized to give hydroxy acetal **9**. Ketone **10** was obtained from **9** by Swern oxidation.

Annelation of **10** to give tricyclic enone **11** was achieved under the standard conditions exemplified in Spencer's work.[14] Namely, formylation of ketone **10** was followed by Robinson annelation employing methyl vinyl ketone, with concomitant removal of the formyl group, to afford **11**. Birch reduction of the unsaturated ketone **11** and reoxidation of the hydroxy group generated at C-12 with pyridinium chlorochromate (PCC) yielded saturated ketone **12**.

To introduce a methyl group at C-14, the ketone **12** was first converted into enone **13**. Accordingly, **12** was thiophenylated by the method of Trost and Massiot,[18] and the resulting phenylthio ether was oxidized with dimethyldioxirane[19] to give the corresponding phenyl sulfoxide, thermolysis of which furnished **13**. Conjugate addition of lithium dimethylcuprate to **13** afforded C-14-methylated ketone **14** as a mixture of the desired, axially methylated α-isomer and its equatorial counterpart. In the ^1H NMR spectrum of **14**, the axial methyl group at C-14 absorbed at $\delta = 0.79$ (d, $J = 7.4$ Hz), due to the shielding effect caused by ring C,[14] while the equatorial one exhibited a doublet at $\delta = 0.99$ (d, $J = 6.4$ Hz). The ratio of these two isomers was unfavorable for our purpose: desired axial methyl/undesired equatorial methyl = 1:2. Different conditions for introducing the methyl group were examined, but resulted in no improvement on this discouraging outcome. Unfortunately, the two isomers of **14** could not be separated, and the mixture was further processed as such.

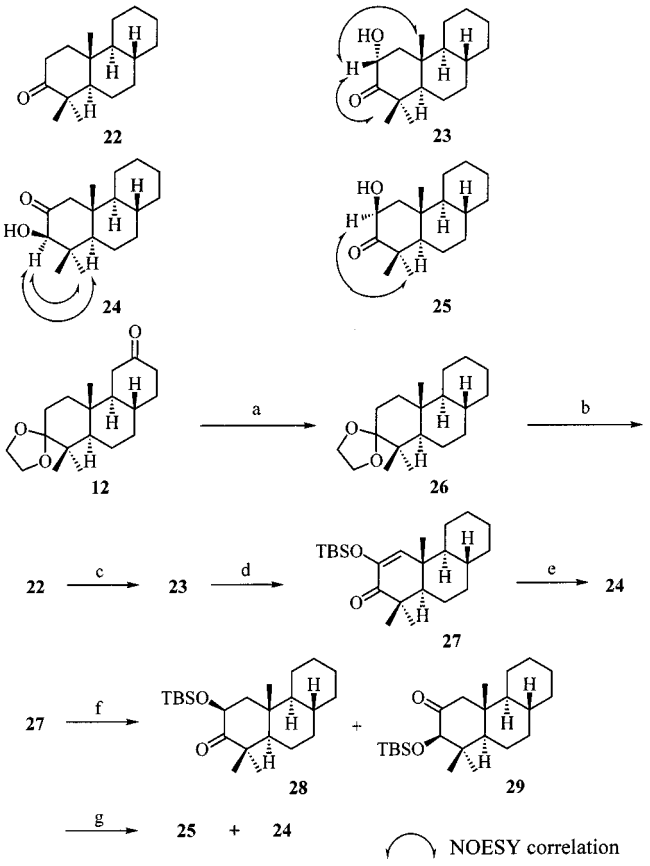
The next step was the attachment of a hydroxymethyl group at C-13 of **14**. Formylation of **14** was followed by reduction of its sodium enolate according to Corey and Smith's method,[20] and the resulting alcohol was protected as a *tert*-butyldiphenylsilyl (TBDPS) ether to furnish **15** (Scheme 4). In order to introduce an oxygen function at C-11, ketone **15** was subjected to Shapiro olefination conditions[21] to give **16** after chromatographic purification. Very fortunately, it was possible at this stage to remove the undesired C-14 β-methyl isomer, and what we obtained was a diastereomeric (at C-13) mixture with the correct stereochemistry at C-14, exhibiting ^1H NMR signals at $\delta = 0.63$ and 0.81 (each d, $J = 7$ Hz, total 3 H). The reason for this unexpected disappearance of the C-14 β-methyl isomer was unclear.

Removal of the TBDPS group of **16** was followed by epoxidation of the resulting olefinic alcohol **17** with *m*-chloroperbenzoic acid (MCPBA) to give epoxide **18**. Dess-Martin oxidation of **18** afforded the corresponding epoxy aldehyde, which was treated with pyrrolidine to give the α,β-unsaturated γ-hydroxy aldehyde **19**. This was subjected to a Wittig methylenation to furnish dienol **20**, which was oxidized with tetrapropylammonium perruthenate (TPAP)[22] to give dienone **21**. Finally, treatment of **21** with dilute hydrochloric acid afforded (+)-2-deoxyphytocassane A (**1**), $[\alpha]_D^{26} = +5.8$ ($c = 0.1$, $CHCl_3$). All spectral data (IR and ^1H and ^{13}C NMR) of the product are in perfect accord with the expected structure **1**. The overall yield of (+)-**1** was 0.04% based on (6*S*,7*S*)-**4** (27 steps).

CD Studies on (+)-2-Deoxyphytocassane A and Related Compounds

Chiroptical methods such as circular dichroism (CD) spectroscopy play a well-established and very important role in stereochemical analysis of natural products.[23] The CD spectrum of (+)-2-deoxyphytocassane A (**1**) shows a positive Cotton effect at 369 nm ($\Delta\varepsilon = +1.63$), due to the n→π* transition of the ring C carbonyl group,[24] while all of the natural phytocassanes A−E show negative Cotton effects at wavelengths between 345 and 369 nm {λ_{ext} [nm] ($\Delta\varepsilon$): A, 369 (−2.78); B, 345 (−5.36); C, 349 (−5.17); D, 368 (−3.27); E, 348 (−4.47)}.[10,11] The natural phytocassanes were therefore concluded to belong to the *ent*-cassane series of diterpenes, antipodal to (+)-**1**. The possibility could not be excluded, however, that structural differences in ring A of (+)-**1** affects its CD spectrum.

We therefore synthesized some model phytocassane compounds (**22**−**25**, Scheme 5), with different ring A functionalities and without any functional group on ring C, and compared their CD spectra with those of the natural and synthetic phytocassanes. For the synthesis of ketone **22**, the ketone **12** was converted into the corresponding tosylhydrazone, which was reduced with sodium cyanoborohydride[25] to give **26**.



Scheme 5. Synthesis of tricyclic ketones **22**−**25**, related to phytocassanes A and D; reagents: (a) $TsNHNH_2$, $NaBH_3CN$, TsOH, DMF, sulfolane (53%); (b) aq. HCl, THF (quant.); (c) i) TMSOTf, Et_3N, CH_2Cl_2; ii) MCPBA, $NaHCO_3$, hexane; iii) $(CO_2H)_2$, MeOH (93%, 3 steps); (d) i) Dess−Martin periodinane, CH_2Cl_2; ii) TBSCl, imidazole, DMF (94%, 2 steps); (e) i) LAH, THF; ii) aq. HCl (58%); (f) i) $NaBH_4$, EtOH; ii) Dess−Martin periodinane, CH_2Cl_2 (quant.); (g) aq. HF, MeCN (43% as 2:5 mixture of **24** and **25**)

This acetal **26** furnished **22** upon acid hydrolysis. Conversion of **22** to hydroxy ketone **23** was achieved by first treating **22** with trimethylsilyl triflate (TMSOTf) in the presence of triethylamine to give the corresponding TMS enol ether, which was epoxidized with MCPBA. The resulting epoxide was treated with acid to afford **23**. The stereochemistry of **23** was confirmed by NOESY correlation between the protons, as shown in Scheme 5. For the synthesis of hydroxy ketone **24**, compound **23** was oxidized with Dess−Martin periodinane and the resulting diketone was converted into the *tert*-butyldimethylsilyl (TBS) enol ether **27**. Reduction of **27** with lithium aluminum hydride (LAH) was followed by acid treatment to give **24**. To synthesize hydroxy ketone **25**, the silyl enol ether **27** was reduced with sodium borohydride, effecting both 1,2- and 1,4-reduction.

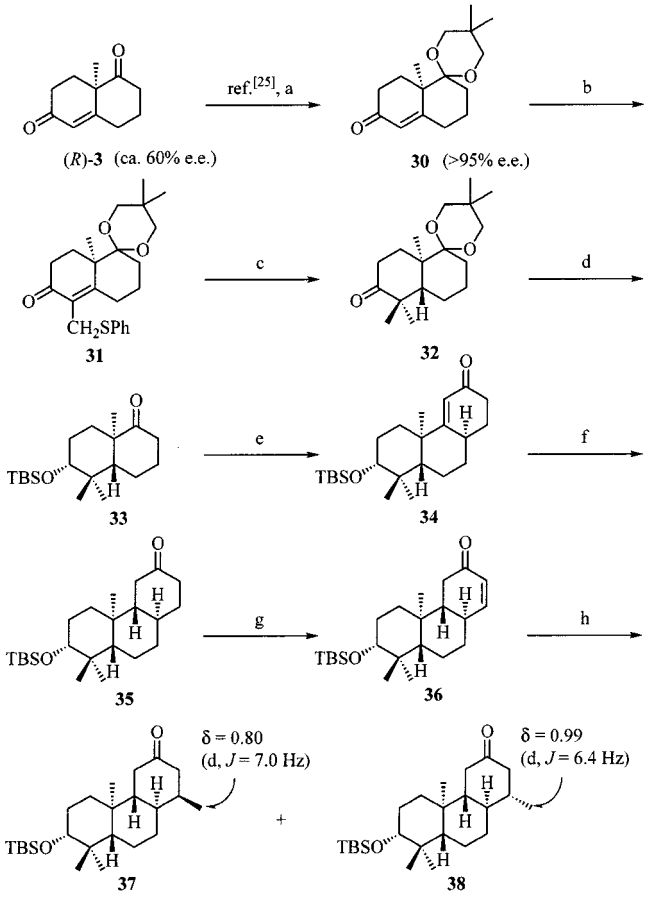
Reoxidation of the hydroxy group at C-3 of the reduction product gave a mixture of **28** and **29**; migration of the TBS group from the C-2 oxygen atom to its C-3 neighbor might have taken place via an enediolate intermediate. Removal of the TBS groups of **28** and **29** with aqueous hydrofluoric acid furnished a mixture of **24** and **25**. The stereochemistries of **24** and **25** were confirmed by NOESY correlation, as shown in Scheme 5. Since **25** was readily isomerizable to **24** even by chromatography on neutral alumina, it proved impossible to separate **25** from **24**, and so the CD absorption of **25** was recorded as a differential spectrum, by subtracting the CD absorption of **24** from that of the mixture of **24** and **25**.

