111. New Triterpenes from the Bark of Western White Pine (*Pinus monticola* DOUGL.)[1])

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Summary

Eleven new triterpenes with the lanostene-type skeleton were isolated from the benzene extract of western white pine bark. Their structures were determined mainly on the basis of physical and spectral data.

As part of a long range study [2] [3] a detailed examination of the extractives of western white pine was undertaken. Extractives to the extent of 25% were obtained by successive extraction with benzene (3.2%), ethanol (7.5%) and water (14.3%). The benzene extract was chromatographed to yield 85 terpenoids including 32 triterpenes [3]. These included 24-methylidenecycloartanol, eleven known and nine new triterpenes with a serratane skeleton [4] [5] and eleven triterpenes with the lanostane skeleton. It is the latter group which forms the subject of this paper.

The unsaponifiable portion of the benzene extract was freed from wax alcohols by formation of the urea channel inclusion complex, and of sterols by precipitation of the digitonides. Subsequently, the petroleum ether insoluble fraction was chromatographed on silica gel to yield among other products eleven novel triterpenes I–XI (s. *Table*) [3]. Structure assignment for I–XI was made mainly on the basis of physical and spectral methods.

Similar characteristics of the physical data of the eleven compounds suggested a common skeleton. Elemental analysis and mass spectral data indicated the presence of C, H and O only, and that at least 30 C-atoms were present. The ^{1}H-NMR. spectra of each compound indicated at least five angular methyl groups,

Table. *Triterpenes I–XI from western white pine*

Compound No.	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Formula	**7**	**10**	**18**	**22**	**24**	**26**	**27**	**29**	**31**	**33**	**36**
% of benzene extract	0.7	0.2	0.04	0.06	0.002	0.005	0.03	0.002	0.02	0.003	0.01

[1]) See [1].

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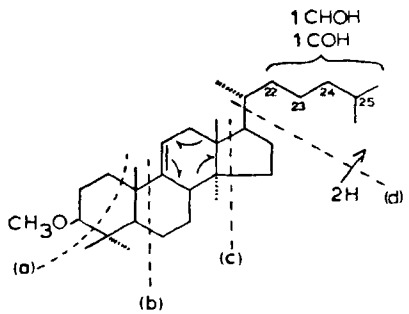
one secondary methyl group, at least one proton geminal to an oxygen substituent (OH or OCH_3, probably at C(3)), and one olefinic proton in the region of 5.2 ppm.

The serratene-type triterpenoid skeleton, known to occur in extractives of *Pinus* SPP. [3–5], was excluded for I–XI by the presence of a secondary methyl group and on the basis of the mass spectral fragmentations, both incompatible with this structural type. The onocerin skeleton and that of the saturated pentacyclic triterpenes could also be eliminated on the basis of spectral data. A common lanostane skeleton was however consistent with the observed physical data. In fact the ^{1}H-NMR. spectra of I–XI exhibited one-proton absorbances in the region of 5.20–5.25 ppm suggesting 9(11)-lanostenes [6–11].

Compound I, m.p. 193–194°, $[\alpha]_D^{22} = +77°$, was shown by elemental analysis and high resolution mass spectrometry to have the molecular formula $C_{31}H_{54}O_3$. The ^{1}H-NMR. spectrum showed only one secondary methyl group at 0.91 ppm (*d*, $J = 6$ Hz), an equatorial, secondary methoxy substituent at 3.36 ppm (*s*) together with a *m* at 2.64 ppm (1 H) arising from the geminal H-atom, a secondary hydroxy group (3.25 ppm, *m*), and an olefinic proton at 5.23 ppm (*m*). The IR. spectrum (KBr) suggested the presence of two hydroxy groups (3500 and 3460 cm^{-1}). The sample formed a monoacetate at ambient temperature and a diacetate only at elevated temperature. This suggestion of both a secondary and tertiary hydroxy groups was consistent with the singlet methyl resonances at 1.17 and 1.22 ppm, tentatively placing one hydroxy group at C(25) of the lanostene skeleton. Facile hydrogenation of the olefinic linkage, together with the vinyl absorbance at 5.23 ppm suggested $\Delta^{9(11)}$-unsaturation. This postulate was secured by mass spectrometric observation of an ion corresponding to the loss of a $C_{10}H_{18}O$ fragment (pathway (b)) characteristic for the loss of ring A in C(3)-oxygenated 9(11)-unsaturated lanostene-type triterpenoids [12]. A significant fragment ion at *m/z* 327 ($C_{23}H_{35}O$) (fragmentation (d)) is also reminiscent of the pathway followed by the tetracyclic lanostene-type triterpenes, representing the loss of side chain plus two protons. The same ion was observed for both the mono- and diacetate of I, thus placing both of the hydroxy groups in the side chain of I, and the methoxy group in ring A, most likely at C(3). Fragments corresponding to fissions (a) and (c) were also observed. A detailed mass spectrometric analysis of the diacetate of I, including high resolution data and analysis of metastable ions, led to the fragmentations outlined in *Scheme 1*. The loss of ketene observed at two stages in the

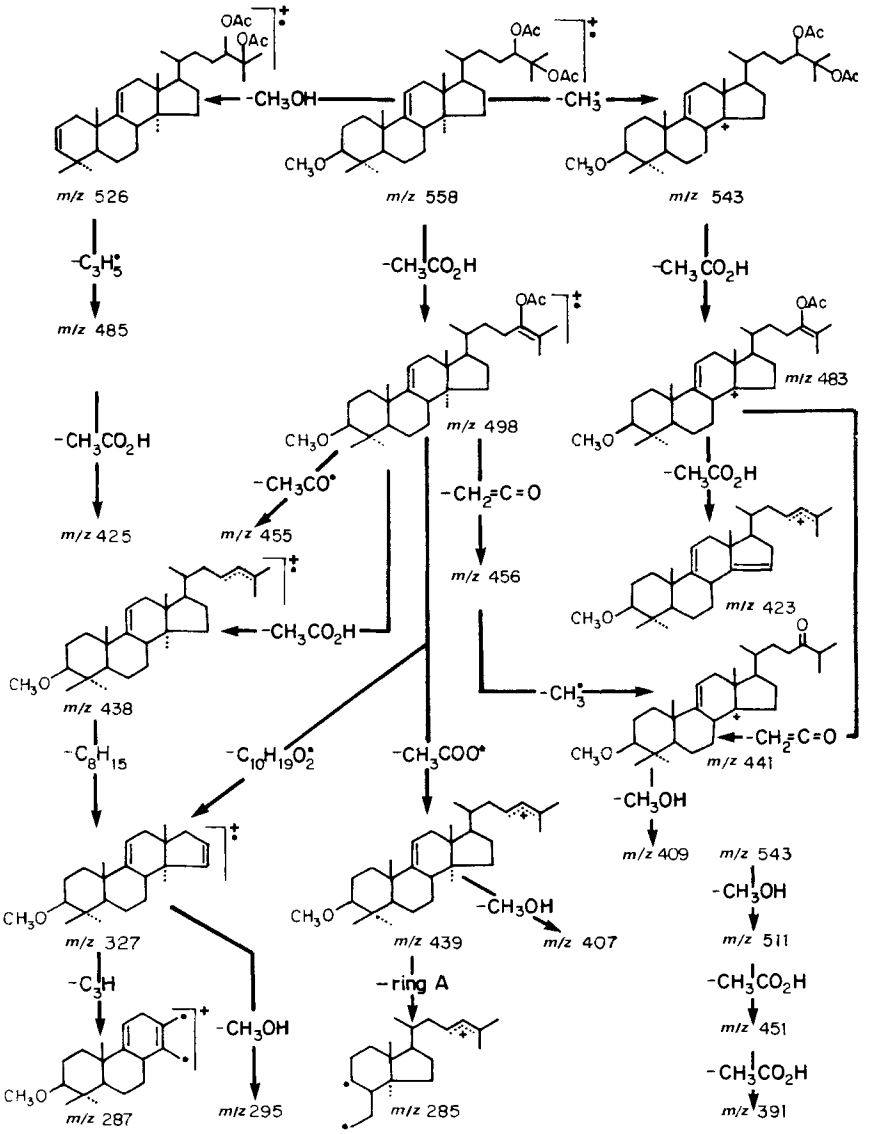


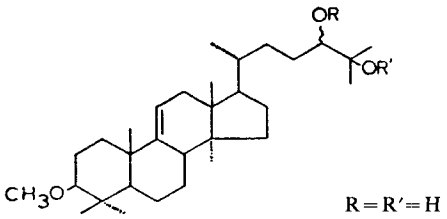
I

fragmentation process suggested a 1,2-relationship for the acetoxy groups [13] [14], *tentatively* placing the secondary hydroxy group on C(24) (s. formula **1**).

Conclusive evidence in support of the tentative structure **1** was obtained as described in *Scheme 2*. The dihydroderivative **2** was treated with periodate to effect vicinal diol cleavage. The aldehyde **3** was then oxidized, and esterification of the resultant acid **4** gave the corresponding ester **5**, confirming the position of the hydroxy groups at C(24) and C(25).

Scheme 1. *Mass spectrometric fragmentation of compound 1-diacetate* (**9**)

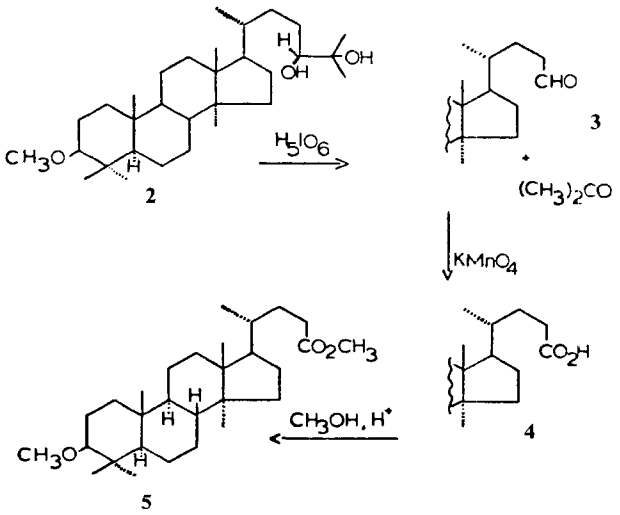




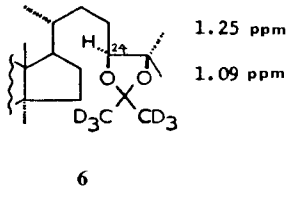
1

The CD. spectrum of compound I ($\Delta\varepsilon = +0.92$, 314 nm, CCl_4, using nickel acetylacetonide shift reagent) revealed a (24 *S*) configuration [15] [16][2]). This assignment was supported by an ^{1}H-NMR. study of the deuterioacetonide **6** derived from the natural diol: Irradiation (110 db) of **6** at the frequency of the methyl group (1.25 ppm) *cis* to H–C(24) (3.62 ppm) provided a nuclear *Overhauser* effect (net intensity increase of 19% in the H–C(24) integral) in accord with expectations.

Scheme 2



The above data completely define the natural triterpene I as *(24S)-3β-methoxy-5α-lanost-9(11)-ene-24S,25-diol* (**7**), its mono- and diacetate having structure **8** and **9**, respectively.



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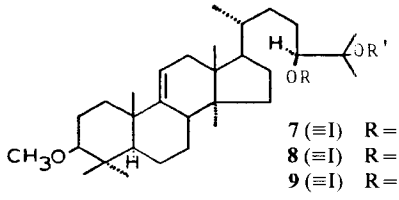
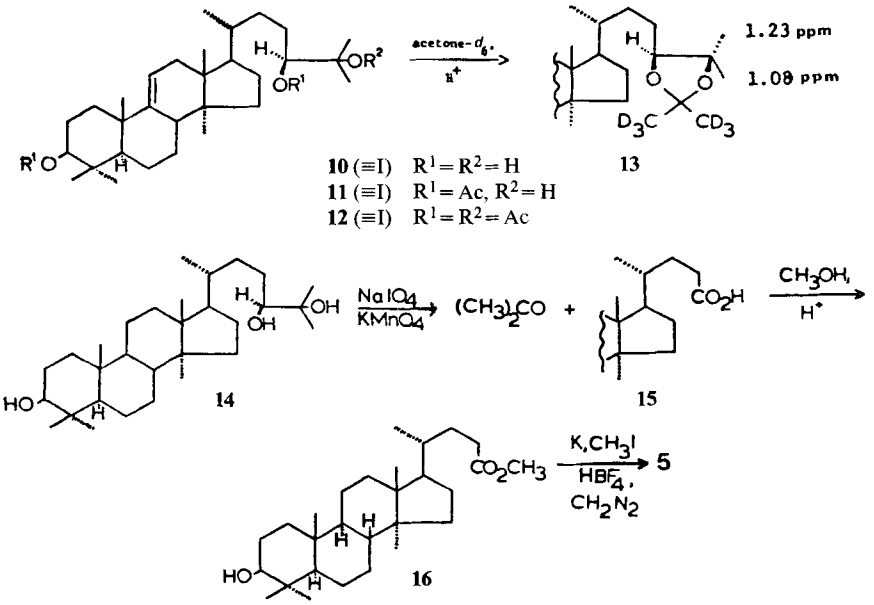


7 (≡I) R = R' = H
8 (≡I) R = Ac, R' = H
9 (≡I) R = R' = Ac

[2]) We are grateful to Professor *K. Nakanishi* for performing this determination.

Compound II had m.p. 214–215° (from acetone/methanol), $[\alpha]_D^{22} = +56°$, and a molecular formula $C_{30}H_{52}O_3$. Again the ^{1}H-NMR. spectrum revealed seven tertiary and only one secondary methyl group, two one-proton multiplets at 3.23 and 3.33 ppm for protons geminal to hydroxy groups, and a vinylic proton signal at 5.24 ppm. In fact the spectrum was remarkably similar to that of **7** with the exception of the signals due to the methoxy group and the proton geminal to it. The latter was replaced by a multiplet at 3.33 ppm. The IR. spectrum indicated the presence of several hydroxy functions and the compound readily formed a diacetate and, with difficulty, a triacetate. Similar fragmentation processes were observed in the mass spectrum of II compared with that of **7**. Based on these findings, compound II appeared to be simply the 3β-hydroxy analogue **10** of the methoxydiol **7**, its di- and triacetate having structure **11** and **12**, respectively.

