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Synthesis of 29-Norlanostane Derivatives[1)]

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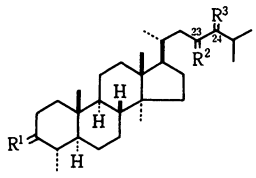
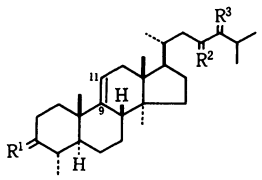
As authentic samples for identification of 29-norlanostane derivatives isolated from plant fossil, 29-norlanostan-24-one and -23-one, 29-norlanost-9(11)-en-24-one, -23-one, and -3-one, 29-norlanost-7-en-3-one, and 29-norlanostan-3-one were synthesized from a commercial lanosterol containing dihydrolanosterol.

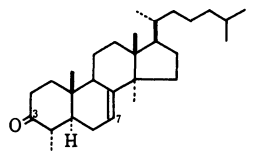
The presence of 29-norlanostane derivatives in very minute quantities was demonstrated in a plant fossil collected at the south deposit, Ningyo-toge in Tottori Prefecture by gas chromatography-mass spectrometry, IR and ^{1}H NMR spectra. In order to identify these compounds, several 29-norlanostane derivatives were synthesized as authentic samples. This paper describes the synthesis of 29-norlanostan-24-one and -23-one (**1** and **2**), 29-norlanost-9(11)-en-24-one, -23-one, and -3-one (**3**, **4**, and **5**), 29-norlanost-7-en-3-one (**6**), and 29-norlanostan-3-one (**7**) from a commercial lanosterol (**8**) containing dihydrolanosterol (**9**).



1 R^1=R^2=H_2, R^3=O
2 R^1=H_2, R^2=O, R^3=H_2
7 R^1=O, R^2=R^3=H_2



3 R^1=R^2=H_2, R^3=O
4 R^1=H_2, R^2=O, R^3=H_2
5 R^1=O, R^2=R^3=H_2



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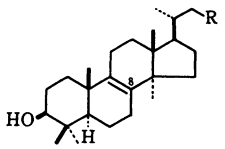
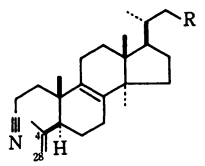
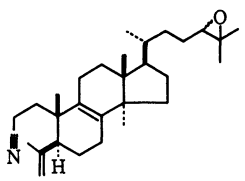


8 R= $-CH_2CH=C(CH_3)_2$
9 R= $-CH_2CH_2CH(CH_3)_2$

Demethylation of 4,4-dimethyl group of a commercial lanosterol (a mixture of lanosterol (**8**) and dihydrolanosterol (**9**)) was effected by the Pinhey's method.[2)] The mixture (**8** and **9**) was subjected to oxidation, oximation, and abnormal Beckmann rearrangement to afford a mixture of seconitrile (**10**) and dihydroseconitrile (**11**)[2)] in about 50% yield. On treatment with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at 0°C, the seconitrile (**10**) afforded a seconitrile epoxide (**12**), which was easily separated from the dihydroseconitrile (**11**) remained intact by column chromatography. The epoxide (**12**) showed peaks at δ 1.28, 1.32, and 2.70 due to two methyl groups and a proton on the oxirane ring, respectively, and δ 1.77 (3H), 4.69 (1H), and 4.95 (1H) assignable to an isopropenyl group in the ^{1}H NMR spectrum. The epoxide (**12**) reacted with boron trifluoride etherate ($BF_3 \cdot OEt_2$)[3)] to give a mixture of a 24-keto derivative (**13**) and a rearranged aldehyde (**14**) in a ratio of 3:1. Optimization of the reaction conditions to improve the yield of the ketone (**13**) was attempted, but failed. Analytical samples of **13** and **14** were obtained by preparative thin-layer chromatography (TLC) and their structures were confirmed by ^{1}H NMR spectrum; the ketone (**13**) showed the signals at δ 1.10 (6H, d, J=7 Hz) and 2.50 (1H, septet, J=7 Hz), indicating the presence of an isobutyryl group, while the aldehyde (**14**) showed a singlet signal at δ 9.47 due to the aldehyde proton. Chromatographic behaviors of **13** and **14** being similar, the mixture of **13** and **14** in a large quantity was separated after reduction. Reduction with sodium borohydride followed by chromatographic separation afforded a secondary alcohol (**15**) and a primary one (**16**). In the ^{1}H NMR spectrum of 24-hydroxy seconitrile (**15**), a multiplet signal assignable to a methine proton of the secondary alcohol was observed at δ 3.30.



10 R= $-CH_2CH=C(CH_3)_2$
11 R= $-CH_2CH_2CH(CH_3)_2$



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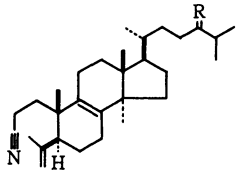
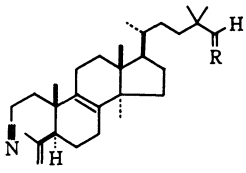


13 R=O
15 R=H,OH



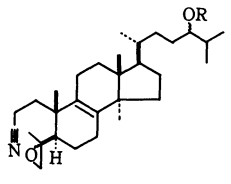
14 R=O
16 R=H,OH

The 24-hydroxy seconitrile (**15**) was epoxidized with MCPBA at 0°C for 2d to afford 4,28-epoxy-24-hydroxy seconitrile (**17**) in 86% yield together with its C-4 epimer in a small amount. The main hydroxy epoxide (**17**), after acetylation, was treated with $BF_3 \cdot OEt_2$ to yield 24-acetoxy-29-norlanost-8-en-3-one (**19**) in a good yield. The α-configuration of the methyl group at C-4 of **19** was demonstrated by the axial-axial coupling (J=11 Hz) observed between $C_{(4)}$-H and

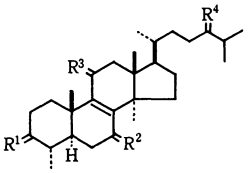
$C_{(5\alpha)}$-H.

Oxidation of 24-acetoxy-29-norlanost-8-en-3-one (**19**) with chromium trioxide[4] afforded 24-acetoxy-29-norlanost-8-ene-3,7,11-trione (**20**), whose molecular formula, $C_{31}H_{46}O_5$, was determined by high-resolution mass spectrum (HR-MS). The Δ^8-triketo derivative (**20**) was then subjected to reduction with zinc in acetic acid[4] to yield a saturated triketone (**21**), to which the molecular formula, $C_{31}H_{48}O_5$, was assigned by HR-MS.

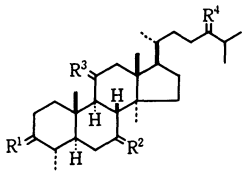
Wolff-Kishner reduction of the saturated triketone (**21**) under usual conditions[5] gave a mixture of 24-hydroxy-29-norlanostan-11-one (**22**) and 29-norlanostan-24-ol (**23**). Since an examination on the reaction conditions revealed that vigorous conditions enhanced the formation of **23**,[6] the following modification was made. The excess hydrazine hydrate was distilled off under reduced pressure before raising temperature. This additional process could suppress the formation of **23**. No occurrence of $C_{(4)}$-CH_3 epimerization in the Wolff-Kishner reduction was proved by the following observation. Reduction of 29-norlanost-8-en-3-one (**24**) (vide infra) under the same conditions as above gave a product (**25**), which was identical with that obtained by hydride reduction of 29-norlanost-8-en-3β-yl mesylate (**26**). 29-Norlanostan-24-ol (**23**) was oxidized to the corresponding 24-one (**1**).



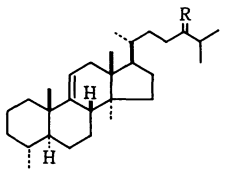
17 R=H
18 R=Ac



19 R^1=O, R^2=R^3=H_2, R^4=H,OAc
20 R^1=R^2=R^3=O, R^4=H,OAc
24 R^1=O, R^2=R^3=R^4=H_2
25 R^1=R^2=R^3=R^4=H_2
26 R^1=α-H,β-OMs, R^2=R^3=R^4=H_2



21 R^1=R^2=R^3=O, R^4=H,OAc
22 R^1=R^2=H_2, R^3=O, R^4=H,OH
23 R^1=R^2=R^3=H_2, R^4=H,OH
27a,b R^1=R^2=H_2, R^3=R^4=H,OH
28a,b R^1=R^2=H_2, R^3=H,OH, R^4=H,OAc

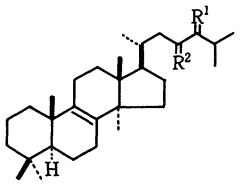


29a,b R=H,OAc
30a,b R=H,OH

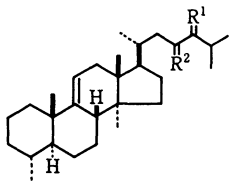
Reduction of 24-hydroxy-29-norlanostan-11-one (**22**) with lithium aluminium hydride (LAH) afforded a pair of C-24 epimeric diols (**27a,b**)[5]. After selective acetylation of the hydroxyl group at C-24, dehydration of each acetoxy alcohol (**28a,b**) was effected by phosphoryl chloride in pyridine[5] to give 29-norlanost-9(11)-en-24-yl acetate (**29a,b**). On deprotection and oxidation, both **29a** and **29b** gave the same compound, 29-norlanost-9(11)-en-24-one (**3**), which showed a multiplet signal at δ 5.27 due to $C_{(11)}$-H and doublet signal at δ 1.09 (6H) due to geminal methyl groups on a carbon atom adjacent to the carbonyl group at C-24. Thus the synthesis of 29-norlanost-9(11)-en-24-one (**3**) was achieved from lanosterol (**8**) in ca. 2% total yield through 17 steps.

Next we investigated transposition of the carbonyl group at C-24 into C-23 without degradation of the side chain using lanost-8-en-24-one (**31**) as a model compound, which was prepared from lanosta-8,24-diene. Although several procedures for 1,2-carbonyl transposition have been reported,[7-10] most of them are limited to cyclic ketones. Application of these procedures to the conversion of 24-one into 23-one was unsuccessful due to unexpectedly large steric effect caused by the presence of bulky lanostane skeleton.