As expected, the ketones **22**−**25**, with no ring C functionality, evinced no CD absorption around 369 nm. The strong CD absorption at 369 nm of (+)-2-deoxyphytocassane A (**1**) must therefore be due to the chirality around its ring C functionalities. The ketones **22**−**25** exhibited CD absorption around 290 nm, due to the n→π* transition of the ring A carbonyl group {λ_{ext} [nm] ($\Delta\varepsilon$): **22**, 309 (−0.38); **23**, 284 (−0.61); **24**, 288 (+0.97); **25**, 289 (+0.04)}. The ketone **25**, with the same hydroxy ketone system as that of phytocassane A, showed a positive Cotton effect at 289 nm, while phytocassane A exhibited a negative Cotton effect at 289 nm ($\Delta\varepsilon = -8.74$).[10] The opposite signs of the CD absorptions − at 369 nm for **1** and also of 289 nm for **25** − in comparison to natural phytocassane A led us to the final conclusion that phytocassanes possess the *ent*-cassane skeleton.

Synthesis of (−)-Phytocassane D (2)

So as to verify the above conclusion that phytocassanes belong to *ent*-cassane series, we set out to synthesize one of the naturally occurring phytocassanes. Phytocassane D (**2**) was chosen as our target, because of the ease of incorporating its ring A functionalities in the later stages of the synthesis. The synthesis of **2** with its correct absolute configuration required us to prepare the (*R*) isomer of Wieland−Miescher ketone [(*R*)-**3**] in enantiomerically pure state. We were reluctant, however, to adopt the established method, of Buchschacher et al.,[15] for its preparation, in the light of the tedious recrystallization procedure necessary to secure pure (*R*)-**3**. After scrutinizing known procedures for the preparation of enantiomerically pure Wieland−Miescher ketone (**3**) and its derivatives, we found that keto acetal (*R*)-**30** (Scheme 6), prepared from enantiomerically enriched (*R*)-**3** (ca. 60% *ee*) according to the method of Swaminathan and co-workers,[26] gave highly crystalline (*R*)-**30** of >95% *ee* (measured by GC analysis), when recrystallized from diethyl ether at room temperature. Crystals of **30** with a different shape (plates) and very low enantiomeric purity (ca. 10% *ee*) were also obtained. Fortunately, these plates were readily removed by picking them out manually, while the mother liquor contained (*R*)-**30** of ca. 60% *ee*, which could be recycled to give an additional quantity of pure (*R*)-**30**.

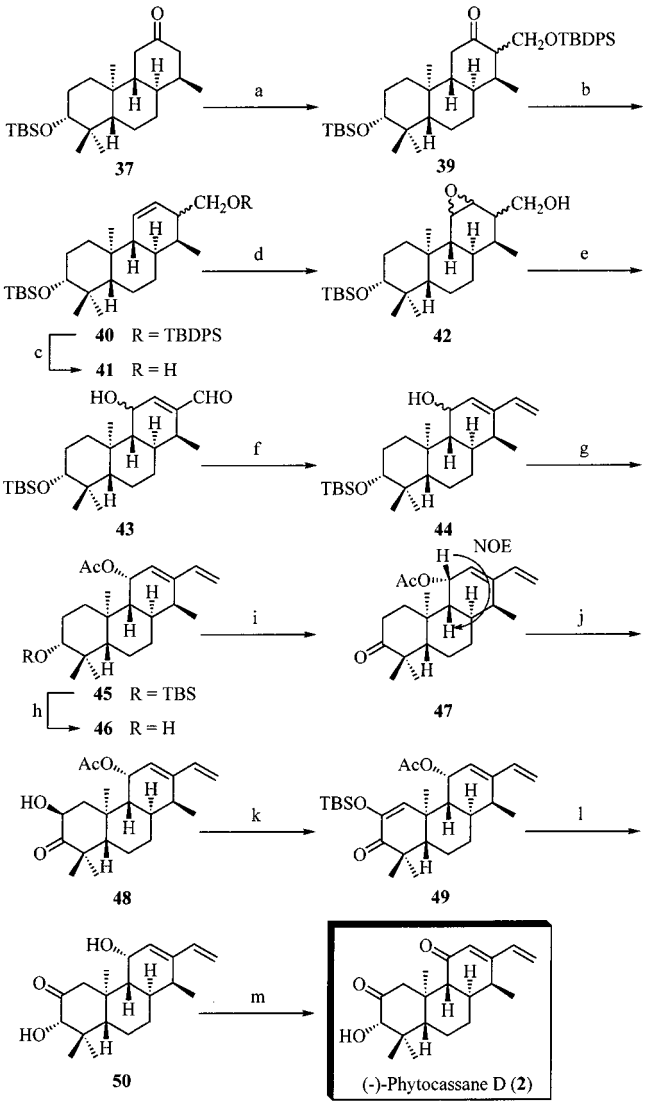
Conversion of the unsaturated ketone **30** into saturated ketone **32** via **31** was executed in the same manner as for



Scheme 6. Synthesis of tricyclic ketone **37**; reagents: (a) recrystallization from Et_2O (71% based on the consumed **30**); (b) PhSH, aq. CH_2O, Et_3N, EtOH (79%); (c) Li, liq. NH_3, H_2O, THF, then MeI, THF (84%); (d) i) LAH, THF; ii) aq. HCl, THF; iii) TBSCl, imidazole, DMF (85%, 3 steps); (e) i) NaH, HCO_2Et, THF, PhMe; ii) $MeCOCH{=}CH_2$, Et_3N; iii) NaOMe, MeOH (78%, 3 steps); (f) i) Li, liq. NH_3, EtOH, THF; ii) PCC, 3-Å MS, CH_2Cl_2 (88%, 2 steps); (g) i) KH, $PhSO_2Me$, THF; ii) $CaCO_3$, PhMe, heat (87%, 2 steps); (h) i) Me_2CuLi, Et_2O (97%, **37**/**38** = 54:46); ii) MPLC separation

the synthesis of (+)-2-deoxyphytocassane A (**1**). Reduction of **32** with LAH was followed by removal of the acetal protective group, to give the corresponding hydroxy ketone. Its hydroxy group was protected as a TBS ether to furnish **33**. Robinson annelation of **33** to give unsaturated tricyclic ketone **34** was followed by Birch reduction, yielding saturated tricyclic ketone **35**. Introduction of the double bond at C-13(14) of **35** was executed by employing methyl phenylsulfinate, according to the method of Resek and Meyers.[27] Although regioselection between C-11 and C-13 was 1:10, this method furnished unsaturated ketone **36** in reproducible yield of 87%. The next and crucial step was the introduction of a methyl group at C-14 of **36**. With substrate **36**, the diastereoselectivity for introduction of the C-14 methyl group was again low: The ratio of desired axial methyl isomer to undesired equatorial methyl isomer was 54:46. It should be remembered though that in the previous case with **13** the ratio was far less favorable (1:2). Perhaps in the case of **36**, the difference in the C-3 functional group might have resulted in some favorable effect on the conformation of ring C, to generate more of the desired axial isomer **37**. Fortunately, isomers **37** and **38** could be separated by medium-pressure liquid chromatography (MPLC), and **37** was secured in 41% yield. The two isomers **37** and **38** could be identified by ^1H NMR analysis (see Scheme 6).

Scheme 7 summarizes the remaining steps required for the completion of the synthesis of (−)-phytocassane D. Conversion of **37** into **39** was executed by a sequence of (i) formylation, (ii) sodium borohydride reduction, (iii) protection of the primary hydroxy group as a TBDPS ether, and (iv) reoxidation of the secondary hydroxy group at C-12 with PCC. The ketone **39** was then subjected to Shapiro



Scheme 7. Synthesis of (−)-phytocassane D (**2**); reagents: (a) i) NaH, HCO_2Et, MeOH; ii) $NaBH_4$, THF, MeOH; iii) TBDPSCl, imidazole, DMF; iv) PCC, 4-Å MS, CH_2Cl_2 (57%, 4 steps); (b) i) $TsNHNH_2$, $MgSO_4$, PPTS, THF; ii) excess LDA, THF then quenched with aq. NH_4Cl (68%, 2 steps); (c) TBAF, THF, room temp. (quant.); (d) MCPBA, $NaHCO_3$, $CHCl_3$ (92%); (e) i) Dess−Martin periodinane, CH_2Cl_2; ii) pyrrolidine, Et_2O (73%, 2 steps); (f) $Ph_3P{=}CH_2$, THF (88%); (g) Ac_2O, DMAP, C_5H_5N (quant.); (h) TBAF, THF, 50−60 °C (68%); (i) PCC, 4-Å MS, CH_2Cl_2 (98%); (j) i) LiHMDS, TMSCl, THF; ii) MCPBA, $NaHCO_3$, hexane; iii) $(CO_2H)_2$, MeOH (38% based on consumed **47**); (k) i) Dess−Martin periodinane, CH_2Cl_2; ii) TBSCl, imidazole, DMF (67%, 2 steps); (l) LAH, THF, then aq. HCl (64%); (m) TPAP, 4-Å MS, MeCN, CH_2Cl_2 (40% based on consumed **50**)

olefination reaction conditions[21] to give olefin **40**. Selective deprotection of the TBDPS protecting group of **40** was followed by epoxidation of the resulting olefinic alcohol **41** with MCPBA to furnish epoxy alcohol **42**. Dess−Martin oxidation of **42** afforded the corresponding epoxy aldehyde, treatment of which with pyrrolidine yielded the α,β-unsaturated γ-hydroxy aldehyde **43**. Olefination of **43** with methylenetriphenylphosphorane gave dienol **44**. The diastereomeric ratio at C-11 of **44**, as determined by ^{1}H NMR analysis, was axial α-hydroxy/equatorial β-hydroxy = 4:1. Acetylation of **44** was followed by removal of the TBS protecting group of the resulting compound **45** to give acetoxy alcohol **46**. In the course of these operations, the minor C-11 β-hydroxy isomer of **44** disappeared, probably thanks to unusually facile *syn* elimination of acetic acid. PCC oxidation of **46** furnished acetoxy ketone **47**, the C-11 stereochemistry of which was established by ^{1}H NMR analysis, by observation of the signal due to the C-11 proton (δ = 5.41, dd, J = 5.8, 7.1 Hz) and also of the NOE between the protons at C-9 and C-11.