Scheme 3



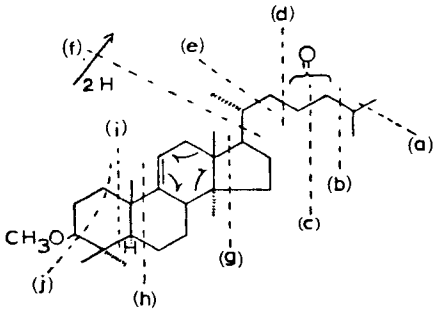
The reactions indicated in *Scheme 3* confirmed this postulate: the dihydro-compound **14** was oxidized to the acid **15**, and esterified to give the known methyl 3β-hydroxy-25,26,27-trinorlanostan-24-oate (**16**)[3]) [17]. Methylation of **16** gave **5** identical with that obtained from **2**.

The deuterioacetonide **13** was examined by ^{1}H-NMR. spectroscopy. Irradiation (110 db) of **13** at the frequency of the methyl group (1.23 ppm) *cis* to H–C(24) (3.60 ppm) provided a nuclear *Overhauser* effect (net intensity increase of 24% in the H–C(24) integral) as expected [23]. The triterpene II was thus defined as *(24S)-5α-lanost-9(11)-ene-3β,24,25-triol* (**10**).

[3]) We would like to thank Dr. *Barnes* for providing a sample of **16** for comparison.

Compound III, m.p. 161–162° (from dichloromethane/hexane), $[\alpha]_D^{20} = +93°$, had molecular formula $C_{31}H_{52}O_2$. The ^{1}H-NMR. spectrum indicated five tertiary methyl signals, a secondary methyl group at 0.88 ppm, two secondary methyl groups at 1.09 ppm, a secondary, equatorial methoxy group at 3.37 ppm, a vinylic proton at 5.23 ppm, and two overlapping one-proton multiplets at 2.3–2.8 ppm. IR. absorbances at 1630 and 1100 cm^{-1} supported the presence of the olefinic and ether functions, while a strong band at 1710 cm^{-1} indicated an aliphatic ketone. Furthermore, the doublet (6 H) at 1.09 ppm suggested a terminal isopropyl group, while the signal for the corresponding methine proton at *ca.* 2.3–2.7 ppm *suggested* [18a] placement of the carbonyl group at C(24).

Conclusive evidence was available from the mass spectral fragmentations, summarized in **17**. Here the significant fragment at *m/z* 441 (76%) due to loss of methyl from M^+ at 456 (67%) was more pronounced than in I and II due to contributions from both loss of an angular methyl group and also to simple ketone β-cleavage (fission a). Ions due to α-cleavage of the isopropyl group (*m/z* 43, and 413; fission b) and the remainder of the molecule (*m/z* 71, and 385; fission c) were also observed. Fragments due to straight β-cleavage (*m/z* 85, and 371; fission d) and *McLafferty* rearrangement (*m/z* 86, and 370) were present. The γ-fission was observable by the ions at *m/z* 99 and 357 (fission e) and loss of the side chain (f) by ions at *m/z* 329 and 127. A more intense ion at *m/z* 327 indicated loss of side chain and two H-atoms. Pronounced fragments due to cleavage of ring D (fission g) to give *m/z* 288 and 168 were noted and loss of ring A (fission h) was supported by ions at *m/z* 302 and 153. Cleavages in ring A were indicated by fragments at *m/z* 342 and 113 (fission i) and at 72 (fission j). Ions at *m/z* 234 and 222 were indicative of *retro-Diels-Alder* cleavage in ring C. Thus III was identified as *3β-methoxy-5α-lanost-9(11)-en-24-one* (**18**).



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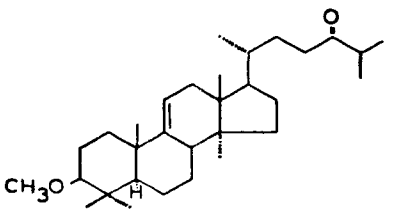


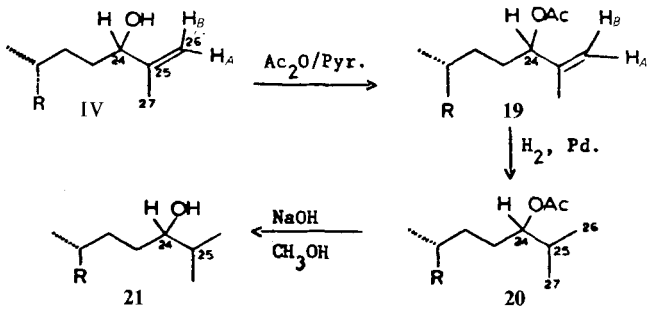
18 (≡III)

Compound IV, m.p. 180–180.5° (from dichloromethane/hexane), $[\alpha]_D^{25} = +86°$, had molecular formula $C_{31}H_{52}O_2$. The IR. spectrum indicated a hydroxy function (3615 cm^{-1}), an exocyclic olefin (1652, and 900 cm^{-1}), and the 9(11)-double bond (1635, and 795 cm^{-1}). The ^{1}H-NMR. spectrum showed five angular methyl absorbances identical with those of triterpenes I–III, a secondary methyl signal at 0.89, and a broad three-proton signal at 1.70 ppm, which together with olefinic resonances at 4.81 (broad quadruplet, $J \simeq 1$ Hz) and 4.89 (broad singlet) ppm

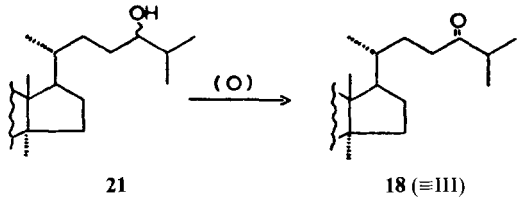
suggested an isopropylidene group. An equatorial methoxy group was indicated by a three-proton singlet at 3.33 ppm, and its geminal H-atom by a one-proton multiplet at 2.62 ppm. A broad one-proton triplet ($J=6$ Hz) was present at 3.99 ppm, and the C(11) vinylic proton resonated at 5.19 ppm.

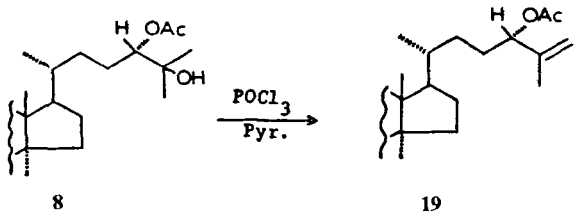
The triterpene IV readily formed a monoacetate **19** which was hydrogenated (→**20**) and subsequently saponified to give **21** (s. *Scheme 4*). The terminal olefin resonances at 4.81, and 4.89 ppm of IV underwent a downfield-shift to 4.88 and 4.93 ppm on acetylation to **19**, suggesting proximity to the hydroxy function.

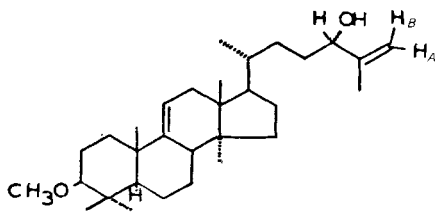
Scheme 4



Scheme 5







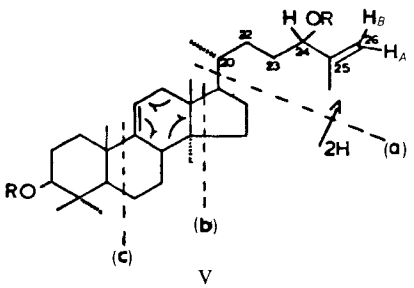
22 (≡IV)

The mass spectrum of IV, through the presence of three significant fragments [*m/z* 327 (M^+ – side chain + 2 H), *m/z* 125 (side chain – 2 H), and *m/z* 109 (side chain – H_2O)], suggested the same lanost-9(11)-ene tetracyclic system with the extra O-atom located in the side chain.

Conclusive chemical evidence in support of the above postulates was obtained by oxidation of **21** to triterpene III (≡**18**), whilst conversion of **8** to acetate **19** of IV indicated (24*S*) configuration in the latter *(Scheme 5)*. Thus triterpene IV was defined as *(24S)-3β-methoxy-5α-lanosta-9(11), 25-dien-24-ol* (**22**).

Compound V had molecular formula $C_{30}H_{50}O_2$. The IR. spectrum revealed two hydroxy groups (3631, and 3619 cm^{-1}), a terminal methylidene group (3100, and 910 cm^{-1}), and a trisubstituted olefinic linkage (1650, and 820 cm^{-1}). The ^{1}H-NMR. spectrum showed the five angular methyl signals for the tetracyclic skeleton, a secondary methyl group at 0.91 and a vinyl methyl group at 1.72 ppm. Three vinyl proton signals were observed at 4.84, 4.93, and 5.26 ppm. A one-proton multiplet at 3.42 ppm was tentatively assigned to an equatorial proton geminal to a hydroxy function. Similarly a broadened triplet at 4.02 ppm was assigned to a side-chain proton geminal to OH and adjacent to a methylidene group. These data suggested a side chain similar to that found for triterpene IV. Compound V readily formed a diacetate, although the yield was comparatively low, probably due to competing elimination processes.

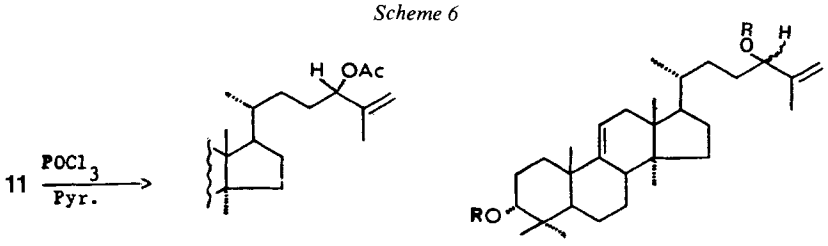
The mass spectrum of V showed strong signals due to loss of a methyl radical and water, indicating formation of the 23,25-diene system (*m/z* 409); the loss of two more H-atoms suggested subsequent formation of the 20,23,25-triene moiety (*m/z* 407). A second molecule of water appeared to be lost from ring A to give *m/z* 391. Fragments due to loss of the side chain plus 2 H-atoms (fission a; *m/z* 127, and 313) were present. That the formation of the diene and triene in the side chain had occurred to some extent prior to fission a was indicated by ions at *m/z* 109 and 107. A fragment ion at *m/z* 295 corresponded to loss of water from the tetracyclic system after fission a. Fragmentation processes b and c were supported by ions at *m/z* 167 and 288, and 302 and 141, respectively. The *retro-Diels-Alder* fission of ring C was supported by fragments at *m/z* 222 and 220.



V

The diacetate **25** of compound V was compared with diacetate **23**, obtained by dehydration of **11** (s. *Scheme 6*). The ^{1}H-NMR. spectra of **23** and **25** were very similar except that H–C(3) of the latter was observed at *ca.* 0.2 ppm lower field [18b], as expected for a C(3) epimer of **23**.

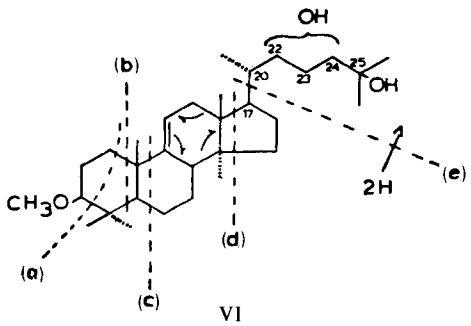
Scheme 6



23 **24** (≡V) R = H
25 (≡V) R = Ac

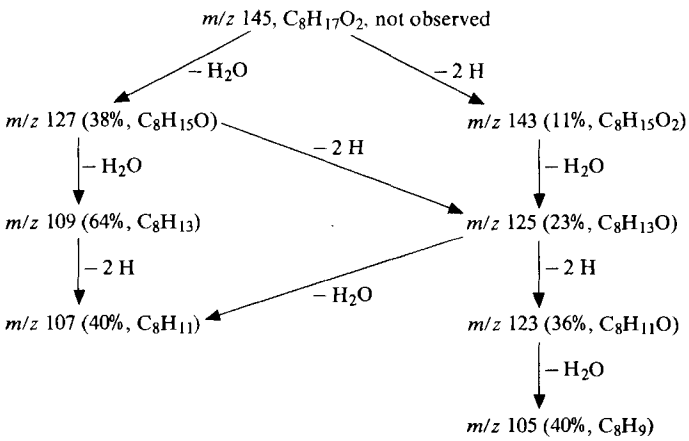
On the basis of these data, V was assigned the structure of *5α-lanosta-9(11),25-diene-3α,24β-diol* (**24**). The configuration at C(24) was not determined. Further support for **24** was obtained by *Jones* oxidation of **24** to 5α-lanosta-9(11),25-diene-3,24-dione, identical with an authentic sample.

Compound VI, m.p. 204–205° (from dichloromethane/hexane), $[\alpha]_D^{20} = +92°$, had molecular formula $C_{31}H_{54}O_3$. Spectral data again indicated a lanostene-type skeleton carrying a 3β-methoxy substituent. A six-proton singlet at 1.17 ppm and a hydroxy absorption in the IR. spectrum suggested a 25-hydroxy-substituted side



VI

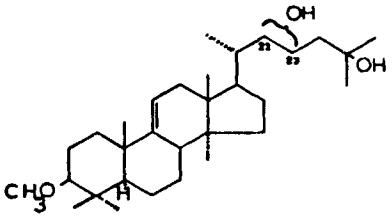
Scheme 7



chain. The magnetic equivalence of the methyl groups at C(25) suggested that C(24) is not an asymmetric C-atom. A one-proton absorbance at 3.32 ppm assigned to a proton geminal to a hydroxy group, together with a significant mass spectral fragment at *m/z* 327 ($C_{23}H_{35}O$), representing loss of the side chain plus 2 H-atoms, suggested that the third oxygen function was located at C(22) or C(23).