We developed a new synthetic route utilizing reduction of a masked α-diketone. Regioselective sulfenylation at C-23 of lanost-8-en-24-one (**31**) was accomplished by application of the inverse addition of the reagent.[9] The anion produced under kinetically controled conditions (see Experimental) was added a solution of diphenyl disulfide in tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) to give a mixture of 23-phenylthiolanost-8-en-24-ones (**32a,b**), which was shown to be C-23 epimers by characteristic septet of $C_{(25)}$-H at 2.92 and 2.97 and double doublet at δ 3.88 and 3.80 due to $C_{(23)}$-H in the ^{1}H NMR spectrum. The mixture was separated by TLC to afford **32a** and **32b**. According to the procedure reported by Trost et al.[9] the α-phenylthio ketones (**32a,b**) were treated with lead tetraacetate in benzene-acetic acid to yield a masked ketone (**33**), which was converted into a dimethyl acetal (**34**) by treatment with iodine in methanol. The carbonyl group in dimethyl acetal (**34**) was then reduced with LAH to give an α-ketol (**35**), the structure of which was supported by ^{1}H NMR spectrum; a double doublet signal at δ 4.66 (J=2.5 and 5 Hz) changed into a doublet signal on addition of D_2O. Acetylation of **35** gave an α-keto acetate (**36**), showing a characteristic signal at δ 4.87 (d, J=4 Hz) in the ^{1}H NMR spectrum. Finally the α-acetoxy ketone (**36**) was reduced with calcium in liquid ammonia to afford the expected product, lanost-8-en-23-one (**37**), total yield of which from the 24-one (**31**) was ca. 20% through 6 steps. Direct deoxygenation of **33**



31 R^1=O, R^2=H_2
32a,b R^1=O, R^2=H,SPh
33 R^1=O, R^2=SPh,OAc
34 R^1=O, R^2=OCH_3,OCH_3
35 R^1=H,OH, R^2=O
36 R^1=H,OAc, R^2=O
37 R^1=H_2, R^2=O



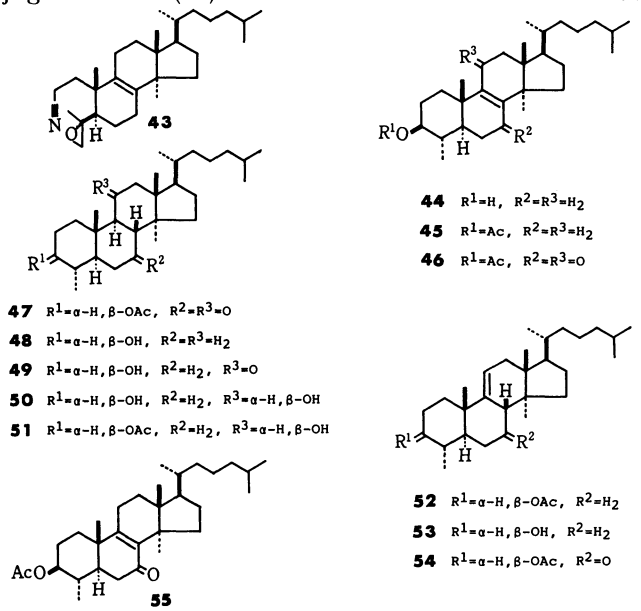
38a,b R^1=O, R^2=H,SPh
39 R^1=O, R^2=SPh,OAc
40 R^1=O, R^2=OCH_3,OCH_3
41 R^1=H,OH, R^2=O
42 R^1=H,OAc, R^2=O

and **34** by Wolff–Kishner reduction resulted in a formation of only a hydrocarbon mixture.

The method mentioned above was applied to the transposition of the carbonyl group of 29-norlanost-9(11)-en-24-one (**3**) into the corresponding 23-one (**4**). Sulfenylation of **3** afforded epimeric 23-phenylthio ketones (**38a,b**), which were subsequently converted into an α-acetoxy-α-phenylthio ketone (**39**), a dimethyl acetal (**40**), and an α-ketol (**41**). On acetylation followed by reduction with calcium in liquid ammonia, **41** gave 29-norlanost-9(11)-en-23-one (**4**) via **42**. The synthesis of a target molecule (**4**) from lanosterol (**8**) was successfully accomplished utilizing the newly developed reduction of a masked α-diketone in 0.4% total yield through 23 steps. 29-Norlanostan-23-one (**2**) was easily derived from **4** by hydrogenation and oxidation. The synthesis of 29-norlanost-9(11)-en-3-one and -7-en-3-one (**5** and **6**) and 29-norlanostan-3-one (**7**) was carried out through similar routes to the compounds **4** and **2**.

The dihydroseconitrile (**11**),[2] prepared from dihydrolanosterol (**9**) (vide supra), was converted into a demethyl derivative, 29-norlanost-8-en-3-one (**24**)[11] through a seconitrile epoxide (**43**). On reduction followed by acetylation, **24** gave an acetate (**45**), which was subjected to allylic oxidation, reduction with zinc, and Wolff–Kishner reduction in turn to afford 29-norlanostan-3β-ol (**48**) and 3β-hydroxy-29-norlanostan-11-one (**49**). The former (**48**), on Jones oxidation, afforded 29-norlanostan-3-one (**7**) and the latter (**49**) was converted into 29-norlanost-9(11)-en-3β-ol (**53**)[12] by reduction, partial acetylation, dehydration, and hydrolysis, which on oxidation gave 29-norlanost-9(11)-en-3-one (**5**).

On the other hand, oxidation of 29-norlanost-8-en-3β-yl acetate (**45**) with chromyl chloride afforded 3β-acetoxy-29-norlanost-9(11)-en-7-one (**54**), which was isomerized by treatment with $BF_3 \cdot OEt_2$ into a conjugate enone (**55**).[13] Wolff–Kishner reduction[14] of **55** following oxidation of the resultant alcohol afforded a mixture of 29-norlanost-7-en-3-one (**6**) and -8-en-3-one (**24**) in a ratio of ca. 2:1. The mixture showed a similar fragmentation to that of 9(11)-en-3-one (**5**) in the mass spectra. In the ^1H NMR spectrum of the mixture, three singlet signals at δ 0.69 (18-Me), 0.86 (30-Me), and 1.09 (19-Me) and a doublet signal at δ 1.00 (28-Me) are assignable to 7-ene (**6**) derivative. Separation of **6** from **24** could not be attained.



Experimental

General Procedures. Melting points were measured on a Mel-temp capillary melting point apparatus (Laboratory Devices) and uncorrected. IR spectra were obtained on a Hitachi 260-30 spectrometer in Nujol mull. ^1H NMR spectra were taken on a Hitachi R-20B (60 MHz) or a Varian EM-390 (90 MHz) or a Brucker WH-270 (270 MHz) spectrometer for solutions in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-D300 mass spectrometer at 70 eV, and the relative intensities were indicated in the parentheses. Optical rotations were measured on a JASCO DIP-181 spectrometer in $CHCl_3$ (*c* 0.10) unless otherwise stated, and UV spectra on a Hitachi 340 spectrometer. TLC was carried out on Kieselgel 60 GF_{254} (E. Merck) coated in 0.25 mm thickness (for analytical) and in 0.5 mm thickness (for preparative). Wakogel C-200 (Wako) was used for column chromatography. Dry solvents were purified by distillation from desiccants as follows: ether/LAH; THF/Na-benzophenone; dichloromethane and carbon tetrachloride/P_2O_5; benzene/Na; toluene and HMPA/CaH_2; pyridine/BaO. Organic extracts were dried over anhydrous sodium sulfate.

Epoxidation of a Mixture of Seconitriles (10 and 11). The seconitrile mixture (**10** and **11**) was obtained by the method described by Pinhey et al.[2] in ca. 50% yield from a commercial lanosterol (**8**) (E. Merck, containing ca. 30% of dihydrolanosterol (**9**)).

The seconitrile mixture (43 g) in dichloromethane (3.4 l) was kept at 0 °C and reacted with MCPBA (16 g) in dichloromethane (0.4 l) in a refrigerator for 3 h. The reaction product was washed with successively cold 5% potassium iodide solution, water, and brine, and dried. Evaporation of the solvent and addition of hexane yielded crystals (6.67 g), which were identified as seconitrile epoxide (**12**), mp 119.5—121.5 °C (needles from hexane); IR 2240 and 1636 cm^{-1}; ^1H NMR (60 MHz) δ=0.75 (3H, s; 18-Me), 0.94 and 0.98 (each 3H, s; 19- and 30-Me), 1.28 and 1.32 (each 3H, s; C(O)C(Me)₂), 1.77 (3H, br s; C=C-Me), 2.70 (1H, t, *J*=6 Hz; C(O)C-H), 4.69 and 4.95 (each 1H, m; C=CH_2); Found *m/z* 437.3653. Calcd for $C_{30}H_{47}ON$: M, 437.3656.

The filtrate was separated by silica-gel chromatography (silica gel: 410 g). Elution (each fraction: 1/4 column volume) was performed with 10% ether–hexane (frs 1—10) and 20% ether–hexane (frs 11—25). Crystallization of frs 6—9 from methanol afforded dihydroseconitrile (**11**; 9.1 g).[2] Fractions 13—22 gave additional seconitrile epoxide (**12**; 14.5 g).

Treatment of Seconitrile Epoxide (12) with $BF_3 \cdot OEt_2$. $BF_3 \cdot OEt_2$ (1.5 ml) was added to a solution of the seconitrile epoxide (**12**; 1.2 g) in toluene (120 ml) and the reaction mixture was stirred at room temperature for 20 min.

Addition of water and extraction with ether furnished a mixture (1.18 g) of seconitrile ketone (**13**) and seconitrile aldehyde (**14**). A part of the mixture (145 mg) was separated by preparative TLC (developed three times with 20% ether–hexane) to afford seconitrile aldehyde (**14**; 21.7 mg) and seconitrile ketone (**13**; 67.9 mg). **13**: Mp 98—99 °C; IR 2240, 1705, 1635, and 894 cm^{-1}; ^1H NMR (60 MHz) δ= 0.74 (3H, s; 18-Me), 0.94 and 0.98 (each 3H, s; 19- and 30-Me), 1.10 (6H, d, J=7 Hz; O=C-CH$\underline{Me}_2$), 1.78 (3H, br s; C=C-Me), 2.50 (1H, septet, J=7 Hz; O=C-C$\underline{H}$Me$_2$), and 4.69 and 4.94 (each 1H, m; C=C$\underline{H}_2$); MS m/z (%) 437 (M^+; 82), 422 (90), 394 (15), 383 (62), 254 (33), 242 (44), and 71 (100); Found: m/z 437.3663. Calcd for $C_{30}H_{47}ON$: M, 437.3656. **14**: An oil; ^1H NMR (60 MHz) δ=0.74 (3H, s; 18-Me), 0.94 and 0.98 (each 3H, s; 19- and 30-Me), 1.06 (6H, s; $C_{(24)}$-Me's), 1.78 (3H, br s; C=C-Me), 4.69 and 4.94 (each 1H, m; C=C$\underline{H}_2$), and 9.47 (1H, s; H-C=O); MS m/z (%) 437 (M^+; 50), 422 (37), 409 (15), 383 (43), 254 (20), 242 (43), and 55 (100).