To attach another oxygen function at C-2 of **47**, this compound was converted into the corresponding silyl enol ether by treatment with lithium hexamethyldisilazide (LiHMDS) and trimethylsilyl chloride (TMSCl). The enol double bond was epoxidized with MCPBA, and the resulting epoxide was treated with methanolic oxalic acid to give hydroxy ketone **48**. The ^{1}H NMR spectrum of **48** showed a pattern similar to that of the model compound **23**. Oxidation of **48** with Dess−Martin periodinane gave the corresponding α-diketone, which furnished TBS enol ether **49** under the conventional silylation conditions. Ketone **49** was reduced with LAH to generate the 3α-hydroxy group, and also to remove the acetyl protecting group at the C-11 hydroxy moiety. Acidic workup after the reduction removed the TBS protective group, too, to give **50**. Finally, selective oxidation of the allylic hydroxy group at C-11 with TPAP afforded (−)-phytocassane D (**2**), $[\alpha]_D^{25} = -170$ ($CHCl_3$), as a gum. Its IR, ^{1}H NMR, and ^{13}C NMR spectra are identical to the spectra of the authentic natural product. Although the overall yield was only 0.002% based on **30** (34 steps), our synthetic (−)-phytocassane D (**2**) possessed a CD spectrum {λ_{ext} = 362 [nm] (Δε = −1.8) and 272 nm (Δε = +3.6)} identical to that of the authentic natural product, and this identity confirms our postulation that phytocassanes belong to the *ent*-cassane series.[13]

Conclusion

The synthesis described above of the naturally occurring (−) enantiomer of phytocassane D (**2**) from the (*R*)-Wieland−Miescher ketone (**3**), in conjunction with the synthesis of the unnatural (+)-2-deoxyphytocassane A (**1**) from (*S*)-**3**, has firmly established the *ent*-cassane stereochemistry of phytocassanes. In summary, the phytocassane group of phytoalexins belongs to the same stereochemical families of *ent*-diterpenes as gibberellins and oryzalexins. The correct stereostructures of phytocassane A−E are shown in Scheme 1.

Experimental Section

General Remarks: Melting points: uncorrected values. − IR spectra: Perkin−Elmer 1640 and Jasco FT/IR-410 spectrometers. − ^{1}H NMR spectra: Jeol JNM-EX 90A (90 MHz), Jeol JNM LA400 (400 MHz) and Jeol JNM LA500 (500 MHz) spectrometers (in $CDCl_3$, TMS at δ = 0.00 or $CHCl_3$ at δ = 7.26 as an internal standard). − ^{13}C NMR spectra: Jeol JNM LA500 spectrometer (125 MHz) (in $CDCl_3$, $CHCl_3$ at δ = 77.0 as an internal standard). − Optical rotations: Jasco DIP-1000 and Jasco P-1020 polarimeters. − CD spectra: Jasco J-725 spectrometer. − Mass spectra: Jeol JMS-SX 102A and Hitachi M-80B spectrometers. − GC analyses: Shimadzu GC-17A and Shimadzu GC-18A. − Column chromatography: Merck Kieselgel 60 Art 7734. − Preparative TLC: Merck Kieselgel 60 F_{254}, 0.5 mm.

(1*RS*,4a*S*,4b*R*,8a*R*,10a*S*)-7-Ethylenedioxy-1,4,4a,4b,5,6,-7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethylphenanthr-3(2*H*)-one (14): To a stirred suspension of CuI (2.13 g, 11.2 mmol) in dry diethyl ether (15 mL), at −10 °C under argon, was added dropwise a solution of MeLi in diethyl ether (1.14 M, 19.6 mL, 22.4 mmol). After stirring for 10 min, this solution was added dropwise to a solution of **13** (1.70 g, 5.59 mmol) in dry diethyl ether (30 mL). Stirring was continued for 30 min, and water was added carefully to the mixture. The mixture was poured into sat. aq. NH_4Cl and filtered through a Celite pad. The filtrate was separated, and the aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (60 g, hexane/ethyl acetate = 9:1) to give 2.03 g (quant.) of **14** as a colorless solid. The isomer ratio was determined by comparison of the ^{1}H NMR signal intensities of the methyl groups (α-Me/β-Me = 1:2). − M.p. 111−117 °C, $[\alpha]_D^{23} = -25.5$ (c = 0.29, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 1710 cm^{-1} (s, C=O), 1100 (s, C−O). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = [0.79 (d, J = 7.4 Hz), 0.85 (s), 0.95 (s), 0.97 (s) each 1 H, CH_3 of α-Me isomer], [0.84 (s), 0.92 (s), 0.96 (s), 0.99 (d, J = 6.4 Hz), each 2 H, CH_3 of β-Me isomer], 1.20−2.53 (m, 16 H, 1,4a,8a,10a-H, 2,4,5,6,9,10-CH_2 of both isomers), 3.8−3.95 (m, 4 H, 2 × CH_2-O of both isomers). − $C_{20}H_{32}O_3$ (320.5): calcd. C 74.96, H 10.06; found C 74.76, H 10.27.

(1*RS*,2*RS*,4a*S*,4b*R*,8a*R*,10a*S*)-2-*tert*-Butyldiphenylsilyloxymethyl-7-ethylenedioxy-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthren-3(2*H*)-one (15): To a stirred solution of **14** (480 mg, 1.51 mmol) in HCO_2Et (12 mL), at −10 °C under argon, was added portionwise 60% NaH (302 mg, 7.55 mmol) over 30 min. Then MeOH (61.0 μL, 1.51 mmol) was added, and the mixture was stirred overnight, with gradual warming to room temperature. After careful addition of water, the mixture was poured into sat. aq. NH_4Cl and extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in dry THF (6 mL). To this solution was added portionwise 60% NaH (302 mg, 7.55 mmol), over 30 min at −30 °C under argon. Then a solution of Red-Al® (65% in toluene, 2.95 mL, 15.1 mmol) was added in one portion. The mixture was immediately warmed to 0 °C and stirred for 15 min. After careful addition of sat. aq. NH_4Cl, the mixture was diluted with diethyl ether and filtered through a Celite pad. The pad was washed with ethyl acetate, and the organic

layer was separated. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was quickly chromatographed on silica gel (15 g, hexane/ethyl acetate = 3:1) to give crude material. This was immediately dissolved in DMF (3 mL), and imidazole (206 mg, 3.03 mmol) and TBDPSCl (434 μL, 1.51 mmol) were added to the mixture. The mixture was stirred overnight and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (15 g, hexane/ethyl acetate = 50:1) to give 160 mg of **15** as a diastereomeric mixture. This was directly employed in the next step without further purification.

(1*R*,2*RS*,4a*R*,4b*R*,8a*R*,10a*S*)-2-*tert*-Butyldiphenylsilyloxymethyl-7-ethylenedioxy-1,2,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethylphenanthrene (16): Ketone **15** (160 mg) was dissolved in dry THF (3 mL), and anhydrous $MgSO_4$ (167 mg, 1.38 mmol) and *p*-$TsNHNH_2$ (62.0 mg, 0.33 mmol) were added to the mixture. The mixture was stirred overnight and filtered through a silica gel pad. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (3 g, hexane/ethyl acetate = 5:1) to give crude hydrazone. This was immediately dissolved in dry THF (3 mL). The solution was added dropwise to a solution of LDA in THF (5 mL) [prepared from diisopropylamine (582 μL, 4.15 mmol) and a solution of *n*BuLi in hexane (1.57 M, 2.64 mL, 4.15 mmol)] at −78 °C under argon. The mixture was stirred overnight with gradual warming to room temperature, and poured into water and sat. aq. NH_4Cl. The aqueous layer was extracted with diethyl ether, and the combined organic extracts were washed with water and sat. aq. NH_4Cl, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (8 g, hexane/ethyl acetate = 150:1) to give 70 mg (8% based on **14**) of **16** as a colorless oil. This was employed in the next step without further purification. − IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 1100 cm^{-1} (s, C−O), 700 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.63, 0.81 (d, *J* = 7 Hz, total 3 H, CH_3), 0.69, 0.84, 0.849, 0.850, 0.91, 0.94 (s, total 9 H, 3 × CH_3), 1.05, 1.06 (s, total 9 H, *t*Bu), 0.80−2.06 (m, 12 H, 5,6,9,10-CH_2, 1,4a,8a,10a-H), 2.55 (m, 1 H, 2-H), 3.47, 3.53, 3.60 [(m), (d, *J* = 8 Hz), (dd, *J* = 6, 9.8 Hz) total 2 H, CH_2-OSi], 3.90−3.99 (m, 4 H, 2 × CH_2-O), 5.43−5.64 (m, 2 H, 3,4-H), 7.35−7.60 (m, 10 H, Ar-H).

(1*R*,4*RS*,4a*S*,4b*S*,8a*R*,10a*S*)-7-Ethylenedioxy-4-hydroxy-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene-2-carbaldehyde (19): To a stirred solution of **18** (13 mg, 37 μmol) in dry CH_2Cl_2 (1 mL) was added Dess−Martin periodinane (24 mg, 56 μmol), in one portion at 0 °C. The mixture was warmed to room temperature, and stirred for 30 min. Then the mixture was diluted with diethyl ether, and sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3 were added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in diethyl ether (1 mL). To the solution was added pyrrolidine (two drops, ca. 20 mg), and the solution was stirred for 1 h at room temperature. The mixture was diluted with diethyl ether and washed with sat. aq. NH_4Cl. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 5:1) to give 11 mg (85% based on **18**) of **19** as a colorless oil. This was employed in the next step without further purification. − IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 3480 cm^{-1} (w, OH), 1685 (s, C=O), 1100 (s, C−O). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.84, 0.91 (d, *J* = 7 Hz, total 3 H, CH_3), 0.86, 0.87, 0.94, 0.97, 0.98, 1.02 (s, total 9 H, 3 × CH_3), 0.8−2.2 (m, 12 H, 5,6,9,10-CH_2, 4a,8a,10a-H, H-O), 2.53, 2.63 (m, 1 H, 1-H), 3.86−3.99 (m, 4 H, 2 × CH_2-O), 4.38 (m, 1 H, 4-H), 6.50 (2 × d, *J* = 1.9 and 7.3 Hz, total 1 H, 3-H), 9.43, 9.45 (2 × s, total 1 H, H-C=O).

(1*R*,4*RS*,4a*S*,4b*S*,8a*R*,10a*S*)-7-Ethylenedioxy-1,4,4a,4b,5,6,-7,8,8a,9,10,10a-dodecahydro-2-vinylphenanthren-4-ol (20): To a suspension of Ph_3PMeBr (41 mg, 0.1 mmol) in dry THF (2 mL) at −78 °C under argon was added dropwise a solution of *n*BuLi in hexane (1.6 M, 61 μL, 0.1 mmol). The mixture was stirred for 30 min at 0 °C. To this mixture was added **19** (13 mg, 0.04 mmol) in dry THF (1 mL). The mixture was stirred for 30 min and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 10:1) to give 10 mg (77%) of **20** as a colorless oil. This was employed in the next step without further purification. − IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 3490 cm^{-1} (w, OH), 1100 (s, C−O), 990 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86, 0.87, 0.91, 0.97, 0.98, 1.00 (s, total 9 H, 3 × CH_3), 0.97, 1.06 (d, *J* = 7 Hz, total 3 H, CH_3), 0.80−1.97, 2.11 [(m), (dt, *J* = 13.5, 3.4 Hz), total 12 H, 5,6,9,10-CH_2, 4a,8a,10a-H, H-O], 2.18, 2.34 [(m), (dq, *J* = 4, 7 Hz), total 1 H, 1-H], 3.88−3.99 (m, 4 H, 2 × CH_2O), 4.19 (m, 1 H, 4-H), 5.02, 5.07 (2 × d, *J* = 11 Hz, 1 H, *H*HC=C), 5.17, 5.24 (2 × d, *J* = 17.8 Hz, 1 H, H*H*C=C), 5.58, 5.59 [(d, *J* = 4.6 Hz), (s), total 1 H, 3H], 6.20, 6.23 (2 × dd, *J* = 11, 17.8 Hz, 1 H, H-C=C).