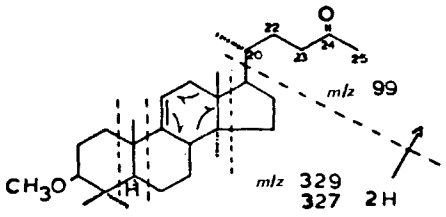
The mass spectrum indicated two distinct losses of water supporting the presence of two hydroxy functions. The fragmentation processes (a)–(d) were observed in the mass spectrum of VI. A fragment corresponding to the side chain (*m/z* 145) was not observed (fission (e)) presumably due to facile elimination processes. Various ions generated from the side chain are given in *Scheme 7*.

Thus the structure of *3β-methoxy-5α-lanost-9(11)-ene-22(or 23),25-diol* (**26**) is suggested for triterpene VI. A 270 MHz ^{1}H-NMR. spectrum of **26** clearly showed a signal at 3.31 ppm (*d×d, J=ca.* 7 and 2.7 Hz) attributable to the proton geminal to the secondary hydroxy group. The multiplicity of this signal indicates a hydroxy group at C(23).

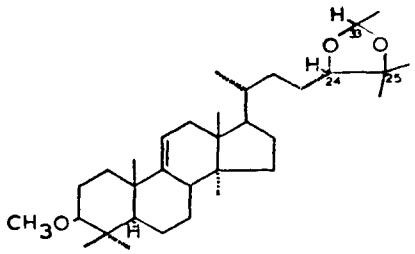


26 (≡VI)

Compound VII, m.p. 161–162° (from dichloromethane/methanol), $[\alpha]_D^{20} = +95°$, had molecular formula $C_{29}H_{48}O_2$. Again spectral data supported a tetracyclic system with a 3β-methoxy function as determined earlier. The IR. spectrum suggested a ketonic carbonyl function (1725 cm^{-1}), a three-proton singlet at 2.12 ppm indicated a methyl ketone, and a doublet at 0.89 ppm was assigned to the C(21)-methyl group. Mass spectral ions at *m/z* 329 and 327 represented the tetracyclic system minus the side chain and further loss of 2 H-atom, respectively. An ion at *m/z* 99 ($C_6H_{11}O$) represented the charged side chain. Other fissions observed in the mass spectrum were as indicated in formula **27**. These data supported a postulate that compound VII was best represented as *3β-methoxy-26,27-dinor-5α-lanost-9(11)-en-24-one* (**27**). Recently, hydrogenation of **27**, reoxidation to the ketone, iodoform degradation and esterification gave **5**.



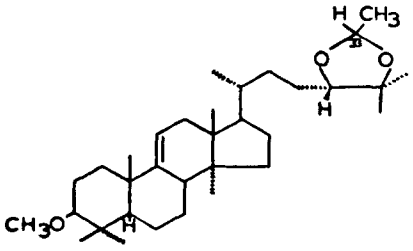
27



28

Compound VIII, m.p. 153–155° (from dichloromethane/hexane), $[\alpha]_D^{20} = +85°$, had molecular formula $C_{33}H_{56}O_3$. Spectral data indicated a tetracyclic system with 9(11)-unsaturation and a 3β-methoxy group. The ^{1}H-NMR. spectrum showed two extra singlet methyl groups (1.08, and 1.23 ppm), and two secondary methyl groups (0.87 ($J = 6$ Hz), and 1.31 ($J = 5$ Hz) ppm). A one-proton multiplet at 3.47 and a low-field one-proton quadruplet at 5.03 ($J = 5$ Hz) ppm were also observed. Two ions, *m/z* 327, and 329, in the mass spectrum confirmed the tetracyclic skeleton, leaving a $C_{10}H_{19}O_2$ fragment for the side chain. The absence of hydroxy and carbonyl absorptions in the IR. spectrum suggested involvement of the remaining two oxygen atoms in a cyclic ether function. Notably the two methyl frequencies at 1.08 and 1.23 ppm were in exactly the same position as those for the acetonide **13**. Thus structure **28** was initially used to rationalize the data. Decoupling experiments confirmed the geminal relationship between the methyl group (1.31 ppm) and methine proton (5.03 ppm) at C(33).

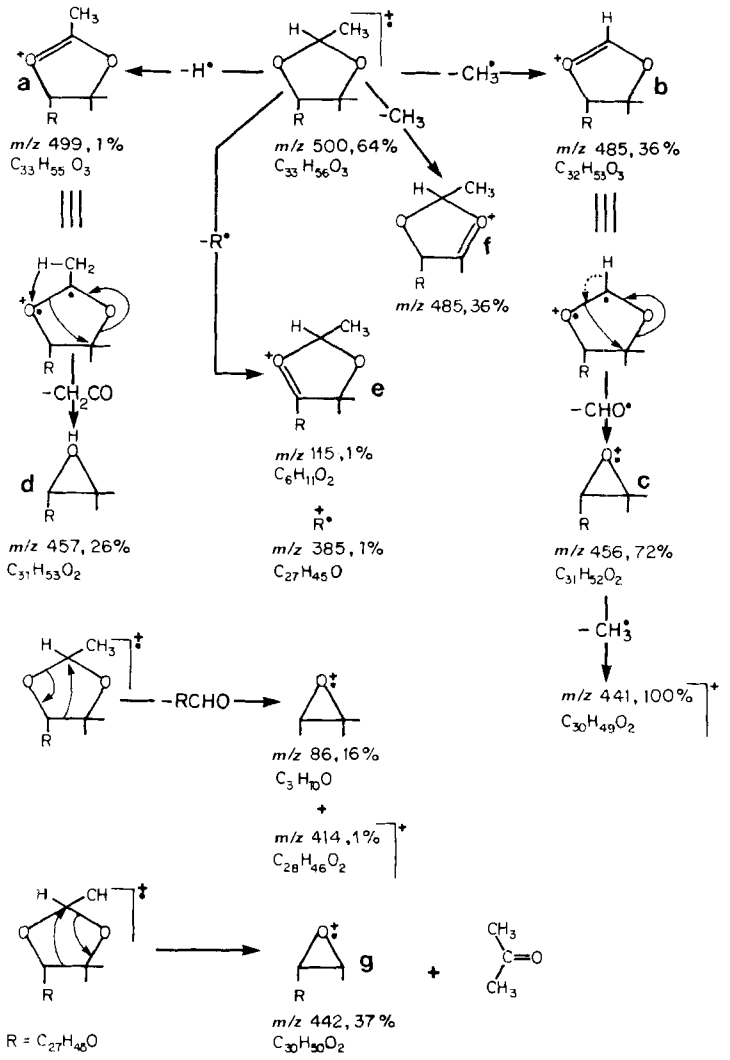
Scheme 8 outlines suggested modes of fission of the side chain (→**a**–**g**) in the mass spectrometer based on literature data for acetonides [19] [20]. In this regard, the $M^+ - 15$ fragment is of course due not only to a combination of the ions **b** and **f** but also to loss of an angular methyl group from the tetracyclic skeleton. Masses due to fissions of rings A, B, C, and D, as discussed earlier, and combinations of those with fragmentations outlined in *Scheme 8* were also present in the mass spectrum of compound VIII.



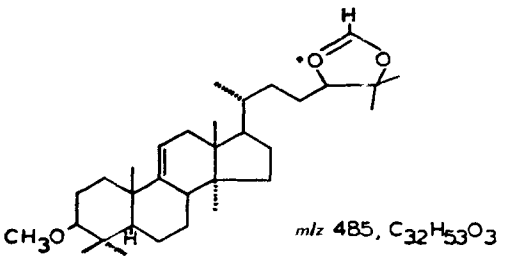
29 (≡VIII)

Conclusive evidence for the structure of VIII, and determination of the configuration at C(24) was obtained by treatment of compound I (≡**7**) with acetaldehyde. The product was identical with a sample of VIII, which is therefore described by the structure of *(24S)-3β-methoxy-24,25-(2'-methyl-1',3'-dioxatrimethylene)-5α-lanost-9(11)-ene* (**29**). The configuration at C(33) (=C(2')) was not determined.

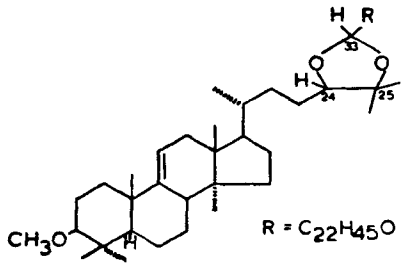
Scheme 8. *Mass spectrometric fragmentations in the side chain of compound VIII* (**29**)



Compound IX had a m.p. of 101.5–103° (from dichloromethane/ethanol), and an $[\alpha]_D^{20} = +48.5°$. High resolution mass measurement gave the highest value at *m/z* 810.7459 corresponding to $C_{54}H_{98}O_4$. Fragments at *m/z* 327, and 329 due to the tetracyclic system were observed arising from the base peak at 485. Further mass spectral fissions of rings A, B, C, and D were very similar to those observed for compound VIII. The latter had also exhibited an ion at *m/z* 485 due to fragment **30** arising by loss of a methyl radical from the molecular ion of VIII. In fact comparison of spectral data for VIII and IX leads to the conclusion that they have the same basic skeleton with differences only in the side chain. The ^{1}H-NMR. spectrum of IX showed a strong broad signal (*ca.* 40 H) at 1.25 ppm



30

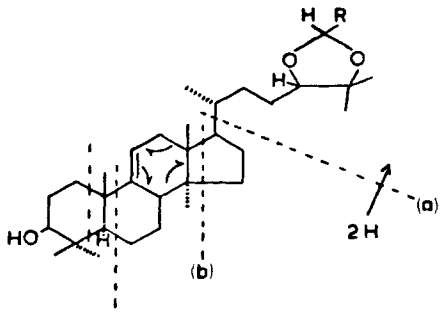


31 (≡IX)

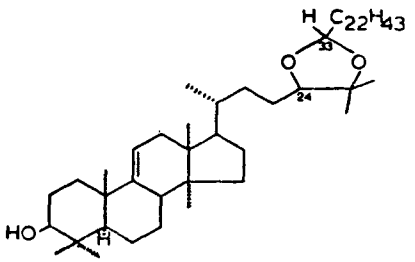
suggesting a hydrocarbon unit attached to the side chain. The one-proton triplet at 4.90 ppm was assigned to a proton geminal to two oxygen substituents and a methylene group. Thus the structure **31** describes the best fit to the data available. The presence of an unassigned one-proton multiplet at 3.73 ppm suggested a secondary hydroxy group in the residue R. Fissions of the side chain analogous to those described in *Scheme 8* supported the assignment **31**. Furthermore, small signals in the mass spectrum indicated that **31** may be accompanied by a mixture of side chain homologs: with M^+ at 807.7595 ($C_{55}H_{99}O_3$), 793 ($C_{54}H_{97}O_3$), 780.7325 ($C_{53}H_{96}O_3$), 779.7276 ($C_{53}H_{95}O_3$), 765.7124 ($C_{52}H_{93}O_3$), and 760.7066 ($C_{53}H_{92}O_2$).

Compound X, m.p. 91–92° (from dichloromethane/methanol), $[\alpha]_D^{20} = +39°$, gave a molecular ion at *m/z* 778 which was measured as 777.7216, representing either M^+ or $M^+ - 1$. The IR. spectrum showed absorbances for a hydroxy group at 3480 cm^{-1}, and for a trisubstituted double bond at 1630 and 810 cm^{-1}. The ^{1}H-NMR. spectrum revealed tertiary methyl groups at 0.66, 0.75, 0.82, 0.99, 1.04, 1.10 and 1.20 ppm, a secondary methyl group at 0.91 (*d*, $J = 6$ Hz) ppm, an axial proton, geminal to an O-atom (3.22 ppm), a one-proton triplet ($J = 5$ Hz) at 4.92, and one-proton multiplets at 3.46, 4.23, and 5.24 ppm. Comparison of this data with that for compounds VIII and IX suggested the same basic skeleton with a 1,3-dioxolane system in the side chain but with a C(3)-hydroxy function. An ^{1}H-NMR. signal, due to approximately 40 protons, at 1.28 ppm again suggested a hydrocarbon residue attached to the side chain.

The mass spectrum exhibited fragments due to fissions of the tetracyclic system as shown in **32**. Ions due to fissions a and b (*m/z* 315 and 313, and 274 and 273, respectively) were predominant. The structure outlined in **32** is equivalent



32



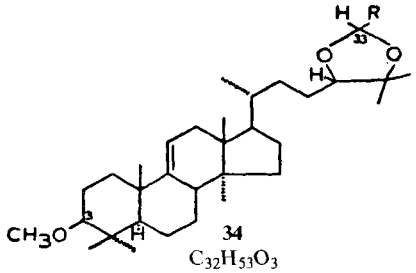
33

to $C_{31}H_{51}O_3$ excluding R. Measurement of the ion at 777.7216 therefore suggested $C_{22}H_{43}$ as the best fit for R. Microanalytical data supported a molecular formula of $C_{53}H_{94}O_3$ for the natural product. The implication of one degree of unsaturation in R was supported by the ^{1}H-NMR. signal at 4.23 ppm. Furthermore, the mass spectrum showed a fragment at *m/z* 735 due to loss of C_3H_7 from M^+ and a signal at 709 corresponding to a loss of C_5H_9, suggesting the double bond be located between the fourth and fifth C-atom from the end of the chain.

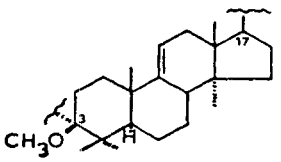
Thus structure **33** is presented as the best fit for the data for compound X. Here again other high molecular weight ions were detected in the mass spectrum suggesting the presence of homologs with M^+ at 793.7419 ($C_{54}H_{97}O_3$), 792.7335 ($C_{54}H_{96}O_3$), 779.7503 ($C_{50}H_{99}O_5$), 779.7276 ($C_{53}H_{95}O_3$), 765.7117 ($C_{52}H_{93}O_3$), 764.7291 ($C_{49}H_{96}O_5$), and 760.7066 ($C_{53}H_{92}O_2$).