Reduction of the Mixture of Seconitrile Ketone (13) and Seconitrile Aldehyde (14). The mixture (6.8 g) of **13** and **14** was treated with sodium borohydride (0.6 g) in methanol (250 ml) at room temperature for 20 min. The usual work-up afforded a mixture (6.8 g) of alcohols, which was separated by silica-gel column chromatography (silica gel: 210 g) eluted with 30% ether–hexane (each fraction: 1/4 column volume). Fractions 7—10 gave a secondary alcohol (**15**; 3.9 g; 57% yield from **12**), and frs 12—14 a primary alcohol (**16**; 1.4 g; 20.5% yield from **12**). **15**: Mp 112.5—113 °C (needles from hexane); IR 3450, 2245, 1635, and 895 cm^{-1}; ^1H NMR (60 MHz) δ= 0.75 (3H, s; 18-Me), 0.83—1.04 (total Me×5), 1.77 (3H, br s; C=C-Me), 3.30 (1H, m; $\underline{H}$-C-OH), and 4.68 and 4.93 (each, 1H, m; C=C$\underline{H}_2$); MS m/z (%) 439 (M^+; 100), 424 (25), and 421 (2); Found: m/z 439.3787. Calcd for $C_{30}H_{49}NO$: M, 439.3812.

Epoxidation of 24-Hydroxy Seconitrile (15). To a solution of 24-hydroxy seconitrile (**15**; 610 mg) in dichloromethane (70 ml) was added MCPBA (453 mg) and the reaction mixture was stood for 2 d in a refrigerator. After the usual work-up, chromatographic separation (silica gel: 30 g, each fraction: 1/4 column volume) eluted with 30% ether–hexane afforded 4,28-epoxy-24-hydroxy seconitrile (**17**; 545.6 mg, 86.2% yield) from frs 25—34, and its epimer at C-4 from frs 21—23. **17**: Mp 112—113 °C; IR 3450 and 2245 cm^{-1}; ^1H NMR (60 MHz) δ=0.75 (3H, s; 18-Me), 0.91 (3H, s; Me), 0.80—1.03 (total Me×3), 1.08 (3H, s, 19-Me), 1.33 (3H, s; C$\overset{O}{\diagup\!\diagdown}$C-Me), 2.69 (2H, s; C$\overset{O}{\diagup\!\diagdown}C\underline{H}_2$), and 3.30 (1H, m; $\underline{H}$-C-OH); MS m/z (%) 455 (M^+; 45), 440 (18), 437 (15), 422 (72), 404 (28), 394 (12), 383 (42), and 354 (31); Found: m/z 455.3748. Calcd for $C_{30}H_{49}NO_2$: M, 455.3761.

Acetylation of 24-Hydroxy Seconitrile Epoxide (17). 24-Hydroxy seconitrile epoxide (**17**; 545 mg) was acetylated in the usual manner and the reaction product was purified by column chromatography (silica gel: 25 g). Elution with 40% ether–hexane afforded 24-acetoxy-4,28-epoxy-3,4-secolanost-8-ene-3-nitrile (**18**; 554 mg; 93% yield) as colorless oil, IR (liquid) 2250, 1740, and 1250 cm^{-1}; ^1H NMR (60 MHz) δ= 0.75 (3H, s; 18-Me), 0.80—1.0 (total Me×4), 1.09 (3H, s; 19-Me) 1.33 (3H, s; C$\overset{O}{\diagup\!\diagdown}$C-Me), 2.05 (3H, s; OAc), 2.69 (2H, s; C$\overset{O}{\diagup\!\diagdown}C\underline{H}_2$), and 4.70 (1H, m; $\underline{H}$-C-OAc); MS m/z (%) 497 (M^+; 12), 482 (10), 479 (3), 464 (3), 454 (4), 443 (12), 437 (10), 422 (100), 404 (28), 394 (20), and 383 (26).

Cyclization of 24-Acetoxy-4,28-epoxy-3,4-secolanost-8-ene-3-nitrile (18). $BF_3 \cdot OEt_2$ (1.5 ml) was added to a solution of the seconitrile epoxide (**18**; 553 mg) in toluene (200 ml) at room temperature under nitrogen and the reaction mixture was heated under reflux for 1.5 h. After addition of water, the reaction product was extracted with ether and the extract was washed with sodium hydrogencarbonate solution and brine, and dried. Evaporation and separation by chromatography on silica gel (25 g) eluted with 15% ether–hexane gave a mixture (58.5 mg) of olefinic compounds from frs 5 and 6 (each fraction: 1/4 column volume) followed by 24-acetoxy-29-norlanost-8-en-3-one (**19**; 229 mg, 44% yield) from frs 9—14. **19**: Mp 140—144 °C (needles from ether–hexane); IR (liquid) 1740, 1708, and 1240 cm^{-1}; $[\alpha]_D$ +35°; ^1H NMR (270 MHz) δ=0.73 (3H, s; 18-Me), 0.85—0.95 (total Me×4), 1.03 (3H, d, J=6 Hz; 28-Me), 1.21 (3H, s; 19-Me), 2.06 (3H, s; OAc), 2.32 (1H, dq, J=11 and 6 Hz; O=C-C$\underline{H}$Me), and 4.73 (1H, m; $\underline{H}$-C-OAc); MS m/z (%) 470 (M^+; 14), 455 (22), 410 (6), 395 (100), 311 (26), 283 (10), 257 (27), 243 (23), and 231 (25); Found: m/z 470.3757. Calcd for $C_{31}H_{50}O_3$: M, 470.3758.

Allylic Oxidation of 24-Acetoxy-29-norlanost-8-en-3-one (19). A solution of chromium trioxide (200 mg) in 90% acetic acid (2 ml) was added to a refluxing solution of 24-acetoxy-29-norlanost-8-en-3-one (**19**; 285 mg) in hexane–acetic acid (1:4, 10 ml). After reflux for 1.5 h, the reaction mixture was poured into a cold aqueous solution of sodium hydrogensulfite. The reaction product was extracted with ether and the extract was washed with 1 M (1 M=1 mol dm^{-3}) sodium hydroxide solution and then with brine. Evaporation gave a residue, which was chromatographed on silica gel (15 g) eluted with 35% ether–hexane (each fraction: 1/4 column volume) to give 24-acetoxy-29-norlanost-8-ene-3,7,11-trione (**20**; 115 mg from frs 16—24; 38% yield) as yellow needles or plates (from ether–hexane), mp 133.5—134.5 °C; IR 1735, 1715, 1690, 1670, and 1240 cm^{-1}; UV (EtOH) 269 nm (log ε 3.86); $[\alpha]_D^{26}$ +103.0°; ^1H NMR (90 MHz) δ=0.85 (3H, s; 18-Me), 0.91 (9H, d, J=7 Hz), 1.06 (3H, d, J=7 Hz; 28-Me), 1.20 (3H, s), 1.49 (3H, s), 2.05 (3H, s; OAc), 2.71 (1H, br s), 3.15 (1H, m), and 4.70 (1H, m; $\underline{H}$-C-OAc), MS m/z (%) 498 (M^+; 20), 483 (3), 470 (3), 456 (6), 438 (45), 423 (15), 413 (10), 327 (15), 273 (20), 272 (25), 260 (27), 245 (30), 234 (15), and 55 (100); Found: m/z 498.3338. Calcd for $C_{31}H_{46}O_5$: M, 498.3343.

Reduction of 24-Acetoxy-29-norlanost-8-ene-3,7,11-trione (20). To a refluxing enone (**20**; 1.81 g) in acetic acid (100 ml), zinc dust (1.5 g) was added portionwise during 1.5 h and the heating was continued for 1 h. Zinc was filtered and washed with hot acetic acid. The filtrate and washings were combined and diluted with ether and the solution was washed with a saturated solution of sodium hydrogencarbonate and brine. The product was crystallized from methanol to give 24-acetoxy-29-norlanostane-3,7,11-trione (**21**; 1.28 g). The filtrate was subjected to silica-gel column chromatography to afford an additional **21** (240 mg). The total yield of **21** was 83.5%. **21**: Mp 182—185.5 °C (colorless stick); IR 1730, 1710, 1690, and 1240 cm^{-1}; $[\alpha]_D^{26}$ +47.5°; ^1H NMR (60 MHz) δ=0.76 (3H, s; 18-Me), 0.80—1.00 (total Me×3), 0.98 (3H, d, J=7 Hz; 28-Me), 1.23 (3H, s; 30-Me), 1.49 (3H, s; 19-Me), 2.05 (3H, s; OAc), and 4.70 (1H, m; $\underline{H}$-C-OAc); MS m/z (%) 500 (M^+; 3), 485 (1), 456 (2), 440 (12), 425 (10), 370 (50), 328 (30), 302 (20), 260 (20), 220 (25), 193 (40), and 109 (100); Found: m/z 500.3492. Calcd for $C_{31}H_{48}O_5$: M, 500.3500