(1*R*,4a*S*,4b*S*,8a*R*,10a*S*)-7-Ethylenedioxy-1,4b,5,6,7,8,8a,9,10,10a-dodecahydro-2-vinylphenanthren-4(4a*H*)-one (21): To a stirred solution of **20** (10 mg, 0.03 mmol) in MeCN (0.5 mL) and CH_2Cl_2 (0.5 mL), were added powdered 4-Å MS (20 mg) and TPAP (10 mg). The mixture was stirred for 30 min at room temperature, and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. NH_4Cl and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 15:1) to give 9 mg (91%) of **21** as a colorless oil. − $[\alpha]_D^{24}$ = +46 (*c* = 0.1, $CHCl_3$). − IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 1650 cm^{-1} (s, C=O), 1100 (s, C−O). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 1.04 (d, *J* = 7 Hz, 3 H, CH_3), 1.10−1.85 (m, 8 H, 7,9,10-CH_2, 5α,8a-H), 1.97 (d, *J* = 13.2 Hz, 1 H, 4a-H), 2.18 (dddd, *J* = 3.7, 3.7, 13, 13 Hz, 1 H, 10a-H), 2.57 (dq, *J* = 4.3, 7 Hz, 1 H, 1-H), 2.89 (ddd, *J* = 4.5, 14, 14 Hz, 1 H, 5β-H), 3.88−3.99 (m, 4 H, 2 × CH_2O), 5.44 (d, *J* = 11 Hz, 1 H, *H*HC=C), 5.65 (d, *J* = 17.7 Hz, 1 H, H*H*C=C), 5.72 (s, 1 H, 3-H), 6.33 (dd, *J* = 11, 17.7, Hz, 1 H, H-C=C). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 14.9, 20.2, 21.0, 23.2, 26.8, 31.2, 33.4, 36.3, 38.2, 38.4, 42.5, 53.0, 56.6, 64.7, 64.8, 112.8, 120.2, 128.9, 136.4, 160.6, 202.0. − MS (FAB^+): found 344.2339 ($C_{22}H_{32}O_2$, M^+), calcd. 344.2349.

(+)-2-Deoxyphytocassane A (1): To a solution of **21** (9 mg, 0.03 mmol) in THF (0.5 mL) was added 1.2 N aq. HCl (0.3 mL). The mixture was stirred for 2 h at room temperature, and diluted with diethyl ether. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and sat. aq. $NaHCO_3$, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 15:1) to give 5 mg (64%) of **1** as a colorless gum. − CD (EtOH) λ_{ext} = 369 nm (Δε = +1.63), 279 nm (Δε = −1.20). − $[\alpha]_D^{26}$ = +5.8 (*c* = 0.1, $CHCl_3$). − IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 2980 cm^{-1} (s, C−H), 2870 (m, C−H), 1700 (s, C=O), 1650 (s, C=O), 1460 (m), 1385 (m), 1230 (w), 1110 (m). −

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 3 H, 20-CH_3), 1.08 (s, 3 H, 18-CH_3), 1.09 (d, *J* = 7 Hz, 3 H, 17-CH_3), 1.11 (s, 3 H, 19-CH_3), 1.42 (br. dd, *J* = 3, 12 Hz, 1 H, 5-H), 1.52 (m, 2 H, 6β,7α-H), 1.66 (m, 2 H, 1α,6α-H), 1.77 (m, 1 H, 7β-H), 1.97 (d, *J* = 13.2 Hz, 1 H, 9-H), 2.22 (m, 1 H, 8-H), 2.38 (ddd, *J* = 4, 5.8, 14 Hz, 1 H, 2α-H), 2.64 (m, 2 H, 1β,14-H), 3.23 (ddd, *J* = 4, 6.5, 14 Hz, 1 H, 2β-H), 5.49 (d, *J* = 10.9 Hz, 1 H, 16-C*H*H), 5.67 (d, *J* = 17.7 Hz, 1 H, 16-CH*H*), 5.76 (s, 1 H, 12-H), 6.35 (dd, *J* = 10.9, 17.7 Hz, 1 H, 15-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.3 (C-17), 14.2 (C-18), 21.7 (C-20), 22.2 (C-6), 26.2 (C-19), 31.1 (C-7), 33.3 (C-14), 34.5 (C-1), 37.9 (C-8), 37.9 (C-8), 38.36 (C-2), 38.45 (C-10), 48.1 (C-4), 55.7 (C-5), 55.9 (C-9), 120.6 (C-16), 128.6 (C-15), 136.3 (C-12), 160.7 (C-13), 201.1 (C-11), 216.8 (C-3). − MS (FAB$^+$): found 300.2094 ($C_{20}H_{28}O_2$, M^+), calcd. 300.2088.

(3*R*,4a*R*,4b*S*,8a*R*,10a*R*)-3,4,4a,4b,5,6,7,8,8a,9,10,10a-Dodecahydro-3-hydroxy-1,1,4a-trimethylphenanthren-2(1*H*)-one (23): To a solution of **22** (260 mg, 1.05 mmol) in dry CH_2Cl_2 (4 mL) at 0 °C under argon were added Et_3N (292 μL, 2.10 mmol) and TMSOTf (228 μL, 1.26 mmol). The mixture was stirred for 30 min and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was immediately dissolved in hexane (8 mL). To the solution were added $NaHCO_3$ (300 mg) and 70% MCPBA (388 mg, 1.57 mmol) at 0 °C. After stirring for 2 h, the mixture was poured into sat. aq. $NaHCO_3$ and extracted several times with diethyl ether. The combined organic extracts were washed twice with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in MeOH (2 mL). To this solution was added $(COOH)_2$ (ca. 10 mg) at room temperature, and the mixture was stirred for 5 min. After dilution with water, the mixture was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (10 g, hexane/ethyl acetate = 40:1) to give 180 mg (65%) of **23** as a colorless oil. − CD (EtOH) λ_{ext} = 284 nm (Δε = −0.61). − n_D^{24} = 1.4480, $[\alpha]_D^{26}$ = −32.9 (*c* = 0.16, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3480 cm^{-1} (m, OH), 1700 (s, C=O), 1050 (s, C−O). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69, 0.8−1.8 [(dt, *J* = 4, 14.4 Hz), (m), total 17 H, 5,6,7,8,9,10-CH_2, 4β,4b,8a,10a-H], 1.11 (s, 3 H, 1α-CH_3), 1.13 (s, 3 H, 1β-CH_3), 1.15 (s, 3 H, 4a-CH_3), 2.44 (dd, *J* = 6.6, 12.7 Hz, 1 H, 4β-H), 3.63 (d, *J* = 3.5 Hz, 1 H, H-O), 4.56 (ddd, *J* = 3.5, 6.6, 13.2 Hz, 1 H, 3-H). − MS (FAB$^+$): found 264.2070 ($C_{17}H_{28}O_2$, M^+), calcd. 264.2091.

(4a*R*,4b*S*,8a*R*,10a*R*)-3-*tert*-Butyldimethylsilyloxy-4a,4b,5,6,7,-8,8a,9,10,10a-decahydro-1,1,4a-trimethylphenanthren-2(1*H*)-one (27): To a solution of **23** (170 mg, 0.64 mmol) in dry CH_2Cl_2 (3 mL) at 0 °C was added Dess−Martin periodinane (410 mg, 0.97 mmol). The mixture was stirred for 1 h and diluted with diethyl ether, followed by sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in DMF (2 mL). To the solution was added imidazole (132 mg, 1.93 mmol) and TBSCl (126 mg, 0.84 mmol). The mixture was stirred overnight at room temperature, and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (8 g, hexane/ethyl acetate = 80:1) to give 228 mg (94% based on **23**) of **27** as a colorless oil. − n_D^{24} = 1.4498, $[\alpha]_D^{26}$ = +14.6 (*c* = 0.28, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 1680 cm^{-1} (s, C=O), 1635 (m, C=C). − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.11 (s, 6 H, 2 × CH_3-Si), 0.8−1.8 (m, 15 H, 5,6,7,8,9,10-CH_2, 4b,8a,10a-H), 0.95 (s, 9 H, *t*Bu), 1.06 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.16 (s, 3 H, CH_3), 6.35 (s, 1 H, H-C=C). − MS (EI): found 319 ($C_{23}H_{40}O_2Si$, M^+ − *t*Bu), calcd. 319.

(2*R*,4a*R*,4b*S*,8a*R*,10a*R*)-1,4,4a,4b,5,6,7,8a,9,10,10a-Dodecahydro-2-hydroxy-1,1,4a-trimethylphenanthren-3(2*H*)-one (24): To a solution of **27** (220 mg, 0.59 mmol) in dry THF (4 mL) at −78 °C was carefully added LAH (67.0 mg, 1.76 mmol). After warming to room temperature over 2 h with stirring, the mixture was cooled to 0 °C. Water was then added carefully, followed by 1.2 N aq. HCl. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (8 g, hexane/ethyl acetate = 30:1) to give 90.0 mg (58%) of **24** as a colorless oil. − CD (EtOH) λ_{ext} = 288 nm (Δε = +0.97). − n_D^{26} = 1.5170, $[\alpha]_D^{26}$ = +19.7 (*c* = 0.35, $CHCl_3$). − IR (film): $\tilde{\nu}_{max}$ = 3485 cm^{-1} (br. m, OH), 1725 (s, C=O), 1070 (m, C−O). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.68 (s, 3 H, 11-CH_3), 0.80 (s, 3 H, 13-CH_3), 0.9−1.1 (m, 2 H, 6α,7β-H), 0.95 (m, 2 H, 4b,5β-H), 1.10−1.23 (m, 2 H, 8a,8α-H), 1.16 (s, 3 H, 12-CH_3), 1.40 (m, 1 H, 10α-H), 1.50 (m, 1 H, 5α-H), 1.52 (dd *J* = 2.5, 12.3 Hz, 1 H, 10a-H), 1.6−1.7 (m, 2 H, 6β,7α-H), 1.75−1.80 (m, 2 H, 8β,10β-H), 2.13 (d, *J* = 12.2 Hz, 1 H, 4α-H), 2.51 (d, *J* = 12.2 Hz, 1 H, 4β-H), 3.41 (d, *J* = 4 Hz, 1 H, H-O), 3.91 (d, *J* = 4 Hz, 1 H, 2-H). − ^{13}C NMR (125 MHz, $CDCl_3$); δ = 14.8 (C-13), 16.5 (C-11), 21.4 (C-10), 25.1 (C-5), 26.1 (C-9), 26.6 (C-8), 29.2 (C-12), 34.9 (C-6), 35.1 (C-7), 36.6 (C-8a), 43.7 (C-4a), 45.7 (C-1), 51.5 (C-4), 53.9 (C-10a), 56.1 (C-4b), 82.7 (C-2), 211.5 (C-3). − MS (FAB$^+$): found 264.2085 ($C_{17}H_{28}O_2$, M^+), calcd. 264.2070.