Compound XI, m.p. 261–261.5° (from dichloromethane/methanol), $[\alpha]_D^{20} = +91°$, gave microanalytical data supporting a molecular formula $C_{58}H_{96}O_5$, which was further substantiated by mass measurement of the molecular ion, 872.7254. The IR. spectrum showed the existence of ether function(s) (1100 cm^{-1}). The ^{1}H-NMR. spectrum did not show the hydrocarbon residue observed in earlier cases, but was quite similar to that for compound VIII. Tertiary methyl signals were observed at 0.66, 0.74, 0.80, 0.98, and 1.05 ppm (6 H each) and at 1.11, and 1.25 ppm (3 H each). Also observed were two overlapping methyl doublets ($J = 6$ Hz) at 0.89 and 0.91 ppm, one-proton multiplets at 2.65 and 3.63 ppm, a one-proton triplet at 4.90 ppm, a two-proton multiplet at 5.25 and a six-proton singlet at 3.37 ppm. These data suggested the possibility of a dimeric compound. Notably only one ^{1}H-NMR. signal was observed for a proton geminal to the methoxy group suggesting that one of the units was substituted at C(3).

The mass spectrum of XI revealed a fragment at *m/z* 485 ($C_{32}H_{53}O_3$; *cf.* fragment **30** from compounds VIII and IX), and at 327 (C(17)–C(20) cleavage and loss of 2 H-atoms). Here however, the ion at 327 was much more abundant than that at 485 suggesting that the tetracyclic system itself is more abundant, *viz* XI could be a dimer. Thus structures **34** ($C_{32}H_{53}O_3$) and **35** ($C_{23}H_{36}O$) were considered as the two likely building units, together with a fragment C_3H_7O needed to make up the molecular formula $C_{58}H_{96}O_5$. Since only one H–C(3) was observed in the ^{1}H-NMR. spectrum, it was tempting to link **34** and **35** *via* C(3) of the latter. The H–C(33) of **34** was observed as a triplet at 4.90 ppm suggesting a methylene bridge between C(33) of **34** and C(3) of **35**. The remaining fragment C_2H_5O was then placed at C(17) in **35** to give **36** as a *tentative* structure for compound XI.

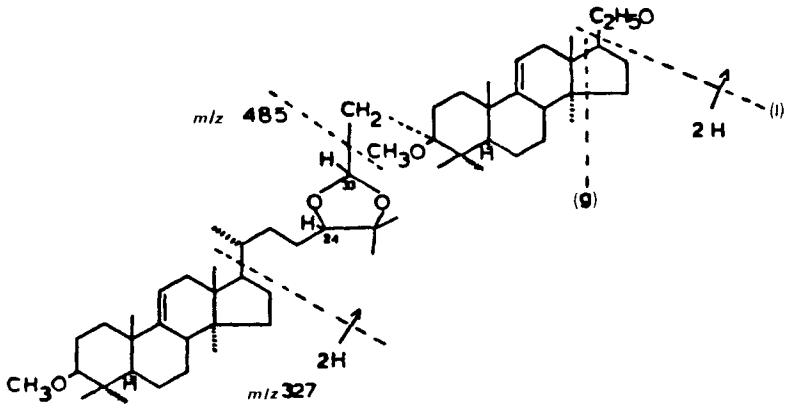


34
$C_{32}H_{53}O_3$



35
$C_{23}H_{36}O$

Mass spectral fragmentation of the 1,3-dioxolane system leading to ions **a** (*m/z* 872), **b** (457), **c** (858), **d** (485), and **e** (456) was observed (s. *Scheme 9*). A fragment at *m/z* 826 due to fission f was noted, while an ion at 86 may be due to fission g. Various fragments arising from the usual fissions of rings A, B, C and D were also observed; however, the aliphatic unit connecting the two tetracyclic systems could not be traced.

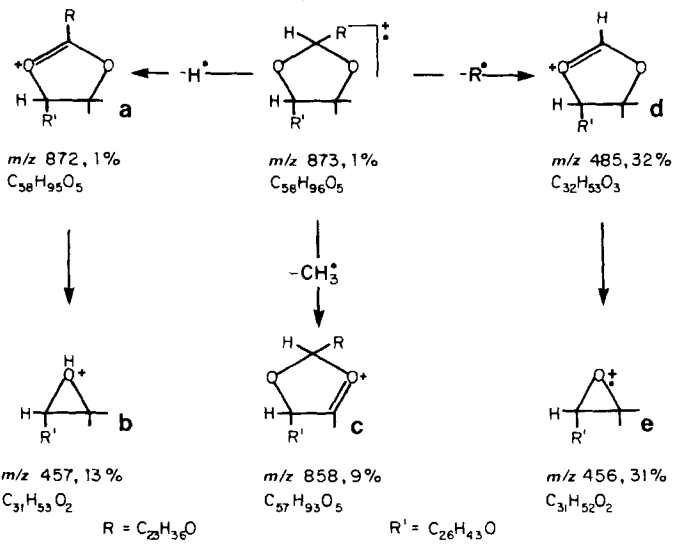


36
$C_{58}H_{96}O_5$

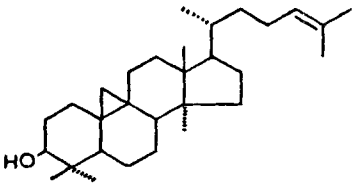
Thus structure **36** remains a *tentative* postulate for compound XI, and other high-mass ions were observed at *m/z* 869.7370 ($C_{59}H_{97}O_4$), 822.6855 ($C_{57}H_{90}O_3$), and 811.6940 ($C_{56}H_{91}O_3$).

The biogeneses of the compounds discussed above can conceivably arise *via* cycloartenol (**37**) by acid catalyzed cleavage of the cyclopropane ring to a

Scheme 9



C(9),C(11)-unsaturation and with appropriate oxygenation of the side chain. The known presence of wax alcohols in the bark extract could account for the side chain substitution patterns in compounds IX and X.



37

Experimental Part

General remarks. M.p. (uncorrected) were determined on a *Kofler* block. Optical rotations were obtained at the sodium D line using a *Perkin-Elmer* model 141 automatic polarimeter. IR. spectra were measured on a *Perkin-Elmer* model 710 or 457 spectrophotometer. The absorption maxima (cm^{-1}) were calibrated with respect to the absorption band of polystyrene at 1610 cm^{-1}. ^{1}H-NMR. spectra were measured at RT. on a *Varian* HA-100 or XL-100 spectrometer. Chemical shift values in ppm are relative to tetramethylsilane (= 0 ppm) used as internal reference (coupling constants J in Hz); s = singlet, d = doublet, t = triplet, qa = quadruplet, m = multiplet, br. = broad. Low resolution MS. (LR.-MS.) were determined on either an *AEI* MS-902 or an *Atlas* CH-4B spectrometer. High resolution MS. (HR.-MS.) were measured on an *AEI* MS-902 instrument. All indicated mass spectral fragmentation pathways were verified by accurate mass measurements and in some cases also by metastable ions. Microanalyses were carried out by Mr. *P. Borda* of the Microanalytical Laboratory, University of British Columbia. Thin layer chromatography was carried out using *Merck* silica gel G plates containing 2% fluorescent indicator. For preparative thin layer chromatography, plates of 1 mm thickness were used. Visualization was effected either by treatment with iodine vapours or spraying with antimony trichloride in glacial acetic acid (40% *w/w*) followed by 5 min heating at 100°. Reagents and solvents were recrystallized or distilled prior to use. A detailed description of the isolation procedure for I–XI has been given elsewhere [3].

Compound I: (24S)-3β-methoxy-5α-lanost-9(11)-ene-24,25-diol (7). The substance obtained from the chromatographic separation was recrystallized from hexane to provide an analytical sample of 7, m.p. 193–194°, $[\alpha]_D^{22} = +77°$ ($c = 1$, $CHCl_3$). – IR. (CCl_4): 3623 (sec. OH); 3577 (H bonded OH). – IR. (KBr): 3500, 3460 (OH); 1635, 790 (C=CH); 1105 (C–O–C). – ^{1}H-NMR.: 0.67, 0.74, 0.81, 0.98, 1.05, 1.17 and 1.22 (7 *s*, 3 H each, 7 CH_3); 0.91 (*d*, $J = 6$, 3 H, H_3C–C(20)); 2.64 (br. *m*, 1 H, H_{ax}–C(3)); 3.25 (*m*, 1 H, H–C(24)); 3.36 (*s*, 3 H, H_3CO_{eq}–C(3)); 5.23 (*m*, 1 H, H–C(11)). – MS.: 474 (13, M^+), 459 (8), 456 (13), 441 (27), 428 (7), 427 (11), 424 (11), 410 (11), 409 (33), 393 (6), 380 (10), 367 (5), 327 (16), 302 (5), 297 (5), 288 (5), 287 (9), 273 (5), 255 (7), 241 (5), 229 (6), 227 (8), 215 (8), 213 (6), 203 (7), 201 (9), 199 (5), 189 (15), 187 (14), 185 (6), 177 (5), 175 (24), 173 (19), 161 (18), 159 (20), 153 (5), 149 (14), 147 (19), 145 (18), 141 (13), 135 (33), 133 (25), 127 (15), 123 (19), 121 (37), 119 (37), 109 (33), 107 (34), 105 (32), 99 (13), 95 (54), 94 (31), 93 (31), 91 (21), 85 (21), 83 (19), 82 (7), 81 (39), 78 (49), 71 (62), 69 (67), 67 (27), 59 (75), 57 (25), 56 (7), 55 (62). – HR.-MS.: 474.4097 ($C_{31}H_{54}O_3$, calc. 474.4071), 327.2656 ($C_{23}H_{35}O$, calc. 327.2687); metastable ions at 444.8, 438.8, 426.7, 424.7, 423.8, 420.7, 412.5, 407.0, 405.9, 397.1, 391.8, 386.6, 379.4, 374.9, 373.8, 364.7, 364.6, 361.5, 355.0, 347.0, 339.7, 337.7, 323.7, 318.9, 272.9, 266.4, 258.5, 255.3, 252.0, 243.9, 238.4, 226.6, 221.8, 213.0, 200.6, 184.7.

$C_{31}H_{54}O_3$ (474.40) Calc. C 78.42 H 11.47% Found C 78.10 H 11.32%

Hydrogenation of 7. Compound 7 (500 mg) in glacial acetic acid (100 ml) was hydrogenated over *Adam*'s catalyst (200 mg) at RT. and atmospheric pressure for 70 h. One mol of H_2 was taken up. The catalyst was removed by filtration and the solvent removed *in vacuo* to provide a white solid (491 mg, 98%), which was recrystallized from benzene/hexane to give an analytical sample of

3β-methoxy-5α-lanostane-24,25-diol (**2**), m.p. 213.5–214.5°, $[\alpha]_D^{24} = +35.4°$ ($c = 0.7$, $CHCl_3$). – IR. (KBr): 3430 (OH); 1105 (C–O–C). – ^{1}H-NMR.: 2.64 (*qa*, $J = 11$, 4, 1H, H–C(3)); 3.29 (*m*, 1H, H–C(24)); no olefinic protons. – HR.-MS.: 476.4229 (1.6%, M^+, $C_{31}H_{56}O_3$, Calc. 476.4224).

$C_{31}H_{56}O_3$ (476.42) Calc. C 78.09 H 11.84% Found C 78.15 H 11.77%

Periodate cleavage of **2**. A suspension of **2** (225 mg) in a solution of $HIO_4 \cdot 2H_2O$ (500 mg) in distilled water (15 ml) was agitated for 4 days at RT. under N_2. Then the mixture was extracted with chloroform, the chloroform solution washed with water, dried over anhydrous Na_2SO_4 and evaporated to yield 192 mg (98%) of a white solid. Recrystallization from benzene afforded an analytical sample of *3β-methoxy-25,26,27-trinor-5α-lanostan-24-al* (**3**), m.p. 180–181°, $[\alpha]_D^{22} = +43.7°$ ($c = 0.6$, $CHCl_3$). – IR. (KBr): 2710, 1720 (CHO); 1105 (C–O–C). – ^{1}H-NMR.: 2.37 (*m*, 2H, 2 H–C(23)); 9.74 (*t*, 1H, H–C(24)). – HR.-MS.: 416.3691 (34%, M^+, $C_{28}H_{48}O_2$, Calc. 416.3653).

$C_{28}H_{48}O_2$ (416.36) Calc. C 80.71 H 11.61% Found C 80.32 H 11.72%

In a second, identical experiment after the 4 day reaction period, the reaction vessel was attached to a vacuum line and part of the volatile fraction trapped in cooled acidic solution of 2,4-dinitrophenylhydrazine. When the latter was allowed to warm to RT. orange crystals (8 mg) precipitated, which after recrystallization from ethanol, were identical (m.p.; mixed m.p.; TLC. on silica gel G with benzene; IR. and ^{1}H-NMR.) with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone.

Permanganate oxidation of **3** *to* **4**. A solution of **3** (52 mg) in acetone (20 ml) was treated with an aqueous $KMnO_4$-solution (25 mg in 0.5 ml water). The mixture was stirred for 2½ h at RT., after which it was diluted with water (10 ml) and treated with methanol (5 ml). The total mixture was then evaporated *in vacuo* to about 10 ml and extracted with methanol/chloroform 1:4. The organic phase was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to yield *3β-methoxy-25,26,27-trinor-5α-lanostan-24-oic acid* (**4**) as a white solid (54 mg, 100%). This material was not purified further because of its polar nature. – IR. (KBr): 3490, 3200–2450, 1705 and 1260 (COOH). – HR.-MS.: 432.3595 (10%, M^+, $C_{28}H_{48}O_3$, Calc. 432.3603).