Wolff–Kishner Reduction of 24-Acetoxy-29-norlanostane-3,7,11-trione (21). A mixture of the trione (**21**; 200 mg), hydrazine hydrate (80%, 2 ml), and diethylene glycol (10 ml)

was refluxed at 130°C for 1.5 h, and the excess hydrazine hydrate was removed in vacuo. Potassium hydroxide (200 mg) was added to the mixture and nitrogen was bubbled for a while. After reflux for 3 h, the mixture was worked up as usual. Addition of methanol to the residue yielded crystals (58 mg), which were identified as 24-hydroxy-29-norlanostan-11-one (**22**). The filtrate was separated by column chromatography (silica gel: 10 g). Elution (each fraction: 1/4 column volume) with 20% ether–hexane (25 ml) and then with 30% ether–hexane (30 ml) gave 29-norlanostan-24-ol (**23**; 8.3 mg) from frs 6—8, and 24-hydroxy-29-norlanostan-11-one (**22**; 72 mg) from frs 13—17. **22**: Mp 156.5—157.5°C (needles from methanol); IR 3500 and 1695 cm^{-1}; $[\alpha]_D^{25}$ +63°; ^1H NMR (270 MHz) δ=0.72 (3H, s; 18-Me), 0.80 (3H, d, J=6 Hz), 0.90 (3H, d, J=7 Hz), 0.92 (6H, d, J=6 Hz), 1.02 (3H, s), 1.09 (3H, s), 2.01 (1H, d, J=13 Hz; $C_{(12)}$-H), 2.53 (1H, d, J=13 Hz; $C_{(12)}$-H'), 2.66 (1H, d, J=13 Hz; $C_{(9)}$-H), and 3.30 (1H, m; H-C-OH); MS m/z (%) 430 (M^+; 64), 415 (6), 412 (8), 397 (3), 387 (7), 319 (14), 311 (8), 273 (10), 260 (15), 233 (8), 223 (7), 191 (100), and 163 (16); Found: m/z 430.3768. Calcd for $C_{29}H_{50}O_2$: M, 430.3809. **23**: Mp 82.5—84.5°C (needles from methanol); IR 3400 cm^{-1}; $[\alpha]_D^{25}$ +35°; ^1H NMR (90 MHz) δ=0.78 (3H, s), 0.80 (3H, s), 0.84 (3H, s), 0.89 (3H, d), 0.93 (6H, d, J=6 Hz; 26- and 27-Me), and 3.31 (1H, m; H-C-OH); MS m/z (%) 416 (M^+; 12), 398 (13), 383 (10), 315 (12), 313 (9), 285 (82), 260 (15), 245 (100), 231 (10), 217 (32), 176 (70), 163 (38), and 109 (60); Found: m/z 416.4005. Calcd for $C_{29}H_{52}O$: M, 416.4016.

Retention of the Configuration at C-4 of 29-Norlanost-8-en-3-one (24) in the Wolff–Kishner Reduction. Wolff–Kishner reduction of 29-norlanost-8-en-3-one (**24**; 50 mg) under the same conditions as those used for 24-acetoxy-29-norlanostane-3,7,11-trione (**21**) afforded 29-norlanost-8-ene (**25**; 21.3 mg) after purification by silica-gel column chromatography, which was completely identical with that obtained by the following procedure.

To a solution of 29-norlanost-8-en-3β-ol (43 mg) in pyridine (5 ml), methanesulfonyl chloride (0.05 ml) was added and the mixture was allowed to stand overnight in a refrigerator. The usual work-up afforded 29-norlanost-8-en-3β-yl mesylate (**26**; 47 mg), a part (24 mg) of which was dissolved in THF (2 ml) and the solution was refluxed for 5 h with lithium triethylhydroborate (in excess) under nitrogen. The excess hydride was destroyed by addition of water and the mixture was extracted with ether. The crude mixture was separated by column chromatography on silica gel (3 g). Elution with hexane gave 29-norlanost-8-ene (**25**; 16.7 mg).

Oxidation of 29-Norlanostan-24-ol (23). A solution of the alcohol (**23**; 13 mg) in acetone (2 ml) was oxidized with Jones reagent at 0°C for 30 min. The usual work-up gave 29-norlanostan-24-one (**1**; 11 mg) as needles (from methanol), mp 92—93°C; IR 1705 cm^{-1}; $[\alpha]_D^{22}$ +22° (c 0.18, $CHCl_3$); ^1H NMR (90 MHz) δ=0.75—0.93 (total Me×5), 1.09 (6H, d, J=7 Hz; O=C-CH$\underline{Me}_2$), and 2.60 (1H, septet, J=7 Hz; O=C-C$\underline{H}$Me$_2$); MS m/z (%) 414 (M^+; 25), 399 (8), 328 (3), 313 (7), 287 (18), 260 (50), 245 (100), 231 (6), 217 (32), 204 (17), 190 (10), and 176 (38); Found: m/z 414.3843. Calcd for $C_{29}H_{50}O$: M, 414.3859.

Reduction of 24-Hydroxy-29-norlanostan-11-one (22). To a solution of 24-hydroxy-11-one (**22**; 300 mg) in ether (50 ml), LAH (50 mg) was added, and the reaction mixture was stirred for 2 h at room temperature. The usual work-up and chromatographic separation on silica gel (15 g) eluted with 20% ether–hexane (each fraction: 1/4 column volume) afforded 29-norlanostane-11,24-diol (**27a**; 83.5 mg) from frs 13—16 and its isomer (**27b**; 82.2 mg) from frs 19—24. Fractions 17 and 18 (100 mg) were further separated in the same manner to give **27a** (29.7 mg) and **27b** (46.0 mg). **27a**: Mp 140.5—141°C (fine needles from methanol); IR 3500 cm^{-1}; $[\alpha]_D^{25}$ +55°; ^1H NMR (90 MHz) δ=0.78 (3H, s), 0.80—1.10 (total Me×6), 3.30 (1H, m; H-$C_{(24)}$-OH), and 4.21 (1H, m; H-$C_{(11)}$-OH); MS m/z (%) 432 (M^+; 6), 414 (16), 399 (10), 396 (4), 381 (4), 285 (4), 276 (6), 258 (20), 245 (14), 243 (14), 240 (16), 229 (3), 217 (6), 193 (22), and 175 (12); Found: m/z 432.3935. Calcd for $C_{29}H_{52}O_2$: M, 432.3965. **27b**: Mp 160—163°C (needles from ether–methanol); IR 3300 cm^{-1}; $[\alpha]_D^{25}$ +39°; ^1H NMR (90 MHz) δ=0.78 (3H, s), 0.80—1.00 (total Me×6), 3.29 (1H, m; H-$C_{(24)}$-OH), and 4.22 (1H, m; H-$C_{(11)}$-OH); MS m/z (%) 432 (M^+; 4), 414 (18), 399 (14), 396 (3), 381 (10), 285 (4), 276 (4), 258 (17), 245 (10), 243 (14), 240 (10), 229 (6), 217 (6), 193 (17), and 175 (10); Found: m/z 432.3926. Calcd for $C_{29}H_{52}O_2$: M, 432.3965.

Acetylation of 29-Norlanostane-11,24-diols (27a and b). The diols (**27a**; 106.9 mg and **27b**; 114.9 mg) were dissolved in pyridine (3 ml) and acetic anhydride (1.5 ml) and stood for 5 h at room temperature, respectively. The usual work-up afforded 24-acetoxy-29-norlanostan-11-ols (**28a**; 123.8 mg and **28b**; 120.4 mg), respectively. **28a**: Mp 148.5—149.5°C (needles from methanol); IR 3540, 1715, and 1260 cm^{-1}; $[\alpha]_D^{26}$ +33°; ^1H NMR (90 MHz) δ=0.77 (3H, s; 30-Me), 0.88 (12H, d, J=7 Hz), 0.99 (3H, s), 1.07 (3H, s), 2.04 (3H, s; OAc), 4.20 (1H, m; H-C-OH), and 4.66 (1H, m; H-C-OAc); MS m/z (%) 474 (M^+; 5), 456 (38), 441 (38), 396 (24), 381 (78), 297 (14), 283 (100), 258 (22), 243 (30), 229 (26), 217 (26), 193 (28), and 109 (46); Found: m/z 474.4014. Calcd for $C_{31}H_{54}O_3$: M, 474.4071. **28b**: Mp 160.5—161°C (fine needles from methanol); IR 3545, 1712, and 1260 cm^{-1}; $[\alpha]_D^{26}$ +49°; ^1H NMR (90 MHz) δ=0.77 (3H, 30-Me), 0.89 (12H, d, J=7 Hz), 0.99 (3H, s), 1.07 (3H, s), 2.04 (3H, s; OAc), 4.22 (1H, m; H-C-OH), and 4.68 (1H, m; H-C-OAc); Found: m/z 474.4053. Calcd for $C_{31}H_{54}O_3$: M, 474.4071.

Dehydration of 24-Acetoxy-29-norlanostan-11-ols (28a and b). Phosphoryl chloride (0.2 ml) was added to a solution of the monoacetate (**28a**; 96.3 mg) in pyridine (5 ml), and the mixture was heated at 90—100°C for 3 h. The reaction mixture was poured into ice–water and extracted with ether. The usual work-up afforded 24-acetoxy-29-norlanost-9(11)-ene (**29a**) in a quantitative yield, mp 102—102.5°C (fine needles from methanol); IR 1730 and 1245 cm^{-1}; $[\alpha]_D^{23}$ +70°; ^1H NMR (90 MHz) δ=0.66 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.76—0.97 (total Me×5), 2.05 (3H, s; OAc), 4.68 (1H, m; H-C-OAc), and 5.28 (1H, m; C=C-H); MS m/z (%) 456 (M^+; 45), 441 (50), 396 (25), 381 (100), 297 (15), 283 (80), 257 (7), 243 (13), 229 (18), 217 (18), and 203 (9); Found: m/z 456.3983. Calcd for $C_{31}H_{52}O_2$: M, 456.3967.

The epimeric acetoxy alcohol (**28b**) was dehydrated in the same procedure to afford 24-acetoxy-29-norlanost-9(11)-ene (**29b**), mp 109.5—110.5°C (glistening plates from methanol); IR 1735 and 1240 cm^{-1}; $[\alpha]_D^{23}$ +81°; ^1H NMR (90 MHz) δ=0.65 (3H, s; 18-Me), 0.74 (3H, s; 30-Me), 0.76—0.97 (total Me×5), 2.04 (3H, s; OAc), 4.68 (1H, m; H-C-OAc), and 5.26 (1H, m; C=C-H); MS m/z (%) 456 (M^+; 27), 441 (40), 396 (26), 381 (100), 297 (14), 283 (75), 257 (6), 243 (14), 229 (18), 217 (16), and 203 (9); Found: m/z 456.3927. Calcd for $C_{31}H_{52}O_2$: M, 456.3967.

Deprotection of 24-Acetoxy-29-norlanost-9(11)-enes (29a and b). The acetate (**29a**; 58.9 mg) in ether was stirred with

LAH (ca. 20 mg) for 1 h at room temperature to afford 29-norlanost-9(11)-en-24-ol (**30a**; 54.9 mg), mp 91—92 °C (colorless plates from methanol); IR 3450 and 1630 cm^{-1}; $[\alpha]_D^{24}$ +76°; ^1H NMR (90 MHz) δ=0.67 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.75—0.97 (total Me×5), 3.30 (1H, m; H-C-OH), and 5.53 (1H, m; C=C-H); MS *m/z* (%) 414 (M^+; 52), 399 (86), 396 (14), 381 (58), 311 (4), 297 (14), 283 (20), 243 (15), 229 (20), 217 (20), and 203 (14); Found: *m/z* 414.3795. Calcd for $C_{29}H_{50}O$: M, 414.3860.