(3*S*,4a*R*,4b*S*,8a*R*,10a*R*)-3-*tert*-Butyldimethylsilyloxy-3,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,1,4a-trimethylphenanthren-2(1*H*)-one (28): To a solution of **27** (30 mg, 0.08 mmol) in EtOH (1 mL) at 0 °C was added $NaBH_4$ (20 mg, 0.5 mmol). After warming to room temperature, the mixture was stirred overnight and poured into sat. aq. NH_4Cl. The aqueous layer was extracted several times with diethyl ether. The combined organic layers were washed with water and sat. aq. NH_4Cl, and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in dry CH_2Cl_2 (2 mL). To this solution was added Dess−Martin periodinane (100 mg, 0.2 mmol) at 0 °C. After warming to room temperature, the mixture was stirred for 1 h and diluted with diethyl ether, followed by sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3 The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 70:1) to give 30 mg (quant.) of a mixture of **28** and **29** (1:3) as a colorless oil. − Properties of the mixture of **28** and **29**: IR (film): $\tilde{\nu}_{max}$ = 1730 cm^{-1} (s, C=O). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = −0.03 (s, CH_3-Si of **29**), 0.01 (s, CH_3-Si of **28**), 0.09 (s, CH_3-Si of **29**), 0.12 (s, CH_3-Si of **28**), 0.73 (s, CH_3 of **28**), 0.77 (s, CH_3 of **29**), 0.83 (s, CH_3 of **29**), 0.90 (s, *t*Bu of **28**), 0.94 (s, *t*Bu of **28**), 1.06 (s, CH_3 of **29**), 1.09 (s, CH_3 of **28**), 1.09 (s, CH_3 of **29**), 0.8−1.9 (m, 5,6,7,8,9,10-CH_2, 4b,8a,10a-H of **29** and 5,6,7,8,9,10-CH_2, 4b,8a,10a-H of **28**), 2.08 (d, *J* = 11.9 Hz, 4α-H of **29**), 2.18 (dd, *J* = 11, 13.5 Hz, 4β-H of **28**), 2.35 (d, *J* = 11.9 Hz, 4β-H of **29**), 3.97 (s, 2-H of **29**), 4.67 (dd, *J* = 8.3, 11 Hz, 3-H of **28**). − MS (FAB$^+$): found 378.2968 ($C_{23}H_{42}O_2Si$, M^+), calcd. 378.2954.

(3*S*,4a*R*,4b*S*,8a*R*,10a*R*)-3,4,4a,4b,5,6,7,8,8a,9,10,10a-Dodecahydro-3-hydroxy-1,1,4a-trimethylphenanthren-2(1*H*)-one (25): To a solu-

tion of the mixture of **28** and **29** (30 mg, 0.08 mmol) in MeCN (1 mL), at 0 °C, was added 47% aq. HF (0.3 mL). After warming to room temperature, the mixture was stirred for 1.5 h and poured into sat. aq. $NaHCO_3$. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (1.2 g, hexane/ethyl acetate = 10:1) to give 9 mg (43%) of a mixture of **25** and **24** (5:2). At this point, 10 mg (33%) of **29** was recovered. − Properties of the mixture of **25** and **24**: IR ($CHCl_3$ solution): $\tilde{\nu}_{max}$ = 3480 cm^{-1} (w, O−H), 1705 (s, C=O). − MS (FAB^+): found 264.2097 ($C_{17}H_{28}O_2$, M^+), calcd. 264.2070. − Properties of **25** (difference spectra): CD (EtOH): λ_{ext} = 289 nm ($\Delta\varepsilon$ = +0.04). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.69 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 0.8−1.8 (m, 15 H, 5,6,7,8,9,10-CH_2, 4β,4b,8a,10a-H), 2.40 (dd, *J* = 12, 13.2 Hz, 1 H, 4α-H), 3.56 (d, *J* = 4.3 Hz, 1 H, H-O), 4.57 (ddd, *J* = 4.3, 7.4, 12 Hz, 1 H, 3-H).

(*R*)-7-(2′,2′-Dimethylpropylenedioxy)-6-methylbicyclo[4.4.0]-1-decen-3-one (30): Compound **30** was prepared from (*R*)-**3** (ca. 60% *ee*) according to Swaminathan's method.[26] The ketone **30** (50 g) was dissolved in diethyl ether (200 mL) at reflux, and the solution was left to stand for 3 d at room temperature. The crystals were collected (11 g, 22%), and the plates (4.6 g, 9%) removed. The enantiomeric purities of the remaining crystals and of the plates were 96.6% *ee* and 10% *ee*, respectively. [The concentrated mother liquor contained 34 g (68%) of **30** of 60% *ee*]. − M.p. 118−120 °C, $[\alpha]_D^{21}$ = −79.1 (*c* = 1.08, $CHCl_3$). − GC analysis; column: Chirasil Dex CB® (25 m × 0.25 mm), carrier gas He (60 kPa), 110 °C (15 min) to 200 °C (2 °C/min), t_R(*S*) = 64.1 (1.7%), t_R(*R*) = 64.9 (98.3%). − $C_{16}H_{24}O_3$ (264.4): calcd. C 72.69, H 9.15; found C 72.74, H 9.25. − The ^1H NMR and IR spectra are identical with those reported.[26]

(1*R*,4a*R*,4b*S*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-1,4,4a,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethylphenanthren-3(2*H*)-one (37): To a stirred suspension of CuI (7.60 g, 39.9 mmol) in dry diethyl ether (80 mL), at 0 °C under argon, was added dropwise a solution of MeLi in diethyl ether (1.14 M, 70.0 mL, 79.8 mmol), and stirring was continued for 15 min. To the resulting solution of Me_2CuLi was added dropwise at −78 °C a solution of **36** (10.0 g, 26.6 mmol) in dry diethyl ether (100 mL). The mixture was gradually warmed to −30 °C over 3 h with stirring, poured into sat. aq. NH_4Cl, and filtered through a Celite pad. The filtrate was separated, and the aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (200 g, hexane/ethyl acetate = 50:1) to give 10.1 g (97%) of a mixture of **37** and **38** as colorless solids (β-Me/α-Me = 54:46). The mixture was subjected to MPLC separation (SiO_2: 600 g, elution with hexane/ethyl acetate = 70:1, 10 mL/min) to give 4.70 g of **37**, 4.27 g of **38** and >900 mg of mixture. Analytical samples were obtained as colorless crystals by recrystallization from hexane/ethyl acetate. − Properties of **37**: M.p. 131−134 °C, $[\alpha]_D^{25}$ = −15.4 (*c* = 0.68, $CHCl_3$). − GC analysis: column: Neutrabond® (30 m × 0.25 mm), carrier gas He (60 kPa), 200 °C (10 min) to 300 °C (3 °C/min), t_R = 38.9. − IR (KBr): $\tilde{\nu}_{max}$ = 1715 cm^{-1} (s, C=O), 1255 (s), 1100 (s), 1080 (s), 880 (s), 835 (s), 770 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.029 (s, 3 H, CH_3Si), 0.034 (s, 3 H, CH_3Si), 0.78 (s, 3 H, CH_3), 0.80 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.80 (m, 1 H, 6α-H), 0.88 (s, 9 H, *t*Bu), 0.90 (s, 3 H, CH_3), 0.91 (s, 3H, CH_3), [0.99 (m), 1.21−1.71 (m), 1.82 (dddd, *J* = 4.0, 4.0, 12.2, 12.2 Hz) total 10 H, 1,4a,8a,10a-H, 5,9,10-CH_2], 2.01 (dd, *J* = 13.2, 13.2 Hz, 1 H, 4α-H), 2.13−2.18 (m, 2 H, 2α,6β-H), 2.26 (ddd, *J* = 2.1, 4.6, 13.2 Hz, 1 H, 4β-H), 2.50 (dd, *J* = 5.8, 13.2 Hz, 1 H, 2β-H), 3.17 (dd, *J* = 4.6, 11.3 Hz, 1 H, 7-H). − $C_{24}H_{44}O_2Si$ (392.7): calcd. C 73.41, H 11.29; found C 73.51, H 11.54. − Properties of isomer **38**: M.p. 117−118 °C, $[\alpha]_D^{25}$ = −5.3 (*c* = 0.64, $CHCl_3$). − GC analysis: column: Neutrabond® (30 m × 0.25 mm), carrier gas He (60 kPa), 200 °C (10 min) to 300 °C (3 °C/min), t_R = 38.6. − IR (KBr): $\tilde{\nu}_{max}$ = 1705 cm^{-1} (s, C=O), 1250 (s), 1100 (s), 1070 (s), 885 (s), 835 (s), 775 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.027 (s, 3 H, CH_3Si), 0.032 (s, 3 H, CH_3Si), 0.77 (s, 3 H, CH_3), 0.84 (m, 1 H, 6α-H), 0.87 (s, 3 H, CH_3), 0.88 (s, 9 H, *t*Bu), 0.90 (s, 3 H, CH_3), 0.99 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.12 (ddd, *J* = 4.0, 11.0, 13.4 Hz, 1 H, 4a-H), 1.24 (ddd, *J* = 4.3, 11.0, 11.0 Hz, 1 H, 5β-H), 1.32−1.66 (m, 8 H, 1,5α,8a,10a-H, 9,10-CH_2), 2.05 (dd, *J* = 13.5, 13.5 Hz, 2 H, 2α,4α-H), 2.14 (dddd, *J* = 4.0, 4.0, 5.0, 13.2 Hz, 1 H, 6β-H), 2.26 (ddd, *J* = 2.7, 3.7, 13.5 Hz, 1 H, 2β-H), 2.32 (ddd, *J* = 2.7, 3.7, 13.5 Hz, 1 H, 4β-H), 3.17 (dd, *J* = 5.0, 11 Hz, 1 H, 7-H). − $C_{24}H_{44}O_2Si$ (392.7): calcd. C 73.41, H 11.29; found C 73.26, H 11.41.