Methyl ester **5** *from* **4**. Compound **4** (50 mg) was treated with anhydrous methanol (75 ml) and conc. sulfuric acid (0.5 ml) for 20 h at RT. The solution was reduced *in vacuo* to about 5 ml and treated with chloroform (20 ml). The solution was washed successively with water, saturated aqueous $NaHCO_3$-solution and water, and was dried over anhydrous Na_2SO_4. Evaporation yielded a white solid material (52 mg, 100%) which after recrystallization from methanol afforded an analytical sample of *methyl-3β-methoxy-25,26,27-trinor-5α-lanostan-24-oate* (**5**), m.p. 173–175.5°, $[\alpha]_D^{20} = +43.9°$ ($c = 0.5$, $CHCl_3$). – IR. (KBr): 1730 and 1175 ($COOCH_3$). – ^{1}H-NMR.: 2.26 (*m*, 2H, 2 H–C(23)); 2.63 (*qa*, $J = 4$, 1H, H–C(3)); 3.32 (*s*, 3H, H_3CO–C(3)); 3.62 (*s*, 3H, CO_2CH_3). – HR.-MS.: 446.3765 (M^+, $C_{29}H_{50}O_3$, Calc. 446.3759).

$C_{29}H_{50}O_3$ (446.38) Calc. C 77.97 H 11.28% Found C 77.78 H 11.12%

Synthesis of mono-acetate **8**. A mixture of **7** (50 mg) and 2 ml of pyridine/acetic anhydride 1:1 was left for 48 h at RT. The mixture was poured into ice-water and extracted with methylene chloride. The extract was washed with aqueous hydrochloric acid (5%), and water, and dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded a crude product which was chromatographed using 5 g silica gel (*Woelm*, activity III). Elution with benzene/ether 95:5 provided *(24S)-3β-methoxy-5α-lanost-9(11)-ene-24,25-diol-24-acetate* (**8**) (33 mg, 61%) followed by a small amount (1.5 mg) of the diacetate (**9**). The monoacetate was recrystallized from hexane/benzene to provide an analytical sample of **8**, m.p. 229–230°, $[\alpha]_D^{22} = +94°$ ($c = 1$, $CHCl_3$). – IR. (CCl_4): 3609 (tert. OH). – IR. (KBr): 3520 (OH); 1725, 1250 (OAc); 1635, 790 (C=CH); 1105 (C–O–C). – ^{1}H-NMR.: 0.65, 0.74, 0.80, 0.97 and 1.05 (5 *s*, 3H each, 5 CH_3); 0.90 (*d*, $J = 6$, 3H, H_3C–C(20)); 1.20 (*s*, 6H, 2 H_3C–C(25)); 2.08 (*s*, 3H, AcO–C(24)); 2.65 (*m*, 1H, H–C(3)); 3.36 (*s*, 3H, H_3CO–C(3)); 4.76 (*qa*, $J = 10$, 3H, H–C(24)); 5.24 (*m*, 1H, H–C(11)). – HR.-MS.: 516.4193 (M^+, $C_{33}H_{56}O_4$, Calc. 516.4178).

$C_{33}H_{56}O_4$ (516.42) Calc. C 76.69 H 10.92% Found C 76.85 H 10.80%

Synthesis of diacetate **9**. Compound **7** (50 mg) was treated with 2 ml of pyridine/acetic anhydride 1:1 for 10 h at 100°. The mixture was cooled to RT., poured into ice-water and extracted with methylene chloride. The extract was washed once with 5% aqueous hydrochloric acid, and twice with water, and was dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded a brown solid residue which was chromatographed on 5 g of silica gel (*Woelm*, activity III). Elution with methylene chloride/methanol 99:1 provided 42 mg (71%) of white crystalline product. Recrystallization from hexane provided an analytical sample of *(24S)-3β-methoxy-5α-lanost-9(11)-ene-24,25-diol-24,25-diacetate* (**9**), m.p. 162–165°, $[\alpha]_D^{23} = +73°$ ($c = 0.4$, $CHCl_3$). – IR. (KBr): 1740, 1260, 1230 (OAc); 1105 (C–O–C). – ^{1}H-NMR.: 1.95 (*s*, 3 H, AcO–C(25)); 2.06 (*s*, 3 H, AcO–C(24)); 2.66 (*m*, 1 H, H–C(3)); 3.36 (*s*, 3 H, H_3CO–C(3)); 5.12 (*qa*, $J = 10$, 3, 1 H, H–C(24)); 5.25 (*m*, 1 H, H–C(11)). – MS.: 558 (7, M^+), 543 (6), 511 (6), 498 (100), 486 (17), 483 (44), 456 (16), 455 (14), 451 (10), 441 (10), 439 (47), 438 (20), 423 (9), 409 (10), 407 (6), 391 (6), 367 (5), 344 (7), 329 (6), 328 (17), 327 (60), 287 (8), 285 (6), 260 (6), 255 (7), 241 (6), 229 (6), 227 (6), 215 (8), 213 (6), 201 (9), 199 (6), 189 (12), 187 (13), 175 (22), 173 (21), 163 (7), 161 (18), 159 (19), 147 (19), 145 (20), 141 (10), 135 (33), 133 (24), 127 (10), 125 (11), 123 (17), 121 (35), 119 (36), 111 (7), 109 (37), 107 (35), 105 (27), 101 (28), 99 (13), 95 (52), 91 (16), 81 (25), 71 (32), 69 (42). – HR.-MS.: 558.4307 ($C_{35}H_{58}O_5$, Calc. 558.4284), 543.4112 ($C_{34}H_{55}O_5$, Calc. 543.4049), 526.4049 ($C_{34}H_{54}O_4$, Calc. 526.4021), 498.4098 ($C_{33}H_{54}O_3$, Calc. 498.4071), 483.3827 ($C_{32}H_{51}O_3$, Calc. 483.3837), 456.3881 ($C_{31}H_{52}O_2$, Calc. 456.3966), 455.3786 ($C_{31}H_{51}O_2$, Calc. 455.3888), 451.3528 ($C_{31}H_{47}O_2$, Calc. 451.3575), 441.3793 ($C_{30}H_{49}O_2$, Calc. 441.3731), 439.3967 ($C_{31}H_{51}O$, Calc. 439.3939), 438.3913 ($C_{31}H_{50}O$, Calc. 438.3860), 423.3593 ($C_{30}H_{47}O$, Calc. 423.3625), 407.3637 ($C_{30}H_{47}$, Calc. 407.3677), 391.3437 ($C_{29}H_{43}$, Calc. 391.3364), 327.2660 ($C_{23}H_{35}O$, Calc. 327.2687), 295.2446 ($C_{22}H_{31}$, Calc. 295.2426), 285.2524 ($C_{21}H_{33}$, Calc. 285.2581); metastable ions at 528.4, 481.0, 470.4, 468.7, 447.9, 444.2, 429.7, 426.6, 421.2, 419.0, 418.0, 415.4, 402.7, 398.5, 393.1, 388.4, 387.0, 385.5, 379.2, 277.4, 370.5, 363.6, 361.4, 346.6, 339.0, 337.7, 316.6, 307.6, 280.2, 266.1, 252.2, 244.1, 240.9, 230.8, 226.7, 214.7, 200.7, 199.0, 186.8, 185.0, 128.6, 117.6, 91.6, 91.2, 89.2, 84.9, 84.2, 77.3, 75.4, 71.5, 68.4, 66.4, 64.0, 63.1, 58.3.

$C_{35}H_{58}O_5$ (558.43) Calc. C 75.22 H 10.46% Found C 74.82 H 10.70%

Synthesis of acetonide-d_6 (**6**) [22]. Compound **7** (50 mg) was treated with acetone-d_6 (2 ml) and perchloric acid (70%, 0.05 ml) for 24 h at RT. The crystalline precipitate was collected to provide 30 mg (55%) of **6**. The motherliquor was poured into ice-cold 3% aqueous $NaHCO_3$-solution and extracted with methylene chloride, the organic phase was washed with water and dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded 21 mg (38%) of crystalline **6**. Recrystallization from hexane provided an analytical sample of *(24S)-24,25-[$^2H_6$]isopropylidenedioxy-3β-methoxy-5α-lanost-9(11)-ene* (**6**), m.p. 191–192°, $[\alpha]_D = +81.2°$ ($c = 0.7$, $CHCl_3$). – IR. (KBr): 1215, 1050 (C–O–C–O–C). – ^{1}H-NMR.: 0.66, 0.74, 0.80, 0.97, 1.05, 1.09 (6 *s*, 3 H each, 6 CH_3); 0.90 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.25 (*d*, $J = 1$, 3 H, H_3C–C(25)); 2.65 (*m*, 1 H, H–C(3)); 3.36 (*s*, 3 H, H_3CO–C(3)); 3.62 (*t*, $J = 6$, 1 H, H–C(24)); 5.25 (*m*, 1 H, H–C(11)); irradiation (110 db) 1.25 ppm provided a net intensity increase at 3.62 ppm of 19%, H–C(3) at 2.65 ppm was used as reference. – HR.-MS.: 520.4774 ($C_{34}H_{52}O_3D_6$, Calc. 520.4763).

$C_{34}H_{52}O_3D_6$ (520.43) (determined as $C_{34}H_{58}O_3$) Calc. C 78.40 H 11.15% Found C 78.19 H 11.08%

Compound II: (24S)-5α-lanost-9(11)-ene-3β,24,25-triol (**10**). The isolated material was recrystallized from acetone/methanol to provide an analytical sample of **10**, m.p. 214–215°, $[\alpha]_D^{22} = +56°$ ($c = 1$, $CHCl_3$). – IR. (KBr): 3425, 1140 (OH); 1635, 790 (C=CH). – IR. (CCl_4): 3707, 3628 (eq. sec. OH); 3584, 3371 (H-bonded OH). – ^{1}H-NMR.: 0.64, 0.73, 0.80, 0.97, 1.03, 1.14 and 1.19 (7 *s*, 3 H each, 7 CH_3); 0.90 (*d*, $J = 6$, 3 H, H_3C–C(20)); 3.23 and 3.33 (2 *m*, 1 H each, H–C(3) and H–C(24)); 5.24 (*m*, 1 H, H–C(11)). – LR.-MS.: 460 (14, M^+), 445 (8), 442 (24), 427 (48), 424 (7), 409 (35), 315 (7), 313 (22), 297 (5), 287 (5), 273 (14), 255 (6), 247 (7), 245 (5), 241 (5), 229 (6), 227 (6), 221 (5), 215 (7), 213 (6), 203 (8), 201 (8), 191 (6), 189 (16), 187 (14), 185 (6), 177 (6), 175 (20), 173 (17), 171 (7), 163 (8), 159 (21), 149 (14), 147 (20), 145 (20), 143 (9), 135 (32), 133 (28), 131 (14), 127 (19), 125 (6), 123 (20), 121 (38), 120 (13), 119 (42), 111 (6), 111 (13), 109 (37), 107 (38), 105 (34), 95 (62), 94 (42), 93 (28), 91 (22), 85 (14), 83 (21), 81 (41), 79 (20), 71 (46), 69 (60), 67 (28), 59 (100). – HR.-MS.: 460.3932 ($C_{30}H_{52}O_3$, Calc. 460.3916); metastable ions at 430.6, 424.8, 412.5, 391.8, 375.8, 373.7, 363.9,

351.8, 349.9, 326.7, 278.0, 258.7, 254.2, 253.2, 252.2, 240.1, 238.3, 224.2, 213.3, 212.4, 210.4, 198.5, 186.6, 174.7, 172.6, 93.6, 89.2 and 77.2.

$C_{30}H_{52}O_3$ (460.40) Calc. C 78.20 H 11.38% Found C 78.05 H 11.38%

Hydrogenation of **10**. A solution of **10** (145 mg) in glacial acetic acid (50 ml) was hydrogenated over *Adam*'s catalyst (100 mg) at RT. and atmospheric pressure for 50 h. One mol-equiv. of H_2 was taken up. The catalyst was removed by filtration and the solvent removed *in vacuo*. The solid white residue (146 mg, 100%) was recrystallized from chloroform to provide an analytical sample of *(24S)-5α-lanostane-3β,24,25-triol* (**14**), m.p. 211–212°, $[\alpha]_D^{22} = +11.7°$ ($c = 0.5$, $CHCl_3$). – IR. (KBr): 3400 (OH). – ^{1}H-NMR. ($CDCl_3$): 3.20 and 3.33 (2 *m*, 1 H each, H–C(3) and H–C(24)). – HR.-MS.: 462.4105 (M^+, $C_{30}H_{54}O_3$, Calc. 462.4072).

$C_{30}H_{54}O_3$ (462.41) Calc. C 77.86 H 11.76% Found C 77.66 H 11.87%

Oxidative cleavage of **14** *to* **15**. A solution of **14** (20 mg) in *t*-butyl alcohol (5 ml) was treated with an aqueous solution (5 ml) of sodium metaperiodate (85 mg), potassium carbonate (21 mg) and potassium permanganate (2.5 mg). The mixture was stirred for 4 h at RT. after which water (10 ml) was added to dissolve a small amount of white precipitate. Using a vacuum line, part of the volatile fraction was removed at RT. and treated as above (s. **2**→**3**) to give 0.6 mg of 2,4-dinitrophenylhydrazone of acetone. The original solution was acidified with acetic acid and a fine white precipitate was obtained. The latter was collected by centrifugation, washed twice with water and dried *in vacuo* to yield 15 mg (83%) of a white amorphous material. Recrystallization from methanol afforded an analytical sample of *3β-hydroxy-25,26,27-trinor-5α-lanostan-24-oic acid* (**15**), m.p. 268–270°. – IR. (KBr): 1720 (COOH); 3430 br. (OH). – HR.-MS.: 418.3445 (M^+, $C_{27}H_{46}O_3$, Calc. 418.3446). Because of its polar character **15** was not further investigated but converted to the corresponding methyl ester.