29-Norlanost-9(11)-en-24-ol (**30b**) was obtained from **29b** by the same method as above. **30b**: Mp 95—96 °C (fine needles from methanol); IR 3300 and 1635 cm^{-1}; $[\alpha]_D^{24}$ +54°; ^1H NMR (90 MHz) δ=0.66 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.82 (3H, d, *J*=7 Hz; 28-Me), 0.90 (6H, d, *J*=7 Hz), 0.92 (3H, d, *J*=6 Hz), 0.95 (3H, s; 19-Me), 3.32 (1H, m; H-C-OH), and 5.27 (1H, m; C=C-H); MS *m/z* (%) 414 (M^+; 50), 399 (100), 381 (64), 311 (4), 297 (15), 283 (22), 243 (20), 229 (24), 217 (25), 203 (15), and 119 (45); Found: *m/z* 414.3831. Calcd for $C_{29}H_{50}O$: M, 414.3860.

Oxidation of 29-Norlanost-9(11)-en-24-ols (30a and b). Jones reagent was added to a solution of 29-norlanost-9(11)-en-24-ol (**30a**; 42.6 mg) in acetone (5 ml) at 0 °C and the mixture was stirred for 20 min. The usual work-up afforded 29-norlanost-9(11)-en-24-one (**3**; 40.4 mg). The same ketone (**3**) was obtained from **30b** in the same manner. **3**: Mp 84—85 °C (colorless plates from methanol); IR 1712 and 1630 cm^{-1}; $[\alpha]_D^{24.5}$ +79°; ^1H NMR (90 MHz) δ=0.66 (3H, s; 18-Me), 0.76 (3H, s; 30-Me), 0.82 (3H, d, *J*=6 Hz; 28-Me), 0.87 (3H, d, *J*=5 Hz; 21-Me), 0.95 (3H, s; 19-Me), 1.09 (6H, d, *J*=7 Hz; O=C-CH$\underline{Me_2}$), 2.40 (2H, dd, *J*=6 and 7.5 Hz), 2.52 (1H, septet, *J*=7 Hz; O=C-C$\underline{H}$Me$_2$), and 5.27 (1H, m; C=C-H); MS *m/z* (%) 412 (M^+; 24), 397 (100), 379 (5), 311 (5), 273 (8), 243 (14), 229 (11), 217 (10), 203 (8), and 127 (30); Found: *m/z* 412.3798. Calcd for $C_{29}H_{48}O$: M, 412.3705.

Lanost-8-en-24-one (31). Lanosta-8,24-diene (540 mg) in THF (40 ml) was stirred with borane solution in THF (BH_3·THF, 1 M, 5 ml) for 1 h at 0 °C. Water (5 ml), 3 M sodium hydroxide (5 ml), and 30% hydrogen peroxide (7 ml) were added and the solution was warmed at ca. 40 °C for 2 h. After the usual work-up, the residue (585 mg) was crystallized from methanol to give lanost-8-en-24-ol (mp 85—89 °C, M^+ 428), which was oxidized with Jones reagent in acetone (20 ml) at 0 °C to afford lanost-8-en-24-one (**31**; 383 mg), mp 88—89 °C (colorless plates from methanol); IR 1715 cm^{-1}; ^1H NMR (270 MHz) δ=0.69 (3H, s; 18-Me), 0.84 (3H, s), 0.88 (6H, s), 0.89 (3H, d, *J*=7 Hz; 21-Me), 0.98 (3H, s; 19-Me), 1.09 (6H, d, *J*=7 Hz; O=C-CH$\underline{Me_2}$), 2.40 (1H, dd, *J*=6 and 8 Hz; O=C-C-H), and 2.53 (1H, septet, *J*=7 Hz; O=C-C$\underline{H}$Me$_2$); MS *m/z* (%) 426 (M^+; 34), 411 (100), 393 (4), 287 (6), 273 (8), 257 (5), 243 (6), 229 (9), and 127 (16); Found: *m/z* 426.3816. Calcd for $C_{30}H_{50}O$: M, 426.3859.

23-Phenylthiolanost-8-en-24-ones (32a and b). Diisopropylamine (0.3 ml; distilled from calcium hydride) was added to a solution of butyllithium (1.25 ml, 1.95 mmol) in THF (5 ml) containing 2,2′-bipyridyl as an indicator at −70 °C under argon atmosphere. After stirring for 40 min at room temperature, the solution was cooled to 0 °C and HMPA (1.5 ml) was added, and then the solution was cooled to −78 °C. A solution of the ketone (**31**; 393 mg, 0.92 mmol) in THF (5 ml) was added dropwise to the solution of lithium diisopropylamide (LDA) above obtained, and stirred for 30 min. Then the resulting anion was put into a solution of diphenyl disulfide (420 mg, 1.9 mmol) in a mixture of THF (2.5 ml) and HMPA (1.25 ml) at room temperature using a syringe. The mixture was stirred for 1.5 h and quenched with 10% ammonium chloride solution. The product was separated by column chromatography on silica gel (32 g). Elution (each fraction: 1/4 column volume) was performed with hexane (frs 1—12) and 2% ether-hexane (frs 13—30) to afford a mixture of α-phenylthio ketones (360 mg) from frs 25—27, which showed peaks at *m/z* 534 (M^+; 35), 519 (100), 463 (25), 411 (28), 409 (32), and 326 (33) in the mass spectrum. The mixture was further separated by preparative TLC (developed twice with 4% ether-hexane). The less polar isomer (**32a**; 153 mg) and the more polar one (**32b**; 180 mg) were obtained. **32a**: Mp 135—136 °C (colorless needles from methanol); $[\alpha]_D^{24}$ −61°; IR 1698, 1580, 1238, 1208, 1097, 900, 740, and 683 cm^{-1}; ^1H NMR (90 MHz) δ=0.62 (3H, s; 18-Me), 0.83 (3H, s; 30-Me), 0.87 (6H, s; 28- and 29-Me), 0.93 (3H, d, *J*=7 Hz), 0.96 (3H, s; 19-Me), 1.04 and 1.09 (each 3H, d, *J*=7 Hz; O=C-CH$\underline{Me_2}$), 2.92 (1H, septet, *J*=7 Hz; O=C-C$\underline{H}$-Me$_2$), 3.88 (1H, dd, *J*=3 and 12 Hz; O=C-C$\underline{H}$-SPh), and 7.3 (5H, m; SPh); Found: *m/z* 534.3878. Calcd for $C_{36}H_{54}OS$: M, 534.3893. **32b**: Mp 65—67 °C (amorphous powder from methanol); $[\alpha]_D^{24}$ +119°; IR (liquid) 1708, 1582, 1240, 908, 735, and 690 cm^{-1}; ^1H NMR (90 MHz) δ=0.72 (3H, s; 18-Me), 0.85 (3H, s; 30-Me), 0.89 (6H, s; 28- and 29-Me), 0.94 (3H, d, *J*=7 Hz; 21-Me), 0.99 (3H, s; 19-Me), 1.04 and 1.06 (each 3H, d, *J*=7 Hz; O=C-CH$\underline{Me_2}$), 2.97 (1H, septet, *J*=7 Hz, O=C-C$\underline{H}$-Me$_2$), 3.80 (1H, dd, *J*=3 and 11 Hz; O=C-C$\underline{H}$SPh), and 7.3 (5H, m; SPh); Found: *m/z* 534.3844. Calcd for $C_{36}H_{54}OS$: M, 534.3893.

Reaction of 23-Phenylthiolanost-8-en-24-ones (32a and b) with Lead Tetraacetate. To a solution of α-phenylthio ketone (**32a**; 45 mg) in a mixture of acetic acid (1 ml) and benzene (9 ml), lead tetraacetate (200 mg containing acetic acid) was added under nitrogen. The mixture was refluxed overnight and then ethylene glycol was added to destroy the excess lead tetraacetate. Brine was added and the mixture was extracted with toluene. After the usual work-up, a residue was purified by column chromatography on silica gel (5 g) eluted with 10% ether-hexane. The α-acetoxy-α-phenylthio ketone (**33**; 28.3 mg) was obtained. The isomeric α-phenylthio ketone (**32b**) afforded the same compound (**33**) on the same treatment. **33**: Mp 170—172 °C; IR 1750, 1720, 1240, 1230, 1210, 760, 750, 710, and 695 cm^{-1}; ^1H NMR (90 MHz) δ=2.08 (3H, s; OAc), 2.37 (1H, dd, *J*=2 and 14 Hz; $C_{(22)}$-H), 2.59 (1H, dd, *J*=2 and 14 Hz; $C_{(22)}$-H′), 3.03 (1H, septet, *J*=6 Hz; O=C-C$\underline{H}$Me$_2$), and 7.35 (5H, m; SPh); MS *m/z* (%) 592 (M^+; 2), 532 (100), 517 (48), 480 (27), 461 (27), 423 (37), 369 (20), 325 (24), 311 (42), 295 (31), 283 (24), and 233 (72); Found: *m/z* 532.3747. Calcd for $C_{36}H_{52}OS$ (M−AcOH): 532.3739.

23,23-Dimethoxylanost-8-en-24-one (34). The α-acetoxy-α-phenylthio ketone (**33**; 70 mg) and iodine (870 mg) were refluxed in methanol (70 ml) overnight. An aqueous solution of sodium thiosulfite was added to the mixture and the solvent was evaporated in vacuo. Extraction with ether and evaporation of the solvent afforded a solid, which was crystallized from methanol to afford 23,23-dimethoxylanost-8-en-24-one (**34**; 41.8 mg), mp 141—143 °C; $[\alpha]_D^{25}$ +46°; IR 1720, 1150, 1090, 1045, 975, and 951 cm^{-1}; ^1H NMR (90 MHz) δ=0.65 (3H, s; 18-Me), 0.77—1.0 (total Me×4), 1.08 (6H, d, *J*=7 Hz; O=C-CH$\underline{Me_2}$), 3.17 and 3.20 (each 3H, s; OMe); MS *m/z* (%) 454 (M^+−MeOH; 16), 439 (11), 415 (38), and 155 (100).