(1*S*,2*RS*,4a*R*,4b*S*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-2-*tert*-butyldiphenylsilyloxymethyl-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethylphenanthren-3(2*H*)-one (39): NaH (60%, 510 mg, 6.38 mmol) was added portionwise over 30 min to a stirred solution of **37** (500 mg, 1.28 mmol) in HCO_2Et (20 mL), at −10 °C under argon. MeOH (52.0 μL, 1.28 mmol) was then added, and the mixture was stirred overnight, warming to room temperature. After careful addition of water, the mixture was poured into sat. aq. NH_4Cl and extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in dry THF (6 mL) and MeOH (2 mL). $NaBH_4$ (72 mg, 1.91 mmol) was added portionwise to the solution, at 0 °C. Then the mixture was stirred for 2 h at room temperature, and poured into sat. aq. NH_4Cl. The aqueous layer was extracted with ethyl acetate, and the combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was quickly chromatographed on silica gel (10 g, hexane/ethyl acetate = 5:1) to give crude diol. This was immediately dissolved in DMF (5 mL), and imidazole (174 mg, 2.55 mmol) and TBDPSCl (424 μL, 1.53 mmol) were added to the mixture at 0 °C. The mixture was stirred for 2 h and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (18 g, hexane/ethyl acetate = 50:1) to give crude alcohol. This was dissolved in CH_2Cl_2 (20 mL). To this solution were added powdered 4-Å MS (700 mg) and PCC (623 mg, 2.89 mmol), at room temperature. The mixture was stirred for 1 h and filtered through silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (16 g, hexane/ethyl acetate = 80:1) to give 478 mg (57% based on **37**) of **39** as colorless foam. − $[\alpha]_D^{21}$ = −6.1 (*c* = 0.47, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 1710 cm^{-1} (s, C=O), 1110 (s), 835 (s), 700 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.02, 0.028, 0.032 (3 × s, total 6 H, CH_3Si), 0.58 (d, *J* = 7.1 Hz, CH_3 of the major isomer), 0.66, 0.74, 0.91 (s, CH_3 of the minor isomer), 0.79, 0.88, 0.91 (s, CH_3 of the major isomer), 0.81 (d, *J* = 7.3 Hz, CH_3 of the minor isomer), 0.89 (s, 9 H, *t*Bu), 1.03, 1.04 (s, total 9 H, *t*Bu), 0.9−1.86 (m, 11.3 H, 1-H of the minor isomer, 4a,8a,10a-H, 5,6,9,10-CH_2), 1.88 (dd, *J* = 13, 13 Hz, 0.3 H, 4α-H of the minor isomer), 1.99 (dd, *J* = 13.5, 13.5 Hz, 0.7 H, 4α-H of the major isomer), 2.08 (dd, *J* = 4.6, 13 Hz, 0.3 H, 4β-H of the minor isomer), 2.19 (dd, *J* = 4.9,

13.5 Hz, 0.7 H, 4β-H of the major isomer), 2.38 (m, 0.7 H, 1-H of the major isomer), 2.51 (br. dd, J = 7.4, 8.9 Hz, 0.3 H, 2-H of the minor isomer), 2.72 (ddd, J = 5.0, 9.0, 13.8 Hz, 0.7 H, 2-H of the major isomer), 3.12−3.18 (m, 1 H, 7-H), 3.69 (dd, J = 9.0, 11 Hz, 0.7 H, C*H*H-O of the major isomer), 3.81 (dd, J = 7.4, 10.1 Hz, 0.3 H, C*H*H-O of the minor isomer), 3.89 (dd, J = 8.6, 10.1 Hz, 0.3 H, CH*H*-O of the minor isomer), 3.98 (dd, J = 5.0, 11 Hz, 0.7 H, CH*H*-O of the major isomer), 7.35−7.68 (m, 10 H, Ar-H). − $C_{41}H_{64}O_3Si_2$ (661.1): calcd. C 74.49, H 9.76; found C 74.30, H 10.15.

(1*S*,2*RS*,4a*R*,4b*S*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-2-*tert*-butyldiphenylsilyloxymethyl-1,2,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethylphenanthrene (40): To a solution of **39** (9.70 g, 14.7 mmol) in THF (80 mL) at room temperature was added anhydrous $MgSO_4$ (7.08 g, 58.8 mmol) and *p*-TsNHNH$_2$ (3.56 g, 19.1 mmol), followed by a catalytic amount (ca. 30 mg) of PPTS. The mixture was stirred overnight and filtered through a silica gel pad. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (200 g, hexane/ethyl acetate = 3:1) to give crude hydrazone. This was immediately dissolved in dry THF (100 mL) under argon. To the solution, at −78 °C, was added dropwise a solution of LDA in dry THF (200 mL) [prepared from diisopropylamine (30.9 mL, 220 mmol) and a solution of *n*BuLi in hexane (2.47 M, 89.1 mL, 4.15 mmol)]. The mixture was stirred overnight, with gradual warming to room temperature, and poured into water and sat. aq. NH_4Cl. The aqueous layer was extracted with diethyl ether, and combined organic extracts were washed with water and sat. aq. NH_4Cl, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (200 g, hexane/ethyl acetate = 100:1) to give 6.44 g (68% based on **39**) of **40** as a colorless solid. This was employed in the next step without further purification. − M.p. 141−145 °C, $[\alpha]_D^{24}$ = −29.6 (c = 0.82, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 1110 cm^{-1} (s), 1080 (s), 835 (s), 700 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03, 0.037, 0.045, (3 × s, total 6 H, CH_3-Si), 0.64 (d, J = 7.0 Hz, CH_3 of the major isomer), 0.65, 0.72, 1.06 (3 × s, CH_3 of the minor isomer), 0.75, 0.80, 0.89 (3 × s, CH_3 of the major isomer), 0.81 (d, J = 6.7 Hz, CH_3 of the minor isomer), [0.83 (dd, J = 2.1, 11.9 Hz), 1.07 (ddd, J = 4.0, 13.1, 17.1 Hz), 1.18−1.81 (m), total 11.25 H, 1-H of the minor isomer, 4a,8a,10a-H, 5,6,9,10-CH_2)], 1.89 (m, 0.75 H, 1-H of the major isomer), 2.05 (m, 0.25 H, 2-H of the minor isomer), 2.55 (m, 0.75 H, 2-H of the major isomer), 3.17−3.22 (m, 1 H, 7-H), 3.46 (dd, J = 9.5, 10.1 Hz, 0.25 H, C*H*H-O of the minor isomer), 3.54 (d, J = 7.9 Hz, 1.5 H, CH_2-O of the major isomer), 3.60 (dd, J = 5.8, 10.1 Hz, 0.25 H, CH*H*-O of the minor isomer), 5.44 (br. d, J = 10.4 Hz, 0.75 H, 4-H of the major isomer), 5.53 (m, 0.25 H, 3-H of the minor isomer), 5.61 (m, total 1 H, 3-H of the major isomer and 4-H of the minor isomer), 7.35−7.68 (m, 10 H, Ar-H). − $C_{41}H_{64}O_2Si_2$ (645.1): calcd. C 76.33, H 10.00; found C 76.40, H 10.20.

(1*S*,2*RS*,4a*R*,4b*S*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-1,2,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-2-hydroxymethyl-1,4b,8,8-tetramethylphenanthrene (41): To a stirred solution of **40** (290 mg, 0.45 mmol) in THF (3 mL), was added TBAF · x H_2O (200 mg, Aldrich) in one portion. The mixture was stirred for 3 h and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (5 g, hexane/ethyl acetate = 10:1) to give 191 mg (quant.) of **41** as colorless solids. This was employed in the next step without further purification. − M.p. 148−155 °C, $[\alpha]_D^{21}$ = −69.2 (c = 0.75, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3360 cm^{-1} (br. m, OH), 1110 (s), 1065 (s), 835 (s). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, CH_3Si), 0.04 (s, 3 H, CH_3Si), 0.68 (d, J = 7.0 Hz, CH_3 of the major isomer), 0.74, 0.79, 0.89 (CH_3 of the major isomer), 0.74, 0.76, 0.89 (CH_3 of the minor isomer), 0.84 (d, J = 7.3 Hz, CH_3 of the minor isomer), 0.89 (s, 9 H, *t*Bu), [0.82−0.87 (m), 1.09 (ddd, J = 3.7, 13.2, 17.1 Hz), 1.21−1.84 (m), total 13 H, 1,4a,8a,10a-H, 5,6,9,10-CH_2, H-O)], 1.97 (m, 0.25 H, 2-H of the minor isomer), 2.46 (m, 0.75 H, 2-H of the major isomer), 3.19 (dd, J = 4.6, 11.3 Hz, 1 H, 7-H), 3.47−3.58 (m, 2 H, CH_2-O), 5.44 (br. d, J = 10.4 Hz, 0.75 H, 4-H of the major isomer), 5.56 (m, 0.25 H, 3-H of the minor isomer), 5.66 (br. d, J = 10.4 Hz, 3-H of the major isomer), 5.71 (br. d, J = 10.4 Hz, 4-H of the minor isomer). − $C_{25}H_{46}O_2Si$ (406.7): calcd. C 73.83, H 11.40; found C 73.46, H 11.78.

(1*S*,2*RS*,3*RS*,4*RS*,4a*R*,4b*R*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-3,4-epoxy-2-hydroxymethyl-1,4b,8,8-tetramethylperhydrophenanthrene (42): To a solution of **41** (191 mg, 0.45 mmol) in $CHCl_3$ (3 mL) were added $NaHCO_3$ (100 mg) and 70% MCPBA (144 mg, 0.59 mmol). The mixture was stirred for 3 h at room temperature, and poured into sat. aq. $NaHCO_3$. The aqueous layer was extracted several times with ethyl acetate. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (5 g, hexane/ethyl acetate = 4:1) to give 174 mg (92% based on **40**) of **42** as colorless solids. This was employed in the next step without further purification. − M.p. 92−95 °C, $[\alpha]_D^{21}$ = −38.3 (c = 0.93, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3310 cm^{-1} (br. m, OH), 1255 (s), 1090 (s), 1070 (s), 880 (s), 835 (s), 770 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, CH_3Si), 0.05 (s, 3 H, CH_3Si), 0.74, 0.75, 0.757, 0.763, 0.78, 0.88, 0.90, 0.92, 1.00, 1.03 (s, total 9 H, 3 × CH_3), 0.67, 0.7−0.97 (d, J = 7 Hz, total 3 H, CH_3), 0.89 (s, 9 H, *t*Bu), 1.18−1.7 (m, 14 H, 1,3,4a,8a,10a-H, 5,6,9,10-CH_2, H-O), [1.88 (br. dd, J = 6.1, 12.5 Hz), 1.94−2.00 (m), 2.05 (ddt, J = 1.7, 5.9, 7.3 Hz), 2.13 (br. dd, J = 7.1, 7.1 Hz), 2.70 (m), total 1 H 2-H], 1.94−2.00 (m, 1 H, 4-H), [3.02−3.14 (m), 3.63−3.73 (m), 3.80 (dd, J = 7.2, 10.2 Hz), 3.87 (dd, J = 7.6, 10.5 Hz) total 2 H, CH_2-O], 3.21 (m, 1 H, 7-H). − $C_{25}H_{46}O_3Si$ (422.7): calcd. C 71.03, H 10.97; found C 70.97, H 11.25.