Methyl ester **16** *from* **15**. A solution of **15** (30 mg) in a mixture of anhydrous methanol (45 ml) and conc. sulfuric acid (0.3 ml) was stirred for 20 h at RT. The solution was concentrated *in vacuo* at RT. to about 10 ml, diluted with 5% aqueous $NaHCO_3$-solution (10 ml) and extracted with methylene chloride. The organic phase was dried over anhydrous Na_2SO_4 and the solvent evaporated *in vacuo* to provide 31 mg (99%) of a white solid. Recrystallization from petroleum ether (30–60°) provided an analytical sample of *methyl 3β-hydroxy-25,26,27-trinor-5α-lanostan-24-oate* (**16**), m.p. 177.5–179°, $[\alpha]_D^{22} = +25°$ ($c = 0.4$, $CHCl_3$). – IR. (KBr): 1750, 1180 ($COOCH_3$); 3570 (OH). – ^{1}H-NMR.: 3.21 (*m*, 1 H, H–C(3)); 3.62 (*s*, 3 H, $COOCH_3$). – HR.-MS.: 432.3574 (M^+, $C_{28}H_{48}O_3$, Calc. 432.3602).

$C_{28}H_{48}O_3$ (432.36) Calc. C 77.73 H 11.18% Found C 77.45 H 10.99%

This material was compared and shown to be identical in every respect (mixed m.p. 177–179°), $[\alpha]_D$; TLC. on silica gel G with CH_2Cl_2/CH_3OH 95:5 ($SbCl_3$, 5 min at 100°), IR., ^{1}H-NMR. and MS.) to an authentic sample [17] of **16**.

Methylation of **16** *to* **5**. – a) A solution of **16** (6 mg) in dry toluene (2 ml) was treated with potassium metal (100 mg) and the mixture was heated to reflux under N_2 and vigorous stirring for 1 h to disperse the molten potassium. The mixture was cooled to RT. and methyl iodide (1 ml) was added. Heating was resumed for 2 h at 100° after which the mixture was cooled in ice and the excess of potassium destroyed by the addition of methanol. Methylene chloride (5 ml) was added, the solution was filtered and the filtrate evaporated to dryness. The residue was taken up in methylene chloride/methanol 4:1 (5 ml), washed once with water and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent yielded an oily residue which was separated by TLC. using silica gel G and petroleum ether (30–60)/ethyl acetate 9:1. Elution with methylene chloride/methanol 4:1 afforded 1.5 mg (25%) of **5**. The aqueous phase was acidified with dilute hydrochloric acid, and a small amount of white precipitate was collected. The latter was dissolved in methylene chloride/methanol 1:1 (5 ml) and treated with an excess of an ethereal diazomethane solution at RT. Evaporation of the solvent yielded 1.5 mg (25%) of **5**.

b) A solution of **16** (10 mg) in dry methylene chloride (0.5 ml) was treated with a solution (0.01 ml) of fluoboric acid (50%, 0.2 ml) in ethyl ether/methylene chloride 3:1 (25 ml). This solution

was cooled to 0° and treated with an ethereal solution (2 ml) of diazomethane (50 mg) which was added in small portions within 30 min. Methylene chloride was added, the solution was filtered and evaporated to dryness to yield 10 mg of **5**. Recrystallization from methylene chloride/methanol gave an analytical sample (7 mg), m.p. 174–176°, $[\alpha]_D^{23} = +39.5°$ ($c = 0.2$, $CHCl_3$). This material was compared to a sample of **5** (from **4**) which had also been recrystallized from the same solvent, m.p. 173–175.5°; a mixed m.p. of 173–175.5° was obtained. Both compounds were identical in every respect ($[\alpha]_D$, IR., ^{1}H-NMR., MS.).

Synthesis of acetonide-d_6 (**13**). A mixture of **10** (20 mg) in acetone-d_6 (1 ml) and perchloric acid 70% (0.05 ml) was stirred for 15 h at RT. The crystalline precipitate was collected, washed with acetone and dried to provide 13 mg (59%) of **13**. The filtrate was poured into ice-cold 3% aqueous $NaHCO_3$-solution (20 ml) and extracted with methylene chloride. The extract was washed with water, dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to yield 10 mg (45%) of **13**. Recrystallization from hexane provided an analytical sample of *(24S)-24,25-[$^2H_6$]isopropylidinedioxy-5α-lanost-9(11)-en-3β-ol* (**13**), m.p. 189–190°, $[\alpha]_D^{22} = +68.3°$ ($c = 0.3$, $CHCl_3$). – IR. (KBr): 1220, 1085 (C–O–C–O–C). – ^{1}H-NMR.: 0.64, 0.73, 0.80, 0.97, 1.03 and 1.08 (6 *s*, 3 H each, 6 CH_3); 1.23 (*d*, $J = 1$, 3 H, H_3C–C(25)); 0.90 (*d*, $J = 6$, 3 H, H_3C–C(20)); 3.22 (*m*, 1 H, H–C(3)); 3.60 (br. *t*, $J = 6$, 1 H, H–C(24)); 5.25 (*m*, 1 H, H–C(11)); irradiation (110 db) at 1.23 ppm provided a net intensity increase at 3.60 ppm of 24% (H–C(3) at 3.22 ppm was used as a reference). – HR.-MS.: 506.4643 (M^+, $C_{33}H_{50}O_3D_6$ requires 506.4605).

$C_{33}H_{50}O_3D_6$ (506.46) (determined as $C_{33}H_{56}O_3$) Calc. C 78.20 H 11.06% Found C 78.16 H 10.80%

Synthesis of diacetate **11** *and triacetate* **12**. A solution of **10** (300 mg) in 5 ml of pyridine/acetic anhydride 1:1 was kept at RT. for 48 h. The mixture was poured onto ice and extracted with methylene chloride. The extract was washed consecutively with dilute hydrochloric acid, water and 5% $NaHCO_3$-solution. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to yield 340 mg of crude material. This mixture was chromatographed on silica gel (*Woelm*, activity III, 15 g). Elution with benzene/ethyl ether 9:1 yielded first *(24S)-5α-lanost-9(11)-ene-3β,24,25-triol-3β,24,25-triacetate* (**12**) (5 mg), followed by **11** (115 mg). Recrystallization of **12** from methanol/methylene chloride afforded white needles, m.p. 208–210°. – IR. (KBr): 1740, 1240 (OAc), 1635, 790 (C=CH). – ^{1}H-NMR.: 0.65, 0.74, 0.88, 0.89 and 1.07 (5 *s*, 3 H each, 5 CH_3); 1.45 and 1.48 (2 *s*, 3 H each, 2 H_3C–C(25)); 1.95, 2.05 and 2.08 (3 *s*, 3 H each, 3 AcO); 4.50 (br. *m*, 1 H, H–C(3)); 5.04 (br. *m*, 1 H, H–C(24)); 5.23 (*m*, H–C(11)). – LR.-MS.: 586 (1, M^+), 527 (15), 526 (36), 511 (17), 484 (7), 483 (7), 469 (7), 468 (12), 467 (35), 466 (21), 453 (6), 451 (21), 424 (5), 423 (5), 410 (6), 409 (19), 407 (11), 392 (7), 391 (23), 357 (6), 356 (27), 355 (100), 309 (7), 301 (6), 297 (9), 295 (21), 288 (5), 285 (5), 283 (5), 281 (7), 271 (5), 269 (8), 257 (6), 255 (17), 253 (7), 243 (6), 241 (14), 239 (9), 229 (14), 227 (15), 225 (6), 215 (19), 213 (16), 211 (6), 203 (13), 201 (16), 199 (14), 189 (22), 175 (31), 173 (45), 161 (34), 145 (37), 135 (45), 131 (27), 123 (28), 121 (55), 109 (68), 107 (62), 105 (55), 95 (78), 81 (67), 71 (26), 69 (81). – HR.-MS.: 586.4223 ($C_{36}H_{58}O_6$, Calc. 586.4233); metastable ions at 454.6, 446.0, 436.4, 430.0, 415.7, 414.5, 413.0, 399.7, 398.6, 383.3, 373.9, 370.5, 355.0, 339.1, 327.1, 313.0, 299.4, 270.6, 258.8, 252.6, 254.3, 241.4, 240.6, 239.8, 238.6, 225.5, 202.6, 199.2, 114.6, 101.3, 91.2, 89.2, 89.0 and 77.2.

Recrystallization of *(24S)-5α-lanost-9(11)-ene-3β,24,25-triol-3β,24-diacetate* (**11**) from methanol/methylene chloride yielded colourless long needles, m.p. 210–211°, $[\alpha]_D^{22} = +83°$ ($c = 1$, $CHCl_3$). – IR. (CCl_4): 3609 (tert. OH). – IR. (KBr): 3460, 1035 (OH); 1740, 1250 (OAc); 1640, 790 (C=CH). – ^{1}H-NMR.: 0.65, 0.75, 0.90, 0.90 and 1.10 (5 *s*, 3 H each, 5 CH_3); 1.21 (*s*, 6 H, 2 H_3C–C(25)); 2.07 and 2.12 (2 *s*, 3 H each, 2 AcO); 4.52 (br. *m*, 1 H, H–C(3)); 4.73 (br. *m*, 1 H, H–C(24)); 5.3 (*m*, 1 H, H–C(11)). – HR.-MS.: 544.4112 (M^+, $C_{34}H_{56}O_5$, Calc. 544.4127).

$C_{34}H_{56}O_5$ (544.41) Calc. C 74.96 H 10.36% Found C 75.25 H 9.89%

Compound III, 3β-methoxy-5α-lanost-9(11)-en-24-one (**18**). The isolated material was recrystallized from methylene chloride/hexane to afford an analytical sample, m.p. 161–162°, $[\alpha]_D^{20} = +93°$ ($c = 1.0$, $CHCl_3$). – IR. (KBr): 1710 (C=O); 1630 (C=CH); 110 (C–O–C). – ^{1}H-NMR.: 0.64, 0.75, 0.82, 0.97 and 1.06 (5 *s*, 3 H each, 5 CH_3); 0.88 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.09 (*d*, $J = 7$, 6 H, 2 H_3C–C(25)); 2.31–2.78 (overlapping *m*, 2 H, H–C(25) and H–C(3)); 3.37 (*s*, 3 H, H_3CO–C(3)); 5.23 (*m*, 1 H,

H–C(11)). – LR.-MS.: 456 (67, M^+), 442 (29), 441 (76), 410 (25), 409 (74), 381 (27), 327 (6), 302 (9), 297 (5), 288 (8), 287 (17), 273 (8), 271 (8), 259 (5), 255 (11), 241 (6), 229 (6), 227 (10), 215 (9), 213 (8), 207 (5), 203 (10), 201 (11), 199 (6), 189 (19), 187 (19), 185 (6), 175 (30), 173 (19), 171 (8), 167 (6), 163 (7), 161 (21), 159 (23), 157 (8), 153 (7), 149 (7), 147 (20), 145 (20), 141 (15), 136 (12), 135 (37), 133 (29), 131 (15), 129 (6), 128 (6), 127 (30), 125 (14), 121 (38), 119 (39), 117 (7), 113 (5), 109 (30), 107 (35), 105 (33), 99 (17), 95 (50), 94 (35), 93 (30), 91 (21), 87 (8), 86 (7), 85 (16), 83 (18), 81 (35), 79 (19), 72 (5), 71 (79), 69 (62), 67 (25), 57 (16), 55 (65), 43 (100). – HR.-MS.: 456.3995 ($C_{31}H_{52}O_2$, Calc. 456.3966); 441.3785 ($C_{30}H_{49}O_2$, Calc. 441.3731), 413.3400 ($C_{28}H_{45}O_2$, Calc. 413.3419), 302.2652 ($C_{21}H_{34}O$, Calc. 302.2608), 288.2401 ($C_{20}H_{32}O$, Calc. 288.2453), 153.1271 ($C_{10}H_{17}O$, Calc. 153.1279), 113.0979 ($C_7H_{13}O$, Calc. 113.0966), 85.0681 (C_5H_9O, Calc. 85.0653), 71.0520 (C_4H_7O, Calc. 71.0496), 71.0847 (C_5H_{11}, Calc. 71.0860): metastable ions at 426.5, 394.5, 379.3, 378.0, 373.9, 361.5, 346.9, 346.3, 342.4, 318.7, 308.0, 293.7, 266.6, 266.3, 254.2, 252.2, 241.8, 230.8, 228.7, 226.5, 212.6, 200.6, 198.6, 186.6, 173.4, 172.8, 172.6, 166.8, 160.8, 103.0, 89.0 and 77.2.

$C_{31}H_{52}O_2$ (456.40) Calc. C 81.52 H 11.48% Found C 81.68 H 11.57%

Compound IV, (24S)-3β-methoxy-5α-lanosta-9(11), 25-dien-24-ol (**22**). The material obtained from the chromatographic separation was recrystallized from methylene chloride/hexane to yield an analytical sample of **22**, m.p. 180–180.5, $[\alpha]_D^{25} = +86°$ ($c = 0.85$, $CHCl_3$). – IR. (CCl_4): 3615 (allylic sec. OH). – IR. (KBr): 3490 (OH); 1652, 900 (C=CH_2); 1635, 795 (C=CH). – ^{1}H-NMR.: 0.63, 0.72, 0.78, 0.94 and 1.03 (5 *s*, 3 H each, 5 CH_3); 0.89 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.70 (*d*, $J = 1$, 3 H, H_3C–C(25)); 2.62 (br. *m*, 1 H, H_{ax}–C(3)); 3.33 (*s*, 3 H, H_3CO_{eq}–C(3)); 3.99 (br. *t*, $J = 6$, 1 H, H–C(24)); 4.81 (*qa*, $J = 1$, 1 H, H–C(26)); 4.89 (*s*, 1 H, H–C(26)); 5.19 (*m*, 1 H, H–C(11)). – LR.-MS.: 456 (40, M^+), 441 (24), 438 (9), 423 (13), 409 (17), 391 (17), 327 (22), 255 (6), 229 (5), 215 (6), 213 (5), 201 (6), 189 (7), 187 (7), 175 (10), 173 (12), 161 (9), 159 (12), 149 (7), 147 (10), 145 (10), 135 (14), 133 (12), 131 (7), 125 (8), 123 (8), 121 (16), 119 (16), 109 (19), 107 (17), 105 (14), 95 (21), 93 (14), 91 (6), 83 (8), 81 (16), 71 (100), 69 (25), 67 (12) and 55 (19). – HR.-MS.: 456.3930 ($C_{31}H_{52}O_2$, Calc. 456.3966), 327.2689 ($C_{23}H_{35}O$, Calc. 327.2687), 125.0954 ($C_8H_{13}O$, Calc. 125.0966), 109.1005 (C_8H_{13}, Calc. 109.1017); metastable ions at 426.5, 407.6, 406.8, 394.1, 380.5, 379.6, 379.3, 374.7, 373.8, 361.8, 346.6, 317.5, 283.8, 266.2, 241.0, 224.5, 186.3, 184.7, 180.8, 127.3, 89.1 and 77.2.