Reduction of Dimethyl Acetal (34). To a solution of the dimethyl acetal (**34**; 33 mg) in ether (6 ml), LAH (ca. 20 mg)

was added with stirring. After 20 min, aqueous ether was added to destroy the excess hydride, and then 0.2 M hydrochloric acid was added to acidify the mixture. The usual work-up gave 24-hydroxylanost-8-en-23-one (**35**; 23.9 mg), amorphous solid; ^{1}H NMR (90 MHz) δ=0.67—1.16 (total Me×8), 2.22 and 2.42 (each 1H, br d, J=9 Hz; $C_{(22)}$-H), 3.37 and 3.43 (total 1H, ca. 2:1, d, J=6 Hz; CH-OH, disappeared on addition of D_2O), 3.98 and 4.06 (total 1H, ca. 1:2, dd, J=3 and 6 Hz; O=C-CH-OH, changed to a doublet (J=3 Hz) on addition of D_2O); MS m/z (%) 442 (M^+; 38), 427 (100), 409 (10), 311 (50), 256 (18), and 230 (19); Found: m/z 442.3778. Calcd for $C_{30}H_{50}O_2$: M, 442.3808.

Acetylation of α-Ketol (35). The α-ketol (**35**; 23.9 mg) was acetylated to afford 24-acetoxylanost-8-en-23-one (**36**; 26.8 mg), an oil; ^{1}H NMR (90 MHz) δ=2.14 (3H, s; OAc), 4.84 and 4.87 (total 1H, ca. 1:2, d, J=4 Hz; O=C-CH-OAc); MS m/z (%) 484 (M^+; 23), 469 (97), 409 (20), 311 (100), 285 (17), and 255 (36); Found: m/z 484.3882. Calcd for $C_{32}H_{52}O_3$: M, 484.3915.

Lanost-8-en-23-one (37). A solution of the α-keto acetate (**36**; 29 mg) in ether (2 ml) was added dropwise to a solution of metalic calcium (20 mg) in liquid ammonia (10 ml, distilled from sodium) at −78 °C with stirring. After 1.5 h, ammonium chloride was added and then ammonia was evaporated. Brine was added and the mixture was extracted with ether. The ether extract was worked up and a residue crystallized from methanol to give lanost-8-en-23-one (**37**; 25.1 mg), mp 82—82.5 °C; $[\alpha]_D^{25}$ +54°; IR 1710 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.76 (3H, s; 18-Me), 0.87 (3H, s; 30-Me), 0.90 (3H, s), 0.91 (3H, s), 0.92 (3H, d, J=6 Hz), 0.93 (3H, d, J=6 Hz), 0.95 (3H, d, J=6 Hz), 1.00 (3H, s; 19-Me), 2.28 (2H, d, J=6 Hz; $C_{(24)}$-H), and 2.46 (1H, dd, J=2 and 15 Hz; $C_{(22)}$-H); MS m/z (%) 426 (M^+; 26), 411 (100), 393 (6), 369 (2), 326 (3), 311 (62), 273 (10), 257 (10), 229 (16), and 85 (52); Found: m/z 426.3883. Calcd for $C_{30}H_{50}O$: M, 426.3861.

Sulphenylation of 29-Norlanost-9(11)-en-24-one (3). The 9(11)-en-24-one (**3**; 124.8 mg) was treated in the same manner as **31** to yield epimers of 23-phenylthio-29-norlanost-9(11)-en-24-ones, **38a** (less polar; 61.0 mg) and **38b** (more polar; 60.5 mg). **38a**: Mp 131 °C (needles from methanol); IR 1710, 1700 (sh), 1630, 740, and 690 cm^{-1}; $[\alpha]_D^{24.5}$ −57°; ^{1}H NMR (90 MHz) δ=0.58 (3H, s; 18-Me), 0.73 (3H, s; 30-Me), 0.82 (3H, d, J=6 Hz; 28-Me), 0.90 (3H, d, J=6 Hz; 21-Me), 0.93 (3H, s; 19-Me), 1.05 and 1.10 (each 3H, d, J=7 Hz; O=C-CHMe$_2$), 2.93 (1H, septet, J=7 Hz; O=C-CHMe$_2$), 3.88 (1H, dd, J=4 and 12 Hz; H-C-SPh), 5.25 (1H, m; H-C=C), and 7.3 (5H, m; SPh); MS m/z (%) 520 (M^+; 7), 505 (4), 449 (100), 411 (6), 339 (14), 313 (10), 283 (7), 245 (8), 243 (8), 229 (16), 217 (20), 203 (21), and 109 (30); Found: m/z 520.3735. Calcd for $C_{35}H_{52}OS$: M, 520.3737. **38b**: An oil; IR (liquid) 1710, 1630, 745, 735, and 690 cm^{-1}; $[\alpha]_D^{24.5}$ +118°; ^{1}H NMR (90 MHz) δ=0.69 (3H, s; 18-Me), 0.73 (3H, s; 30-Me), 0.83 (3H, d, J=7 Hz; 28-Me), 0.93 (3H, d, J=7 Hz; 21-Me), 0.97 (3H, s; 19-Me), 1.04 and 1.07 (each 3H, d, J=7 Hz; O=C-CHMe$_2$), 2.97 (1H, septet, J=7 Hz; O=C-CHMe$_2$), 3.83 (1H, dd, J=4 and 10 Hz; H-C-SPh), 5.27 (1H, m; H-C=C), and 7.3 (5H, m; SPh); MS m/z (%) 520 (M^+; 8), 449 (100), 411 (8), 339 (14), 313 (10), 283 (6), 245 (12), 243 (12), 229 (16), 217 (20), 203 (24), 194 (30), and 109 (30); Found: m/z 520.3681. Calcd for $C_{35}H_{52}OS$: M, 520.3737.

Reaction of 23-Phenylthio-29-norlanost-9(11)-en-24-ones (38a and 38b) with Lead Tetraacetate. The α-phenylthio ketone (**38a**; 46.7 mg) reacted with lead tetraacetate in the same manner as **32a**, and the product was separated by column chromatography on silica gel (5 g). Elution with 10% ether-hexane gave the starting material (**38a**; 14.4 mg) and 23-acetoxy-23-phenylthio-29-norlanost-9(11)-en-24-one (**39**; 29 mg, 56% yield). The same compound (**39**) was obtained from the isomer (**38b**). **39**: Mp 137—138.5 °C (needles from methanol); IR 1750, 1720, 1630, 1215, 965, and 745 cm^{-1}; $[\alpha]_D^{25}$ +64°; ^{1}H NMR (90 MHz) δ=0.63 (3H, s; 18-Me), 0.72 (3H, s; 30-Me), 0.83 (3H, d, J=6 Hz; 28-Me), 0.94 (3H, s; 19-Me), 1.03 (3H, d, J=7 Hz; 21-Me), 1.08 and 1.14 (each 3H, d, J=7 Hz; O=C-CHMe$_2$), 2.08 (3H, s; OAc), 2.58 (1H, d, J=14 Hz; $C_{(22)}$-H), 3.03 (1H, septet, J=7 Hz, O=C-CHMe$_2$), 5.25 (1H, m; C=C-H), and 7.3 (5H, m; SPh); MS m/z (%) 518 (M^+−AcOH; 24), 503 (6), 447 (3), 409 (4), 297 (22), 283 (63), 243 (10), 234 (50), 217 (12), 206 (100), 191 (20), 163 (60), and 115 (70); Found: m/z 518.3571. Calcd for $C_{35}H_{50}OS$ (M−AcOH): 518.3581.

23,23-Dimethoxy-29-norlanost-9(11)-en-24-one (40). Treatment of **39** (81.8 mg) with iodine by the same method as **33** furnished a dimethyl acetal (**40**), which was purified by column chromatography on silica gel (5 g). Elution with 4% ether-hexane afforded 43.9 mg (66% yield) of **40** as needles (from methanol), mp 122.5—125 °C; IR 1720, 1630, 1270, 1150, 1090, 1065, 1040, 1020, 970, and 950 cm^{-1}; $[\alpha]_D^{26}$ +66°; ^{1}H NMR (90 MHz) δ=0.63 (3H, s; 18-Me), 0.74 (3H, s; 30-Me), 0.82 (3H, d, J=6 Hz; 28-Me), 0.94 (3H, s; 19-Me), 1.09 (6H, d, J=7 Hz; O=C-CHMe$_2$), 3.15 (1H, septet, J=7 Hz; O=C-CHMe$_2$), 3.19 and 3.22 (each 3H, s; OMe), and 5.27 (1H, m; C=C-H); MS m/z (%) 440 (M^+−MeOH; 2), 425 (0.2), 401 (100), 313 (2), 283 (2), 245 (2), 231 (1), 229 (1), 217 (2), and 203 (10); Found: m/z 440.3554. Calcd for $C_{30}H_{48}O_2$ (M−MeOH): 440.3652.

Reduction of 23,23-Dimethoxy-29-norlanost-9(11)-en-24-one (40). The dimethyl acetal (**40**; 43 mg) was reduced and hydrolyzed and the resulting product was purified by chromatography on silica gel (5 g) eluted with 10% ether-hexane to give 24-hydroxy-29-norlanost-9(11)-en-23-one (**41**; 31.6 mg, 81% yield) as white powder (from methanol), mp 112—115 °C; IR (liquid) 3500, 1710, 1635, 1280, 1260, 1180, 1130, 1020, and 760 cm^{-1}; $[\alpha]_D^{26}$ +53°; ^{1}H NMR (90 MHz) δ=0.70 (3H, s; 18-Me), 0.76 (3H, s; 30-Me), 0.72 (3H, d, J=7 Hz; 21-Me), 0.84 (3H, d, J=6 Hz; 28-Me), 0.96 (3H, s; 19-Me), 0.91 and 1.09 (each 3H, d, J=7 Hz; CHMe$_2$), 2.55 (1H, br d, J=13 Hz; $C_{(22)}$-H), 3.37 and 3.43 (total 1H, ca. 3:2, d, J=5 Hz; H-C-OH, disappeared on addition of D_2O), 3.97 and 4.06 (total 1H, ca. 2:3, dd, J=3 and 5 Hz; H-C-OH, changed into a doublet (J=3 Hz) on addition of D_2O), and 5.28 (1H, m; C=C-H); MS m/z (%) 428 (M^+; 22), 413 (100), 395 (8), 355 (15), 312 (15), 297 (60), 283 (13), 243 (18), 229 (13), 217 (17), 215 (20), 203 (20), and 189 (20); Found: m/z 428.3703. Calcd for $C_{29}H_{48}O_2$: M, 428.3653.