(1*S*,4*RS*,4a*R*,4b*R*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-4-hydroxy-1,4b,8,8-tetramethylphenanthrene-2-carbaldehyde (43): To a stirred solution of **42** (170 mg, 0.40 mmol) in dry CH_2Cl_2 (4 mL) at 0 °C was added Dess−Martin periodinane (256 mg, 0.60 mmol) in one portion. The mixture was warmed to room temperature, and stirred for 30 min. Then the mixture was diluted with diethyl ether, and sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3 were added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in diethyl ether (3 mL). To this solution was added pyrrolidine (3 drops, ca. 30 mg) and the solution was stirred for 2 h at room temperature. The mixture was diluted with diethyl ether and washed with sat. aq. NH_4Cl. After concentration in vacuo, the residue was chromatographed on silica gel (4 g, hexane/ethyl acetate = 7:1) to give 123 mg (73% based on **42**) of **43** as a colorless oil. This contained unknown and inseparable impurities, and was therefore directly employed in the next step without further purification. − IR (KBr): $\tilde{\nu}_{max}$ = 3450 cm^{-1} (br. w, OH), 1690 (s, C=O), 1100 (s), 1075 (s), 835 (s), 775 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.038, 0.045, 0.054 (3 × s, total 6 H, CH_3-Si), 0.78, 0.89, 0.92 (s, CH_3 of the major isomer), 0.84 (d, J = 7 Hz, CH_3 of the minor isomer), 0.89 (s, 9 H, *t*Bu), 0.92 (d, J = 6.8 Hz, CH_3 of

the major isomer), 1.2−2.0 (m, 11 H, 4a,5β,8a,10a-H, 6,9,10-CH_2, H-O), 1.83, 2.07 (ddd, J = 3.4, 3.4, 12.9 Hz, total 1 H, 5α-H), 2.54 (dq, J = 3.9, 6.8 Hz, 0.8 H, 1-H of the major isomer), 2.66 (dq, J = 5.4, 7 Hz, 0.2 H, 1-H of the minor isomer), 3.22 (m, 1 H, 7-H), 4.37 (br. dd, J = 4.2, 6.1 Hz, 0.8 H, 4-H of the major isomer), 4.55 (m, 0.2 H, 4-H of the minor isomer), 6.50 (d, J = 4.2 Hz, 0.8 H, 3-H of the major isomer), 6.59 (d, J = 4.4 Hz, 0.2 H, 3-H, of the minor isomer), 9.45,9.46 (2×s, total 1 H, H-C=O). − MS (EI): found 420 ($C_{25}H_{44}O_3Si$, M^+), calcd. 420.

(1*S*,4*RS*,4a*R*,4b*R*,7*R*,8a*S*,10a*R*)-7-*tert*-Butyldimethylsilyloxy-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethyl-2-vinylphenanthren-4-ol (44): To a suspension of Ph_3PMeBr (306 mg, 0.86 mmol) in dry THF (3 mL), at −78 °C under argon, was added dropwise a solution of *n*BuLi in hexane (1.57 M, 476 μL, 0.71 mmol). The mixture was stirred for 30 min at 0 °C. This Wittig reagent was added to a solution of **43** (120 mg, 0.29 mmol) in dry THF (2 mL) at −78 °C. The mixture was stirred for 1 h at 0 °C and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (3 g, hexane/ethyl acetate = 60:1) to give 105 mg (88%) of **44** as colorless solids. This was employed in the next step without further purification. − M.p. 139−153 °C, $[\alpha]_D^{22}$ = −5.3 (c = 1.4, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3600 cm^{-1} (w), 3455 (br. m, OH), 3090 (vw), 1605 (w, C=C), 1100 (s), 1070 (s), 835 (s), 775 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.03, 0.04, 0.05 (3×s, total 6 H, CH_3-Si), 0.77, 0.85, 0.92 (3 × s, CH_3 of the major isomer), 0.83, 0.89, 1.14 (3 × s, CH_3 of the minor isomer), 0.89 (s, 9 H, *t*Bu), 0.90 (d, J = 7 Hz, CH_3 of the minor isomer), 0.98 (d, J = 7.0 Hz, CH_3 of the major isomer),1.16−1.94 (m, 11 H, 4a,5β,8a,10a-H, 6,9,10-CH_2, H-O), 1.80, 2.07 (ddd, J = 3.4, 3.4, 13 Hz, total 1 H, 5α-H), 2.35 (dq, J = 4.0, 7.0 Hz, 0.8 H, 1-H of the major isomer), 2.47 (dq, J = 5.2, 7.1 Hz, 0.2 H, 1-H of the minor isomer), 3.22 (m, 1 H, 7-H), 4.18 (br. ddd, J = 4.3, 4.9, 6.5 Hz, 0.8 Hz, 4-H, of the major isomer), 4.34 (br. ddd, J = 4.3, 4.7, 9.2 Hz, 0.2 H, 4-H of the minor isomer), 5.07 (d, J = 11.0 Hz, 1 H, *H*HC=C), 5.23 (d, J = 17.7 Hz, 0.2 H, H*H*C=C of the minor isomer), 5.25 (d, J = 17.4 Hz, 0.8 H, H*H*C=C of the major isomer), 5.57 (d, J = 4.3 Hz, 0.8 H, 3-H of the major isomer), 5.66 (d, J = 4.7 Hz, 0.2 H, 3-H of the minor isomer), 6.22 (dd, J = 11.0, 17.7 Hz, 0.2 H, H-C=C of the minor isomer), 6.24 (dd, J = 11.0, 17.4 Hz, 0.8 H, H-C=C of the major isomer). − $C_{26}H_{46}O_2Si$ (418.7): calcd. C 74.58, H 11.07; found C 74.56, H 11.54.

(1*S*,4*R*,4a*R*,4b*R*,7*R*,8a*S*,10a*R*)-4-Acetoxy-7-*tert*-butyldimethylsilyloxy-1,4,4a,4b,5,6,7,8,8a,9,10,10a-dodecahydro-1,4b,8,8-tetramethyl-2-vinylphenanthrene (45): To a solution of **44** (5 mg, 0.01 mmol) in pyridine (0.3 mL) at room temperature were added Ac_2O (1 drop, ca. 10 mg) and a catalytic amount of DMAP (ca. 2 mg). The mixture was stirred for 7 h and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $CuSO_4$, water, and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was purified by PTLC to give 7 mg (quant.) of **45** as a colorless foam. This was employed in the next step without further purification. − $[\alpha]_D^{23}$ = −102 (c = 0.72, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 1730 cm^{-1} (s, C=O), 1605 (w, C=C), 1240 (s, OAc), 1100 (s), 835 (s), 775 (s). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, CH_3Si), 0.04 (s, 3 H, CH_3-Si), 0.75 (s, 3 H, CH_3), 0.86 (s, 3 H, CH_3), 0.88 (s, 9 H, *t*Bu), 0.90 (s, 3 H, CH_3), 0.99 (d, J = 6.8 Hz, 3 H, CH_3), 1.15−1.69 (m, 11 H, 4a,8a,10a-H, 5,6,9,10-CH_2), 2.02 (s, 3 H, CH_3-C=O), 2.37 (dq, J = 3.9, 6.8 Hz, 1 H, 1-H), 3.20 (dd, J = 4.4, 11.2 Hz, 1 H, 7-H), 5.09 (d, J = 10.8 Hz, 1 H, *H*HC=C), 5.27 (d, J = 17.6 Hz, 1 H, H*H*C=C), 5.36 (dd, J = 4.6, 5.6 Hz, 1 H, 3-H), 6.22 (dd, J = 10.8, 17.6 Hz, 1 H, H-C=C). − $C_{28}H_{48}O_3Si$ (460.8): calcd. C 72.99, H 10.50; found C 72.90, H 10.78.

(2*R*,4a*R*,4b*R*,5*R*,8*S*,8a*R*,10a*S*)-5-Acetoxy-1,2,3,4,4a,4b,5,-8,8a,9,10,10a-dodecahydro-1,1,4a,8-tetramethyl-7-vinylphenanthren-2-ol (46): A mixture of **45** (870 mg, 1.89 mmol) and a solution of TBAF in THF (1.00 M, 25.0 mL, 25.0 mmol) was stirred for 3 h at 50−60 °C and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (15 g, hexane/ethyl acetate = 15:2) to give 447 mg (68% based on **44**) of **46** as colorless solids. An analytical sample was obtained by recrystallization from hexane/ethyl acetate as colorless needles. − M.p. 135−137 °C, $[\alpha]_D^{23}$ = +165 (c = 1.01, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3290 cm^{-1} (br. m, OH), 1730 (s, C=O), 1605 (w, C=C), 1235 (s, OAc). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.92 (br. dd, J = 2.2, 11.7 Hz, 1 H, 10a-H), 1.00 (d, J = 6.8 Hz, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 1.19−1.74 (m, 11 H, 4b,8a-H, 3,4,9,10-CH_2, H-O), 2.05 (s, 3 H, CH_3-C=O), 2.39 (dq, J = 3.9, 6.8 Hz, 1 H, 8-H), 3.24 (br. ddd, J = 4.9, 5.9, 11.0 Hz, 1 H, 2-H), 5.10 (d, J = 10.8 Hz, 1 H, *H*HC=C), 5.28 (d, J = 17.6 Hz, 1 H, H*H*C=C), 5.37 (dd, J = 4.6, 5.5 Hz, 1 H, 5-H), 5.57 (d, J = 4.6 Hz, 1 H, 6-H), 6.23 (dd, J = 10.8, 17.6 Hz, 1 H, H-C=C). − $C_{22}H_{34}O_3$ (346.5): calcd. C 76.26, H 9.89; found C 76.39, H 10.22.

(4a*R*,4b*R*,5*R*,8*S*,8a*R*,10a*S*)-5-Acetoxy-3,4,4a,4b,5,8,8a,9,10,10a-dodecahydro-1,1,4a,8-tetramethyl-7-vinylphenanthren-2(1*H*)-one (47): To a solution of **46** (430 mg, 1.24 mmol) in CH_2Cl_2 (8 mL) at room temperature were added powdered 4-Å MS (800 mg) and PCC (670 mg, 3.11 mmol). The mixture was stirred for 5 h and filtered through silica gel. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel (14 g, hexane/ethyl acetate = 15:1) to give 418 mg (98%) of **47** as a colorless solid. An analytical sample was obtained as colorless needles by recrystallization from hexane/ethyl acetate. − M.p. 120−123 °C, $[\alpha]_D^{22}$ = +185 (c = 0.83, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3095 cm^{-1} (w), 1720 (s, C=O), 1700 (s, C=O), 1605 (w, C=C), 1240 (s, OAc). − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 7.1 Hz, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.33−1.79 (m, 9 H, 4,9,10-CH_2, 4b,8a,10a-H), 2.00 (s, 3 H, CH_3-C=O), 2.25 (ddd, J = 2.9, 4.6, 15.1 Hz, 1 H, 3β-H), 2.42 (dq, J = 3.9, 7.1 Hz, 1 H, 8-H), 2.67 (ddd, J = 6.1, 15.1, 15.1 Hz, 1 H, 3α-H), 5.11 (d, J = 11.0 Hz, 1 H, *H*HC=C), 5.28 (d, J = 17.6 Hz, 1 H, H*H*C=C), 5.41 (dd, J = 5.8, 7.1 Hz, 1 H, 5-H), 5.57 (d, J = 5.8 Hz, 1 H, 6-H), 6.23 (dd, J = 11.0, 17.6 Hz, 1 H, H-C=C). − $C_{22}H_{32}O_3$ (344.5): calcd. C 76.70, H 9.36; found C 76.86, H 9.61.