$C_{31}H_{52}O_2$ (456.40) Calc. C 81.52 H 11.48% Found C 81.62 H 11.31%

Synthesis of (24S)-3β-methoxy-5α-lanosta-9(11),25-dien-24-ol acetate (**19**). The motherliquor from compound IV recrystallization was evaporated and the residue treated for 5 h at RT. with a mixture of acetic anhydride/pyridine, 1:1 and worked up in the usual fashion. Chromatography on silica gel with benzene provided **19**. Recrystallization from methylene chloride/hexane provided an analytical sample, m.p. 167–169°, $[\alpha]_D^{20} = +85°$ ($c = 1.0$, $CHCl_3$). – IR. (KBr): 1748, 1242 (OAc); 1630, 790 (C=CH); 1650, 898 (C=CH_2); 1100 (C–O–C). – ^{1}H-NMR.: 0.63, 0.72, 0.78, 0.95 and 1.03 (5 *s*, 3 H each, 5 CH_3); 0.87 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.70 (*d*, $J = 1$, 3 H, H_3C–C(25)); 2.02 (*s*, 3 H, AcO–C(24)); 2.63 (*m*, 1 H, H–C(3)); 3.34 (*s*, 3 H, H_3CO–C(3)); 4.88 (*qa*, $J = 1$, 1 H, H–C(26)); 4.93 (*s*, 1 H, H–C(26)); 5.12 (*t*, $J = 6$, 1 H, H–C(24)); 5.21 (*m*, 1 H, H–C(11)). – LR.-MS.: 498 (9, M^+), 483 (9), 451 (11), 438 (31), 423 (26), 391 (26), 328 (40), 327 (82), 123 (17), 110 (5), 109 (46) and 107 (38). – HR.-MS.: 499.4136 ($C_{33}H_{54}O_3$, Calc. 499.4150).

$C_{33}H_{54}O_3$ (499.42) Calc. C 79.46 H 10.91% Found C 79.79 H 11.19%

Hydrogenation of **19** *to* **20**. A solution of **19** (50 mg) in 1,2-dimethoxyethane (10 ml) was hydrogenated over 10% Pd/C (10 mg) at RT. and atmospheric pressure for a period of 0.5 h. One mol-equiv. of H_2 was taken up. The catalyst was removed by filtration and evaporation of the solvent yielded a crystalline residue (50 mg, 99%). Recrystallization from methylene chloride/methanol gave an analytical sample of *(24S)-3β-methoxy-5α-lanostan-24-ol* (**20**), m.p. 184–185°, $[\alpha]_D^{20} = +91°$ ($c = 1$, $CHCl_3$). – IR. (KBr): 1740, 1245 (OAc); 1635, 815 (C=CH); 1105 (C–O–C). – ^{1}H-NMR.: 0.64, 0.73, 0.79, 0.96 and 1.04 (5 *s*, 3 H each, 5 CH_3); 0.88 (*d*, $J = 6$, 9 H, H_3C–C(20) and 2 H_3C–C(25)); 2.02 (*s*, 3 H, AcO–C(24)); 2.63 (*m*, 1 H, H–C(3)); 3.35 (*s*, 3 H, H_3CO–C(3)); 4.70 (*m*, 1 H, H–C(24)); 5.24 (*m*, 1 H, H–C(11)). – HR.-MS.: 500.4216 (M^+, $C_{33}H_{56}O_3$, Calc. 500.4228).

$C_{33}H_{56}O_3$ (500.42) Calc. C 79.20 H 11.20% Found C 78.80 H 11.52%

Synthesis of **21**. A solution of **20** (40 mg) in benzene (5 ml) was treated with 2N methanolic NaOH (10 ml) for 40 h at RT. The mixture was treated with ice-cold water (10 ml) and extracted with benzene. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to yield 33 mg (90%) of solid (**21**), recrystallization from methylene chloride/methanol afforded an analytical sample of *(24S)-3β-methoxy-5α-lanosta-9(11)-en-24-ol* (**21**), m.p. 161.5–163°, $[\alpha]_D^{20} = +81°$ ($c = 1$, $CHCl_3$). – IR. (CCl_4): 3632 (sec. OH). – IR. (KBr): 1635, 815 (C=CH); 1100 (C–O–C). – ^{1}H-NMR.: 0.68, 0.77, 0.82, 0.99 and 1.07 (5 *s*, 2 H each, 5 CH_3); 0.90 and 0.95 (2 *d*, overlapping, 3 H, 6 H, 3 H–C(20) and 2 H_3C–C(25)); 2.69 (*m*, 1 H, H–C(3)); 3.36 (*m*, 1 H, H–C(24)); 3.39 (*s*, 3 H, H_3CO–C(3)); 5.28 (*m*, 1 H, H–C(11)). – HR.-MS.: 458.4056 (M^+, $C_{31}H_{54}O_2$, Calc. 458.4123).

$C_{31}H_{54}O_2$ (458.41) Calc. C 81.23 H 11.79% Found C 81.03 H 12.06%

Synthesis of 3β-methoxy-5α-lanost-9(11)-en-24-one (**18**). Compound **21** (20 mg) in acetone (10 ml) was treated with *Kiliani* reagent (0.1 ml, 0.6 g sodium dichromate dihydrate in 0.8 g conc. sulfuric acid and 2.7 ml water) at 0° and under N_2. After the reaction mixture had turned a yellow red colour, methanol was added and the mixture extracted with benzene to yield 20 mg of solid. Chromatography on silica gel (*Woelm*, activity III, benzene) and recrystallization from hexane provided an analytical sample which was identical in every respect (m.p., undepressed mix. m.p., $[\alpha]_D$, IR., ^{1}H-NMR.) with the natural compound III.

Synthesis of **19** *from* **8**. To a solution of **8** (900 mg) in pyridine (70 ml), phosphorus oxychloride (15 ml) was added dropwise. The mixture was left for 40 h at RT. and poured into ice water. Extraction with benzene yielded 810 mg (98%) of **19**. Recrystallization from methylene chloride/hexane provided an analytical sample. This material was identical in every respect (m.p., undepressed mix. m.p., $[\alpha]_D$, IR.,^{1}H-NMR.) with the acetate obtained from compound IV.

Compound V, 5α-lanosta-9(11),25-diene-3α,24-diol (**24**). The material eluted from the chromatography column was recrystallized from methylene chloride/hexane to provide an analytical sample, m.p. 181–184°. – IR. (CCl_4): 3631 (sec. ax. OH); 3619 (sec. OH, allylic). – IR. (KBr): 3620 (OH); 3100, 910, 840 (C=CH_2); 1650, 820 (C=CH). – ^{1}H-NMR. ($CDCl_3$): 0.66, 0.76, 0.82, 0.96 and 1.07 (5 *s*, 3 H each, 5 CH_3); 0.91 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.72 (br. *s*, 3 H, H_3C–C(25)); 3.42 (*m*, 1 H, H–C(3)); 4.02 (br. *t*, $J = 6$, 1 H, H–C(24)); 4.84 (*m*, 1 H, H–C(26)); 4.93 (*m*, 1 H, H–C(26)); 5.26 (*m*, 1 H, H–C(11)). – MS.: 442 (26, M^+), 427 (20), 424 (10), 413 (15), 409 (72), 407 (8), 393 (14), 391 (18), 374 (10), 341 (5), 323 (6), 313 (38), 297 (5), 295 (5), 273 (9), 271 (6), 269 (5), 259 (5), 257 (6), 255 (14), 247 (6), 245 (5), 241 (10), 229 (10), 227 (9), 217 (5), 215 (12), 213 (11), 203 (11), 201 (11), 199 (7), 191 (6), 189 (19), 187 (19), 185 (8), 175 (32), 173 (24), 163 (13), 161 (24), 159 (24), 157 (9), 149 (19), 147 (24), 145 (23), 137 (12), 135 (37), 133 (30), 131 (17), 127 (7), 125 (12), 123 (21), 122 (10), 121 (45), 119 (46), 109 (57), 107 (47), 105 (39), 97 (14), 95 (66), 93 (41), 91 (28), 83 (23), 81 (52), 79 (26), 77 (11), 71 (47), 69 (77), 67 (35), 57 (26), 55 (87) and 43 (100). – HR.-MS.: 442.3813 (M^+, $C_{30}H_{50}O_2$, Calc. 442.3810).

Synthesis of 5α-lanosta-9(11),25-diene-3α,24-diol-3α,24-diacetate (**25**). Compound V (**24**) (25 mg) was treated with acetic anhydride (1 ml) and pyridine (1 ml) over a period of 20 h at RT. The mixture was poured into ice-water and extracted with methylene chloride to provide a crude product which was chromatographed on silica gel (5 g, *Woelm*, neutral, activity III). Benzene eluted 10 mg (33%) of **25** which was recrystallized from methylene chloride/methanol to provide an analytical sample, m.p. 139–140°. – IR. (KBr): 1740 (OAc); 1652 (C=C); 1250 (C–O). – ^{1}H-NMR.: 0.60, 0.72, 0.81, 0.88 and 1.02 (5 *s*, 3 H each, 5 CH_3); 1.67 (br. *s*, 3 H, H_3C–C(25)); 2.00 (*s*, 6 H, 2 AcO); 4.61 (*m*, 1 H, H–C(3)); 4.83 (*m*, 1 H, H–C(26)); 4.89 (*m*, 1 H, H–C(26)); 4.97-5.35 (*m*, 2 H, H–C(11) and H–C(24)). – HR.-MS.: 526.3980 (M^+, $C_{34}H_{54}O_4$, Calc. 526.4021).

Synthesis of (24S)-5α-lanosta-9(11),25-diene-3β,24-diol-3α,24-diacetate (**23**). Compound **11** (20 mg) in pyridine (5 ml) was treated with phosphorus oxychloride (0.5 ml) and kept for 40 h at RT. The mixture was poured into ice-water and extracted with benzene to provide 19.1 mg (99%) of crystalline material. Recrystallization from methylene chloride/methanol provided an analytical sample, m.p. 217–218°, $[\alpha]_D^{20} = +38°$ ($c = 1$, $CHCl_3$). – IR. (KBr): 3050 (C=CH_2); 1745 (OAc); 1655 (=C); 1245 (C–O). – ^{1}H-NMR.: 0.63, 0.72, 0.85, 0.88 and 1.06 (5 *s*, 3 H each, 5 CH_3); 0.88 (*d*, $J = 6$, H_3C–C(20)); 1.70 (br. *s*, 3 H, H_3C–C(25)); 2.01 (*s*, 6 H, 2 AcO); 4.44 (*m*, 1 H, H–C(3)); 4.88 (*m*, 1 H, H–C(26)); 4.94 (*m*, 1 H, H–C(26)); 5.03–5.29 (*m*, 2 H, H–C(11) and H–C(24)). – HR.-MS.: 526.4046 (M^+, $C_{34}H_{54}O_4$, Calc. 526.4021).

$C_{34}H_{54}O_4$ (526.40) Calc. C 77.52 H 10.33% Found C 77.45 H 10.39%

3β-Methoxy-5α-lanost-9(11)-ene-22(or 23),25-diol (**26**). The isolated material was recrystallized from methylene chloride/hexane to yield an analytical sample, m.p. 204–205°, $[\alpha]_D^{20} = +92°$ ($c = 0.9$, $CHCl_3$). – IR. (CCl_4): 3607 (tert. OH). – IR. (KBr): 1630, 815 (C=CH); 1105 (C–O–C). – ^{1}H-NMR.: 0.65, 0.75, 0.80, 0.97 and 1.05 (5 *s*, 3 H each, 5 CH_3); 0.91 (*d*, $J = 6$, H_3C–C(20)); 1.17 (*s*, 6 H, 2 H_3C–C(25)); 2.63 (*m*, 1 H, H–C(3)); ~3.32 (*m*, 1 H); 3.37 (*s*, 3 H, H_3CO–C(3)); 5.24 (*m*, 1 H, H–C(11)). – MS.: 474 (11, M^+), 459 (11), 456 (42), 441 (52), 439 (9), 423 (38), 409 (50), 407 (7), 399 (8), 391 (8), 384 (11), 383 (28), 367 (8), 329 (9), 327 (58), 313 (6), 302 (13), 297 (14), 295 (7), 289 (9), 288 (8), 287 (16), 285 (9), 283 (7), 273 (12), 269 (7), 261 (18), 259 (8), 255 (12), 247 (6), 245 (6), 241 (14), 229 (16), 227 (16), 215 (18), 203 (21), 201 (19), 191 (22), 189 (28), 187 (57), 175 (39), 173 (32), 170 (9), 167 (10), 163 (16), 161 (37), 159 (28), 153 (7), 149 (20), 147 (25), 145 (20), 143 (11), 137 (20), 135 (57), 133 (32), 127 (38), 125 (23), 123 (36), 121 (56), 113 (8), 111 (21), 109 (64), 107 (40), 105 (40), 99 (27), 97 (18), 87 (12), 85 (30), 73 (14) and 71 (82). – HR.-MS.: 474.4079 ($C_{31}H_{54}O_3$, Calc. 474.4071), 456.3973 ($C_{31}H_{52}O_2$, Calc. 456.3966), 438.3810 ($C_{31}H_{50}O$, Calc. 438.3860), 327.2690 ($C_{23}H_{35}O$, Calc. 327.2687), 143.1068 ($C_8H_{15}O_2$, Calc. 143.1071), 127.1139 ($C_8H_{15}O$, Calc. 127.1122), 125.0937 ($C_8H_{13}O$, Calc. 125.0966), 123.0939 ($C_8H_{11}O$, Calc. 123.0820), 109.0993 (C_8H_{13}, Calc. 109.1017), 107.0847 (C_8H_{11}, Calc. 107.0860) and 105.0681 (C_8H_9, Calc. 105.0704).