Acetylation of 24-Hydroxy-29-norlanost-9(11)-en-23-one (41). The α-ketol (**41**; 31 mg) was acetylated to give 24-acetoxy-29-norlanost-9(11)-en-23-one (**42**) quantitatively, mp 93.5—95 °C (needles from methanol); IR 1745, 1730, 1720, 1235, and 1025 cm^{-1}; $[\alpha]_D$ +71°; ^{1}H NMR (90 MHz) δ=0.70 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.81 (3H, d, J=8 Hz; 21-Me), 0.96 (3H, s; 19-Me), 0.91 and 0.99 (each 3H, d, J=7 Hz; CHMe$_2$), 2.15 (3H, s; OAc), 4.35 and 4.38 (total 1H, ca. 2:3, d, J=4 Hz; H-C-OAc), and 5.28 (1H, m; C=C-H); MS m/z (%) 470 (M^+; 12), 455 (80), 410 (3), 395 (12), 355 (12), 312 (26), 297 (100), 283 (15), 243 (18), 230 (11), 229 (10), 217 (13), 215 (17), 203 (14), 201 (14), and 189 (17); Found: m/z 470.3823. Calcd for $C_{31}H_{50}O_3$: M, 470.3760.

29-Norlanost-9(11)-en-23-one (4). The keto acetate (**42**;

26 mg) was treated in the same manner as **36**, and the product was separated by column chromatography on silica gel (5 g). Elution with 5% ether–hexane gave 29-norlanost-9(11)-en-23-one (**4**; 14.8 mg, 65% yield). Further elution with 10% ether–hexane afforded an epimeric mixture of 29-norlanost-9(11)-en-23-ols (4.3 mg). **4**: Mp 88—89 °C (needles from methanol); IR 1715 and 1630 cm^{-1}; $[\alpha]_D^{22}$ +89° (*c* 0.20, $CHCl_3$); ^1H NMR (270 MHz) δ=0.70 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.83 (3H, d, *J*=6 Hz; 28-Me), 0.88 (3H, d, *J*=7 Hz; 21-Me), 0.905 and 0.92 (each 3H, d, *J*=6 Hz; 26- and 27-Me), 0.95 (3H, s; 19-Me), 2.25 (2H, d, *J*=6 Hz; $C_{(24)}$-H_2), 2.43 (1H, dd, *J*=2 and 15 Hz; $C_{(22)}$-H), and 5.28 (1H, m; C=C-H); MS *m/z* (%) 412 (M^+; 21), 398 (20), 397 (100), 312 (45), 297 (67), 283 (8), 230 (20), 215 (16), and 119 (36); Found: *m/z* 412.3750. Calcd for $C_{29}H_{48}O$: M, 412.3705. HR-MS *m/z* 397.3490 ($C_{28}H_{45}O$), *m/z* 312.2837 ($C_{23}H_{36}$), *m/z* 297.2592 ($C_{22}H_{33}$), *m/z* 283.2430 ($C_{21}H_{31}$), *m/z* 230.2080 ($C_{17}H_{26}$), and *m/z* 215.1808 ($C_{16}H_{23}$).

29-Norlanostan-23-one (2). A solution of 29-norlanost-9(11)-en-23-one (**4**; 28 mg) in acetic acid (2 ml) was stirred with platinum oxide (25 mg) under hydrogen at 90 °C overnight. The catalyst was filtered off and washed with ether. The filtrate and washings were combined, evaporated, and chromatographed on silica gel (5 g). Elution (each fraction: 1/4 column volume) was performed with 5% ether–hexane (frs 1—8) and 20% ether–hexane (frs 9—22). An epimeric mixture of 29-norlanostan-23-ols was eluted in frs 12—21 (18 mg), and was treated with Jones reagent in acetone (5 ml) at 0 °C for 20 min. The usual work-up and crystallization from methanol afforded 29-norlanostan-23-one (**2**; 17.8 mg) as needles in 63.3% yield from **4**. **2**: Mp 103.5—105 °C; IR 1710 cm^{-1}; $[\alpha]_D^{22}$ +25° (*c* 0.39, $CHCl_3$); ^1H NMR (270 MHz) δ= 0.80 (3H, d, *J*=6 Hz), 0.80 (3H, s), 0.82 (3H, s), 0.83 (3H, s), 0.86 (3H, d, *J*=6 Hz), 0.90 (3H, d, *J*=7 Hz), 0.91 (3H, d, *J*= 6 Hz), 2.10 (1H, d, *J*=15 Hz; $C_{(22)}$-H), 2.24 (2H, d, *J*=6 Hz; $C_{(24)}$-H_2), and 2.42 (1H, br d, *J*=15 Hz; $C_{(22)}$-H′); MS *m/z* (%) 414 (M^+; 4), 399 (4), 314 (100), 299 (44), 245 (63), 217 (16), 203 (8), and 176 (46); Found: *m/z* 414.3810. Calcd for $C_{29}H_{50}O$: M, 414.3860. HR-MS *m/z* 399.3526 ($C_{28}H_{47}O$), *m/z* 314.3011 ($C_{23}H_{38}$), *m/z* 299.2772 ($C_{22}H_{35}$), *m/z* 245.2301 ($C_{18}H_{29}$), *m/z* 217.1930 ($C_{16}H_{25}$), *m/z* 203.1803 ($C_{15}H_{23}$), and *m/z* 176.1546 ($C_{13}H_{20}$).

29-Norlanost-8-en-3β-ol (44). 29-Norlanost-8-en-3-one (**24**, mp 105.5—107 °C; lit,[11] 109—111 °C), obtained from the dihydroseconitrile (**11**), was reduced with LAH to give 29-norlanost-8-en-3β-ol (**44**) in a quantitative yield, mp 140.5—142 °C (lit,[15] 135—137 °C); IR 3300 and 1020 cm^{-1}; ^1H NMR (90 MHz) δ=0.72 (3H, s; 18-Me), 0.84 (3H, s; 30-Me), 0.92 (Me×3), 0.99 (3H, s; 19-Me), and 3.11 (1H, m; H-C-OH); MS *m/z* (%) 414 (M^+; 20), 399 (100), 381 (20), 273 (10), 259 (12), and 245 (8).

Acetylation of 29-Norlanost-8-en-3β-ol (44). The alcohol (**44**; 100 mg) was acetylated to give 29-norlanost-8-en-3β-yl acetate (**45**; 80 mg) after crystallization from methanol, mp 98—98.5 °C (lit,[15] 89—90 °C); IR 1740 and 1245 cm^{-1}; ^1H NMR (90 MHz) δ=0.71 (3H, s; 18-Me), 0.84 (3H, s; 30-Me), 0.91 (Me×3), 0.99 (3H, s; 19-Me), 2.05 (3H, s; OAc), and 4.41 (1H, dt, *J*=5 and 10 Hz; H-C-OAc); MS *m/z* (%) 456 (M^+; 34), 441 (100), 396 (3), 381 (52), 287 (8), 273 (13), 259 (3), 241 (8), 229 (8), and 227 (10).

Allylic Oxidation of 29-Norlanost-8-en-3β-yl Acetate (45). The acetate (**45**; 417 mg) was oxidized with chromium trioxide in acetic acid, and the reaction product was separated by chromatography on silica gel (16 g). Elution (each fraction: 15 ml) was carried out successively with 5, 10, 15, 20, 25, and 30% ether–hexane (each 30 ml). Fractions 9—12 afforded 3β-acetoxy-29-norlanost-8-ene-7,11-dione (**46**; 327 mg), mp 154—155 °C (yellow needles from methanol); IR 1740, 1680, and 1245 cm^{-1}; ^1H NMR (90 MHz) δ=0.80—0.95 (total Me×3), 1.21 (3H, s), 1.33 (3H, s), 2.06 (3H, s; OAc), and 4.44 (1H, dt, *J*=5 and 10 Hz; H-C-OAc); MS *m/z* (%) 484 (M^+; 26), 424 (12), and 409 (4); Found: *m/z* 484.3512. Calcd for $C_{31}H_{48}O_4$: M, 484.3552.

3β-Acetoxy-29-norlanostane-7,11-dione (47). The dienone (**46**; 240 mg) was dissolved in acetic acid (10 ml) and treated with zinc dust (1.2 g). The resulting residue (240 mg) was crystallized from methanol to afford 3β-acetoxy-29-norlanostane-7,11-dione (**47**; 140 mg), mp 180.5—181 °C; IR 1730, 1710, and 1245 cm^{-1}; ^1H NMR (90 MHz) δ=0.72 (3H, s), 0.76—0.92 (total Me×4), 1.24 (3H, s), 1.27 (3H, s), 2.06 (3H, s; OAc), and 4.41 (1H, dt, *J*=5 and 10 Hz; H-C-OAc); MS *m/z* (%) 486 (M^+; 100), 471 (16), 426 (25), 373 (12), 318 (20), 287 (40), 250 (15), 237 (30), 220 (30), 207 (30), and 177 (52); Found: *m/z* 486.3683. Calcd for $C_{31}H_{50}O_4$: M, 486.3708.

Wolff–Kishner Reduction of 3β-Acetoxy-29-norlanostane-7,11-dione (47). A mixture of the dione (**47**; 230 mg), hydrazine hydrate (2 ml), and diethylene glycol (4 ml) was refluxed at 130 °C for 1.5 h, and then potassium hydroxide (0.8 g) was added after the reaction mixture was cooled to room temperature. The excess hydrazine hydrate was removed by distillation until the vapor temperature reached ca. 200 °C, and the solution was refluxed for 2 h. After the usual work-up, the reaction product was crystallized from methanol to give 29-norlanostan-3β-ol (**48**; 87 mg). The filtrate was chromatographed on silica gel (12 g) eluted with 10% ether–hexane (frs 1—2), 20% ether–hexane (frs 3—4), 30% ether–hexane (frs 5—6), 40% ether–hexane (frs 7—8), and 50% ether–hexane (frs 9—12). Fractions 9 and 10 afforded 29-norlanostan-3β-ol (**48**; 29 mg) and fractions 11 and 12 gave 3β-hydroxy-29-norlanostan-11-one (**49**; 60 mg). **48**: Mp 154.5—155 °C; IR 3300 cm^{-1}; ^1H NMR (90 MHz) δ=0.79—1.0 (Me× 7), and 3.09 (1H, dt, *J*=5 and 10 Hz; H-C-OH); MS *m/z* (%) 416 (M^+; 26), 411 (3), 276 (35), 261 (100), 232 (20), and 192 (66); Found: *m/z* 416.4022. Calcd for $C_{29}H_{52}O$: M, 416.4017. **49**: Mp 153 °C (needles from methanol); IR 3300, 1700, 1165, 1040, and 970 cm^{-1}; ^1H NMR (90 MHz) δ=0.72 (3H, s; 18-Me), 0.83—0.90, (Me×3), 0.95 (3H, d), 1.03 (3H, s), 1.09 (3H, s), 2.39 (1H, s), 2.48 (1H, br s), 2.76 (1H, dt, *J*=13.5 and 3 Hz), and 3.07 (1H, dt, *J*=5 and 10 Hz; H-C-OH); MS *m/z* (%) 430 (M^+; 26), 412 (5), 303 (26), 276 (8), and 207 (100); Found: *m/z* 430.3808. Calcd for $C_{29}H_{50}O_2$: M, 430.3809.