(3*S*,4a*R*,4b*R*,5*R*,8*S*,8a*R*,10a*S*)-5-Acetoxy-3,4,4a,4b,5,8,8a,-9,10,10a-dodecahydro-3-hydroxy-1,1,4a,8-tetramethyl-7-vinylphenanthren-2(1*H*)-one (48): To a solution of **47** (410 mg, 1.19 mmol) in dry THF (4 mL), at −78 °C under argon, was added dropwise a solution of LiHMDS in THF (1.00 M, 1.79 mL, 1.79 mmol). The mixture was stirred for 1 h, and TMSCl (294 μL, 2.38 mmol) was added to the mixture. After stirring for 10 min, the solution was poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in hexane (6 mL) at 0 °C. To this solution were added $NaHCO_3$ (600 mg) and 70% MCPBA (441 mg, 1.79 mmol). The mixture was stirred for 1.5 h and poured into sat. aq. $NaHCO_3$. The aqueous layer was extracted several

times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$, and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in MeOH (8 mL). A catalytic amount (ca. 10 mg) of $(CO_2H)_2$ was added at room temperature to the solution. The mixture was stirred for 10 min and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and sat. aq. $NaHCO_3$, and dried with $MgSO_4$. After concentration in vacuo, the residue was chromatographed on silica gel (15 g, hexane/ethyl acetate = 10:1) to give 143 mg (33%) of **48** as a colorless oil. At this stage, 50 mg of starting material **47** was recovered. The yield was therefore estimated as 38%. The product contained unknown and inseparable impurities, and therefore was directly employed in the next step. − IR (KBr): $\tilde{\nu}_{max}$ = 3480 cm^{-1} (br. w, OH), 1725 (s, C=O), 1605 (w, C=C), 1240 (s, OAc). − ^1H NMR (500 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3), 1.31−1.81 (m, 8 H, 4b,4β,8a,10a-H, 9,10-CH_2), 2.01 (s, 3 H, CH_3-C=O), 2.18 (dd, *J* = 6.1, 12.7 Hz, 1 H, 4α-H), 2.42 (dq, *J* = 4.0, 7.0 Hz, 1 H, 8-H), 3.58 (d, *J* = 3.9 Hz, 1 H, H-O), 4.54 (ddd, *J* = 4.0, 6.1, 16.8 Hz, 1 H, 3-H), 5.12 (d, *J* = 11 Hz, 1 H, *H*HC=C), 5.27 (d, *J* = 17.6 Hz, 1 H, H*H*C=C), 5.42 (dd, *J* = 4.6, 6.4 Hz, 1 H,5-H), 5.60 (d, *J* = 4.6 Hz, 1 H, 6-H), 6.23 (dd, *J* = 11, 17.6 Hz, 1 H, H-C=C). − MS (EI): found 360 ($C_{22}H_{32}O_4$, M^+), calcd. 360.

(4a*R*,4b*R*,5*R*,8*S*,8a*R*,10a*S*)-5-Acetoxy-3-*tert*-butyldimethylsilyloxy-4a,4b,5,8,8a,9,10,10a-decahydro-1,1,4a,8-tetramethyl-7-vinylphenanthren-2(1*H*)-one (49): To a solution of **48** (8 mg, 0.02 mmol) in dry CH_2Cl_2 (0.5 mL) at 0 °C was added Dess−Martin periodinane (14 mg, 0.03 mmol). The mixture was stirred for 1 h and diluted with diethyl ether, followed by sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was dissolved in DMF (0.5 mL). To this solution was added imidazole (8.0 mg, 0.1 mmol) and TBSCl (7.0 mg, 0.04 mmol). The mixture was stirred overnight at room temperature, and poured into water. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with water and brine, and dried with $MgSO_4$. After concentration in vacuo, the residue was purified by PTLC to give 7.0 mg (67% based on **48**) of **49** as a colorless gum. − $[\alpha]_D^{17}$ = +88.9 (*c* = 0.27, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 1735 cm^{-1} (s, C=O), 1680 (s, C=O), 1630 (w, C=C), 1235 (s, OAc), 840 (s). − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.10 (s, 3 H, CH_3-Si), 0.14 (s, 3 H, CH_3-Si), 0.92 (s, 9 H, *t*Bu), 1.03 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.42−1.88 (m, 7 H, 4b,8a,10a-H, 9,10-CH_2), 2.06 (s, 3 H, CH_3-C=O), 2.43 (dq, *J* = 4.3, 7.1 Hz, 1 H, 8-H) 5.13 (d, *J* = 10.8 Hz, 1 H, *H*HC=C), 5.29 (d, *J* = 17.6 Hz, 1 H, H*H*C=C), 5.54 (br. dd, *J* = 4.6, 5.8 Hz, 1 H, 5-H), 5.63 (d, *J* = 4.6 Hz, 1 H, 6-H), 6.14 (s, 1 H, 4-H), 6.23 (dd, *J* = 10.8, 17.6 Hz, 1 H, H-C=C). − MS (FAB$^+$): found 473.3073 ($C_{28}H_{44}O_4Si$, $[M + H]^+$), calcd. 472.3009.

(2*S*,4a*R*,4b*R*,5*R*,8*S*,8a*R*,10a*S*)-1,4,4a,4b,5,8,8a,9,10,10a-Decahydro-2,5-dihydroxy-1,1,4a,8-tetramethyl-7-vinylphenanthren-3(2*H*)-one (50): LAH (2 mg, 0.06 mmol) was added carefully to a solution of **49** (7 mg, 0.02 mmol) in dry THF (0.5 mL) at −78 °C. After gradual warming to 4 °C over 3 h, the mixture was stirred for an additional 1 h. Water was then added carefully, followed by 1.2 N aq. HCl. The aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with sat. aq. $NaHCO_3$ and dried with $MgSO_4$. After concentration in vacuo, the residue was purified by PTLC to give 3 mg (64%) of **50** as colorless solids. An analytical sample was obtained as colorless needles by recrystallization from hexane/ethyl acetate. − M.p. 155−157 °C, $[\alpha]_D^{17}$ = +7.8 (*c* = 0.16, $CHCl_3$). − IR (KBr): $\tilde{\nu}_{max}$ = 3405 cm^{-1} (br. s, OH), 1700 (s, C=O), 1605 (w, C=C), 1405 (s). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.70 (s, 3 H, CH_3), 0.85 (s, 3 H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.42−1.82 (m, 8 H, 4b,8a,10a-H, 9,10-CH_2, 5-H-O), 2.41 (dq, *J* = 4.0, 7.0 Hz, 1 H, 8-H), 2.58 (d, *J* = 12.8 Hz, 1 H, 4-C*H*H), 2.68 (d, *J* = 12.8 Hz, 1 H, 4-CH*H*), 3.44 (d, *J* = 5.2 Hz, 1 H, 2-H), 3.96 (dd, *J* = 1.4, 5.2 Hz, 1 H, 2-H-O), 4.16 (br. m, 1 H, 5-H), 5.11 (d, *J* = 10.7 Hz, 1 H, *H*HC=C), 5.27 (d, *J* = 17.7 Hz, 1 H, H*H*C=C), 5.56 (d, *J* = 4.3 Hz, 1 H, 6-H), 6.24 (dd, *J* = 10.7, 17.7 Hz, 1 H, H-C=C). − $C_{20}H_{30}O_3$ (318.5): calcd. C 75.43, H 9.50; found C 75.06, H 9.28.

(−)-Phytocassane D (2): To a stirred solution of **50** (15 mg, 0.05 mmol) in MeCN (1.5 mL) and CH_2Cl_2 (1.5 mL) were added powdered 4-Å MS (50 mg) and TPAP (17 mg, 0.05 mmol). The mixture was stirred for 15 min at room temperature, and poured into the mixture of sat. aq. $Na_2S_2O_3$ and diethyl ether. After filtration through a Celite pad, the aqueous layer was extracted several times with diethyl ether. The combined organic extracts were washed with brine and dried with $MgSO_4$. After concentration in vacuo, the residue was purified by PTLC to give 4.0 mg (27%) of **2** as a colorless gum. At the same time, 5.0 mg of starting material **50** was recovered, and therefore the yield was estimated as 40%. − CD (EtOH) λ_{ext} = 362 nm (Δε = −1.8), 272 (Δε = +3.6). − $[\alpha]_D^{25}$ = −170 (*c* = 0.15, $CHCl_3$). − IR (CCl_4 solution): $\tilde{\nu}_{max}$ = 3485 cm^{-1} (br. w, OH), 2970 (s, C−H), 2925 (s, C−H), 2855 (m, C−H), 1715 (s, C=O), 1660 (s, C=O), 1590 (w, C=C), 1455 (w), 1390 (m), 1295 (m), 1265 (m), 1205 (m), 1135 (w), 1100 (w), 1060 (m), 990 (m), 965 (w), 920 (m), 895 (w), 660 (w). − ^1H NMR (500 MHz, $CDCl_3$): δ = 0.69 (s, 3 H, 18-CH_3), 0.90 (s, 3 H, 20-CH_3), 1.10 (d, *J* = 7.1 Hz, 3 H, 17-CH_3), 1.20 (s, 3 H, 19-CH_3), 1.43−1.64 (m, 3 H, 5,6α,7β-H), 1.80 (dddd, *J* = 3.3, 3.3, 3.3,12.5 Hz, 1 H, 7α-H), 1.86 (dddd, *J* = 3.0, 3.3, 4.0, 12.9 Hz, 1 H, 6β-H), 2.15 (d, *J* = 12.9 Hz, 1 H, 9-H), 2.19 (dddd, *J* = 3.3, 3.7, 12.5, 13.0 Hz, 1 H, 8-H), 2.45 (d, *J* = 13.1 Hz, 1 H, 1β-H), 2.65 (dq, *J* = 3.7, 7.1 Hz, 1 H, 14-H), 3.49 (d, *J* = 4.9 Hz, 1 H, H-O), 3.82 (d, *J* = 13.1 Hz, 1 H, 1α-H), 3.94 (ddd, *J* = 1.2, 1.5, 4.9 Hz, 1 H, 3-H), 5.50 (d, *J* = 10.7 Hz, 1 H, 16-C*H*H), 5.69 (d, *J* = 17.7 Hz, 1 H, 16-CH*H*), 5.77 (s, 1 H, 12-H), 6.35 (dd, *J* = 10.7, 17.7 Hz, 1 H, 15-H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5, 16.0, 16.4, 21.1, 29.2, 30.9, 33.2, 38.2, 44.0, 45.1, 52.6, 53.8, 56.5, 82.2, 120.8, 128.4, 136.2, 161.1, 200.5, 211.1. These spectral data were identical with authentic spectra of phytocassane D. − MS (FAB$^+$): found 317.2127 ($C_{22}H_{32}O_2$, $[M + H]^+$), calcd. 316.2038.[28]

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[28] Supporting information for this article, including the preparative procedures and spectral properties of compounds **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**, **13**, **17**, **18**, **22**, **26**, **31**, **32**, **33**, **34**, **35**, and **36**, is available on the WWW under http://www.wiley-vch.de/home/eurjoc.

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