Compound VII: 3β-methoxy-26,27-dinor-5α-lanost-9(11)-en-24-one (**27**). The material obtained from the chromatographic separation was recrystallized from methylene chloride/methanol to provide an analytical sample, m.p. 161–162, $[\alpha]_D^{20} = +95°$ ($c = 1.2$, $CHCl_3$). – IR. (KBr): 1725 (C=O); 1635, 815 (C=CH); 1100 (C–O–C). – ^{1}H-NMR.: 0.64, 0.74, 0.80, 0.98 and 1.04 (5 *s*, 3 H each, 5 CH_3); 0.89 (*d*, $J = 6$, 3 H, H_3C–C(20)); 2.12 (*s*, 3 H, H_3C–C(24)); 2.41 (br. *m*, 2 H, H_2C–C(24)); 2.63 (*m*, 1 H, H–C(3)); 3.35 (*s*, 3 H, H_3CO–C(3)); 5.23 (*m*, 1 H, H–C(11)). – LR.-MS.: 428 (100, M^+), 413 (83), 395 (6), 381 (65), 363 (5), 287 (6), 274 (9), 259 (8), 255 (6), 245 (6), 241 (6), 229 (5), 227 (8), 215 (8), 205 (5), 203 (7), 201 (9), 189 (17), 187 (18), 175 (28), 173 (20), 167 (6), 161 (20), 159 (22), 147 (20), 145 (20), 141 (10), 139 (7), 135 (32), 133 (28), 125 (13), 123 (16), 121 (32), 119 (35), 111 (5), 109 (27), 107 (34), 105 (31), 99 (41), 95 (49), 91 (20), 85 (13), 83 (17), 81 (28), 71 (51), 69 (46), 59 (6), 58 (37), 57 (7) and 55 (60). – HR.-MS.: 428.3608 ($C_{29}H_{48}O_2$, Calc. 428.3653), 329.2919 ($C_{23}H_{37}O$, Calc. 329.2843), 327.2679 ($C_{23}H_{35}O$, Calc. 327.2687), 99.0810 ($C_6H_{11}O$, Calc. 99.0809).

$C_{29}H_{48}O_2$ (428.37) Calc. C 81.25 H 11.29% Found C 81.15 H 11.12%

Compound VIII: (24S)-3β-methoxy-24,25-(2′-methyl-1′,3′-dioxatrimethylene)-5α-lanost-9(11)-ene (**29**). The isolated material was recrystallized from hexane/methylene chloride to provide an analytical sample, m.p. 153–155°; a sublimed sample (180°, 0.01 mm) had a m.p. 149.5–152°, $[\alpha]_D^{20} = +85°$ ($c = 0.6$, $CHCl_3$). – IR. (KBr): 1635, 815 (C=CH); 1190, 1165, 1140, 1100 (C–O–C–O–C). – ^{1}H-NMR.: 0.62, 0.71, 0.77, 0.94, 1.02, 1.08 and 1.23 (7 *s*, 3 H each, 7 CH_3); 0.87 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.31 (*d*, $J = 5$, 3 H, H_3C–C(33)); 2.62 (*m*, 1 H, H–C(3)); 3.35 (*s*, 3 H, H_3CO–C(3)); 3.47 (*m*, 1 H, H–C(24)); 5.03 (*qa*, $J = 5$, 1 H, H–C(33)); 5.25 (*m*, 1 H, H–C(11)); irradiation of the quadruplet at 5.03 ppm (107 db) caused the doublet at 1.31 ppm to collapse to a singlet. – LR.-MS.: 500 (64, M^+), 485 (36), 458 (5), 457 (26), 456 (72), 453 (14), 442 (37), 441 (100), 438 (16), 424 (5), 423 (8), 409 (73), 328 (10), 327 (34), 302 (8), 295 (5), 288 (8), 287 (8), 273 (7), 255 (6), 227 (5), 215 (5), 213 (7), 201 (5), 189 (7), 187 (6), 175 (9), 173 (10), 161 (8), 159 (10), 149 (5), 145 (8), 135 (12), 121 (15), 119 (17), 109 (14), 107 (15), 105 (14), 95 (21), 93 (13), 91 (10), 86 (16), 85 (8), 83 (8), 81 (30), 71 (46) and 69 (20). – HR.-MS.: 500.4149 ($C_{33}H_{56}O_3$, Calc. 500.4228), 485.4043 ($C_{32}H_{53}O_3$, Calc. 485.3994), 329.2836 ($C_{23}H_{37}O$, Calc. 329.2843), 327.2702 ($C_{23}H_{35}O$, Calc. 327.2687); metastable ions at 470.4, 426.9, 417.7, 415.8, 405.8, 401.6, 401.0, 394.5, 380.4, 379.4, 373.8, 369.1, 361.7, 361.2, 341.7, 337.7, 326.8, 286.5, 267.3, 266.2, 258.8, 254.4, 252.2, 234.6, 226.8, 213.8, 200.5, 172.6, 160.6, 133.2, 93.6, 91.4, 89.2, 89.0 and 77.2.

$C_{33}H_{56}O_3$ (500.42) Calc. C 79.14 H 11.27% Found C 78.41 H 11.08% (sublimed sample)

Conversion of 7 *to* **29**. Compound **7** (50 mg) in acetaldehyde (2 ml) was treated with perchloric acid, 70% (0.05 ml). The solution was kept for 1 h at RT., poured into ice-water and extracted with methylene chloride to provide 48 mg (91%) of material. Recrystallization from hexane/methanol afforded an analytical sample of **29** identical with that obtained above.

3β-Methoxy-24,25-(2′-R-1′,3′-dioxatrimethylene)-5α-lanost-9(11)-ene (R = $C_{22}H_{45}O$, **31**). The material eluted from the chromatography column was recrystallized from methylene chloride/ethanol to

yield an analytical sample of **31**, m.p. 101.5–103°, $[\alpha]_D^{20} = +48.5°$ ($c = 1.0$, $CHCl_3$). – IR. (KBr): 1635, 815 (C=CH); 1107 (C–O–C). – ^{1}H-NMR.: 0.65, 0.74, 0.79, 0.96, 1.05, 1.09 and 1.19 (7 *s*, 3 H each, 7 CH_3); 0.90 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.25 (*s*, ~40 H, hydrocarbon chain); 2.65 (*m*, 1 H, H–C(3)); 3.36 (*s*, 3 H, H_3CO–C(3)); ~3.5 (*m*, 1 H, H–C(24)); 3.73 (*m*, 1 H); 4.90 (*t*, $J = 5$, 1 H, H–C(33)); 5.24 (*m*, 1 H, H–C(11)). – LR.-MS.: 811 (2, M^+), 810 (2), 764 (5), 485 (100), 457 (18), 456 (45), 453 (25), 441 (98), 439 (10), 426 (9), 424 (12), 409 (76), 407 (11), 393 (5), 329 (5), 327 (42), 297 (7), 295 (7), 287 (9), 273 (7), 241 (6), 229 (7), 227 (6), 213 (6), 203 (8), 201 (8), 189 (12), 187 (12), 175 (17), 173 (17), 161 (14), 159 (14), 149 (11), 147 (12), 135 (20), 121 (19), 119 (16), 109 (26), 107 (15), 97 (20), 95 (33), 93 (11), 91 (8), 85 (18), 83 (24), 71 (46) and 69 (43). – HR.-MS.: 810.7459 ($C_{54}H_{98}O_4$, Calc. 810.7465), 485.3963 ($C_{32}H_{53}O_3$, Calc. 485.3994), 329.2857 ($C_{23}H_{37}O$, Calc. 329.2843), 327.2663 ($C_{23}H_{35}O$, Calc. 327.2687); metastable ions at 413.5, 366.3, 360.8, 350.6, 348.0, 320.3, 253.2, 196.9, 185.8 and 181.8.

$C_{54}H_{98}O_4$ (810.75) Calc. C 80.0 H 12.1% Found C 81.37 H 12.14%

An attempted sublimation of 2 mg material at 0.01 Torr-vacuum and 180° resulted in waxy material driven from the sample and a solid residue. The former yielded a typical low intensity hydrocarbon mass spectrum with masses up to about *m/z* 320. The solid residue exhibited a base peak and molecular ion at *m/z* 485 ($C_{32}H_{53}O_3$), the fragmentation pattern was identical with the corresponding region of the starting material.

3β-Methoxy-24,25-(2'-R-1',3'-dioxatrimethylene)-5α-lanost-9(11)-ene (R = $C_{22}H_{43}$, **33**). The isolated material was recrystallized from methylene chloride/methanol to provide an analytical sample of **31**, m.p. 91–92°, $[\alpha]_D^{20} = +39°$ ($c = 0.7$, $CHCl_3$). – IR. (CCl_4): 3627 (sec. eq. OH). – IR. (KBr): 3480 (OH); 1630, 810 (C=CH). – ^{1}H-NMR.: 0.66, 0.75, 0.82, 0.99, 1.04, 1.10 and 1.20 (7 *s*, 3 H each, 7 CH_3); 0.91 (*d*, $J = 6$, 3 H, H_3C–C(20)); 1.28 (*s*, ~40 H, hydrocarbon chain); 3.22 (*m*, 1 H, H–C(3)); 3.46 (*m*, 1 H, H–C(24)); 4.23 (*m*, 1-2 H, olefinic?); 4.92 (*t*, $J = 5$, 1 H, H–C(33)); 5.24 (*m*, 1 H, H–C(11)). – LR.-MS.: 778 (1, M^+), 764 (3), 471 (15), 453 (28), 442 (7), 425 (13), 409 (53), 407 (8), 391 (6), 381 (8), 313 (13), 297 (8), 295 (11), 273 (5), 257 (5), 255 (7), 241 (6), 229 (7), 227 (7), 215 (7), 213 (7), 201 (9), 189 (12), 187 (13), 175 (18), 173 (16), 161 (15), 159 (16), 147 (17), 145 (15), 139 (5), 135 (26), 133 (21), 131 (11), 127 (23), 123 (24), 122 (7), 121 (25). 119 (27), 111 (23), 109 (43), 107 (22), 105 (21), 97 (44), 95 (62), 91 (13), 85 (35), 83 (53), 82 (62), 81 (53), 71 (67) and 69 (71). – HR.-MS.: 777.7216 ($M - 1^+$, $C_{53}H_{93}O_3$, Calc. 777.7125), 735.6947 ($C_{50}H_{87}O_3$, Calc. 735.6654), 315.2539 ($C_{22}H_{35}O$, Calc. 315.2687), 313.2530 ($C_{22}H_{33}O$, Calc. 313.2530), 274.2329 ($C_{19}H_{30}O$, Calc. 274.2296), 273.2241 ($C_{19}H_{29}O$, Calc. 273.2218).

$C_{53}H_{94}O_3$ (778.73) Calc. C 81.3 H 12.2% Found C 81.38 H 11.96%

Compound XI (**36**). The isolated material was recrystallized from methylene chloride/methanol to provide an analytical sample of **36**, m.p. 261–261.5°, $[\alpha]_D^{20} = +91°$ ($c = 1.2$, $CHCl_3$). – IR. (KBr): 1100 (C–O–C). – ^{1}H-NMR. ($CDCl_3$): 0.66 and 0.74 (2 *s*, 6 H each, 4 CH_3); 0.80, 0.98 and 1.05 (3 *s*, 6 H each, 6 CH_3); 1.11 and 1.25 (*s*, 3 H each, 2 CH_3); 0.89 and 0.91 (*d*, $J = 6$, 3 H each, 2 H_3C–C(20)); 2.65 (*m*, 1 H, H–C(3)); 3.37 (*s*, 6 H, 2 H_3CO–C(3)); ~3.63 (*m*, 1 H, H–C(24)); 4.90 (*t*, $J = 5$, 1 H, H–C(33)); 5.25 (*m*, 2 H, 2 H–C(11)). – LR.-MS.: 872 (2, M^+), 858 (9), 826 (7), 485 (32), 457 (13), 456 (31), 453 (14), 441 (74), 439 (10), 425 (18), 414 (27), 413 (11), 409 (81), 407 (14), 399 (65), 397 (23), 383 (21), 381 (19), 367 (84), 355 (6), 349 (12), 339 (11), 329 (9), 328 (12), 327 (49), 313 (10), 297 (15), 295 (15), 288 (11), 287 (14), 285 (10), 283 (8), 273 (14), 271 (13), 269 (9), 260 (12), 259 (12), 257 (11), 255 (20), 243 (12), 242 (7), 241 (19), 239 (8), 229 (22), 227 (22), 217 (11), 215 (25), 213 (24), 203 (24), 201 (28), 199 (155), 191 (18), 189 (33), 185 (18), 177 (14), 175 (56), 173 (48), 171 (18), 167 (12), 165 (10), 163 (20), 161 (48), 159 (46), 157 (16), 149 (32), 147 (44), 145 (41), 143 (16), 141 (20), 135 (72), 133 (56), 131 (30), 127 (37), 125 (21), 121 (74), 119 (77), 117 (13), 111 (21), 109 (21), 107 (64), 105 (57), 99 (21), 97 (21), 95 (100), 93 (48), 91 (33), 86 (7), 85 (40), 83 (28), 81 (67), 79 (30), 71 (69), 69 (82) and 67 (35). – HR.-MS.: 872.7254 ($C_{58}H_{96}O_5$, Calc. 872.7257), 825.6915 ($C_{56}H_{89}O_4$, Calc. 825.6761), 485.3867 ($C_{32}H_{53}O_3$, Calc. 485.3994), 327.2660 ($C_{23}H_{35}O$, Calc. 327.2687).

$C_{58}H_{96}O_5$ (872.73) Calc. C 79.8 H 11.01% Found C 79.67 H 11.04%

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