29-Norlanostan-3-one (7). Jones oxidation of **48** (29 mg) furnished 29-norlanostan-3-one (**7**; 27 mg), mp 118—119 °C (needles from methanol); IR 1710, 1180, 1140, and 980 cm^{-1}; $[\alpha]_D^{22}$ +42° (*c* 0.12, $CHCl_3$); ^1H NMR (270 MHz) δ=0.79 (3H, s), 0.81 (3H, s), 0.87 (9H, d, *J*=6 Hz), 0.97 (3H, d, *J*=6 Hz; 28-Me), and 1.11 (3H, s; 19-Me); MS *m/z* (%) 414 (M^+; 8), 399 (5), 274 (42), 259 (100), 245 (7), 231 (30), 218 (28), and 190 (48); Found: *m/z* 414.3857. Calcd for $C_{29}H_{50}O$: M, 414.3860.

29-Norlanostane-3β,11β-diol (50). A solution of the hydroxy ketone (**49**; 47 mg) in ether (5 ml) was refluxed with LAH (38 mg) for 2 h. The usual work-up gave a residue (52 mg), which crystallized from methanol to give 29-norlanostane-3β,11β-diol (**50**) as needles, mp 173.5 °C; IR 3400, 1040, 1030, and 975 cm^{-1}; ^1H NMR (90 MHz) δ=0.75—0.91 (Me×5), 1.01 (3H, s), 1.12 (3H, s), 3.09 (1H, dt, *J*=5 and

11 Hz; H-$C_{(3)}$-OH), and 4.25 (1H, m; H-$C_{(11)}$-OH); MS *m/z* (%) 432 (M^+; 3), 414 (13), 399 (15), 381 (15), 274 (44), 259 (26), 241 (16), 224 (66), 209 (40), and 208 (44); Found: *m/z* 432.3959. Calcd for $C_{29}H_{52}O_2$: M, 432.3965.

Acetylation of 29-Norlanostane-3β,11β-diol (50). The diol (**50**; 46 mg) was acetytlated to afford 3β-acetoxy-29-norlanostan-11β-ol (**51**; 51.3 mg), mp 167—168 °C (needles from methanol); IR 3480, 1710, 1280, 1035, and 980 cm^{-1}; ^1H NMR (90 MHz) δ=0.78 (3H, s; 30-Me), 0.87 (9H, d, *J*=6 Hz), 0.89 (3H, d, *J*=5 Hz), 1.00 (3H, s), 1.12 (3H, s), 2.05 (3H, s; OAc), 4.25 (1H, m; H-C-OH), and 4.40 (1H, dt, *J*=5 and 10 Hz; H-C-OAc); MS *m/z* (%) 474 (M^+; 2), 456 (6), 441 (6), 414 (1), 316 (28), 256 (15), 250 (38), 241 (24), and 224 (57); Found: *m/z* 474.4093. Calcd for $C_{31}H_{54}O_3$: M, 474.4073.

Dehydration of 3β-Acetoxy-29-norlanostan-11β-ol (51). Dehydration of the 11β-ol (**51**; 50 mg) was effected in the same way as that used for **28a** and **28b**. The product was purified by chromatography on silica gel (5 g) to afford 29-norlanost-9(11)-en-3β-yl acetate (**52**; 29 mg), mp 114 °C (needles from methanol) (lit,[12a] mp 113.5—115 °C); IR 1740, 1635, 1250, 1030, and 980 cm^{-1}; ^1H NMR (90 MHz) δ=0.66 (3H, s; 18-Me), 0.74—0.95 (total Me×5), 1.00 (3H, s; 19-Me), 2.05 (3H, s; OAc), 4.40 (1H, m; H-C-OAc), and 5.34 (1H, m; C=C-H); MS *m/z* (%) 456 (M^+; 68), 441 (100), 396 (7), and 381 (35); Found: *m/z* 456.3983. Calcd for $C_{31}H_{52}O_2$: M, 456.3967.

29-Norlanost-9(11)-en-3β-ol (53). The acetate (**52**; 27 mg) was hydrolyzed with potassium hydroxide in boiling methanol to give 29-norlanost-9(11)-en-3β-ol (**53**; 23 mg) after crystallization from methanol as needles. **53**: Mp 148—149 °C; IR 3300, 1635, 1040, 1020, and 975 cm^{-1}; ^1H NMR (90 MHz) δ=0.66 (3H, s; 18-Me), 0.75 (3H, s; 30-Me), 0.88 (9H, d, *J*=6 Hz), 0.97 (3H, d, *J*=6 Hz; 28-Me), 0.99 (3H, s; 19-Me), 3.10 (1H, dt, *J*=5 and 10 Hz; H-C-OH), and 5.35 (1H, m; C=C-H); MS *m/z* (%) 414 (M^+; 21), 399 (100), 381 (20), 311 (4), 273 (7), 259 (9), 245 (6), and 243 (8).

29-Norlanost-9(11)-en-3-one (5). The alcohol (**53**; 21 mg) was oxidized with Jones reagent to afford 29-norlanost-9(11)-en-3-one (**5**) quantitatively, mp 102—102.5 °C (needles from methanol); IR 1720, 1205, 1150, 1140, and 980 cm^{-1}; $[\alpha]_D^{22}$+71° (*c* 0.07, $CHCl_3$); ^1H NMR (270 MHz) δ=0.69 (3H, s; 18-Me), 0.74 (3H, s; 30-Me), 0.868 (3H, d, *J*=6.4 Hz), 0.872 (3H, d, *J*=6.6 Hz), 0.882 (3H, d, *J*=6.1 Hz), 1.01 (3H, d, *J*=6.4 Hz; 28-Me), 1.23 (3H, s; 19-Me), and 5.35 (1H, dd, *J*=5.5 and 4.5 Hz); MS *m/z* (%) 412 (M^+; 18), 397 (100), 299 (6), 285 (2), 257 (7), 243 (12), 231 (12), and 217 (4); Found: *m/z* 412.3726. Calcd for $C_{29}H_{48}O$: M, 412.3705.

Oxidation of 29-Norlanost-8-en-3β-yl Acetate (45) with Chromyl Chloride. Chromyl chloride (0.015 ml) in dichloromethane (0.8 ml) was added to a solution of 29-norlanost-8-en-3β-yl acetate (**45**; 50 mg) in dichloromethane (1 ml) at −60 °C, and the solution was stirred for 1 h at −30 °C. Sodium hydrogensulfite solution was added to the solution and the product was extracted with ether. The usual work-up afforded 9(11)-en-7-one (**54**), which was isomerized immediately by $BF_3 \cdot OEt_2$ in benzene (3 ml). After 2 d, the solution was diluted with ether and washed with sodium hydrogencarbonate solution and dried. On evaporation and crystallization from hexane, 3β-acetoxy-29-norlanost-8-en-7-one (**55**; 27.6 mg) was obtained. The filtrate was chromatographed on silica gel (5 g) eluted with 10% ether-hexane, 15% ether-hexane, and then 20% ether-hexane (each 20 ml) to afford additional crystals of **55** (8 mg) from frs 18—20 (each fraction: 1/4 column volume). **55**: Mp 143.5 °C (cubics from hexane); IR 1740, 1650, 1580, and 1245 cm^{-1}; UV (EtOH) 252 nm (log ε 4.0); ^1H NMR (90 MHz) δ=0.67 (3H, s), 0.87 (9H, d, *J*=7 Hz), 0.93 (3H, s), 1.19 (3H, s), 2.05 (3H, s; OAc), and 4.8 (1H, m; H-C-OAc); MS *m/z* (%) 470 (M^+; 50), 455 (100), 410 (3), 395 (4), 357 (10), 302 (11), 264 (6), 229 (12), and 215 (9); Found: *m/z* 470.3779. Calcd for $C_{31}H_{50}O_3$: M, 470.3759.

A Mixture of 29-Norlanost-7-en-3-one (6) and 29-Norlanost-8-en-3-one (24). A mixture of the enone (**55**; 25 mg), hydrazine hydrate (0.5 ml), and diethylene glycol (2 ml) was refluxed at 130 °C for 2 h. After cooling, potassium hydroxide (3 pellets) was added to the mixture and the temperature was raised at 220 °C. Reflux was continued for 2 h and the mixture was worked up as usual to afford a mixture of alcohols.

Without purification, the mixture of alcohols was oxidized with Jones reagent in acetone to afford a mixture of 29-norlanost-7-en-3-one (**6**) and 29-norlanost-8-en-3-one (**24**), which was purified by chromatography on silica gel (5 g). Elution (each fraction: 1/2 column volume) was performed with 10% ether-hexane. Fractions 4—6 gave crystals (13.6 mg), which were shown to be a 2:1 mixture of **6** and **24** by ^1H NMR measurement. The mixture of **6** and **24**: IR 1715, 1310, 1230, 1185, 1175, and 820 cm^{-1}; MS *m/z* (%) 412 (M^+; 36), 397 (100), 299 (6), 285 (4), 257 (16), 243 (13), and 231 (20). ^1H NMR (270 MHz) signals ascribable to **6** δ=0.69 (3H, s; 18-Me), 0.86 (3H, s; 30-Me), 1.00 (3H, d, *J*=7 Hz; 28-Me), 1.09 (3H, s; 19-Me), and 5.21 (1H, m; H-C=C<).

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