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The Transformation of 11-Deoxojervine into 18-Functional *C*-Nor-*D*-homosteroids[1, 2]

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Deoxojervine, a *C*-nor-*D*-homosteroidal alkaloid, has been transformed into 17β-acetyl-12α-etiojervan-3β-ol acetate in 3 steps. Treatment with base gave the 17α-epimer. Reduction of the 17β-isomer with $NaBH_4$ afforded 17β-ethyl-12α-etiojervane-3β,20β-diol 3-acetate as a single product whereas reduction of the 17α-isomer afforded 17β-ethyl-12α-etiojervane-3β,20β-diol 3-acetate and the 20α isomer in an approximate 1:1 ratio. Irradiation of 17β-ethyl-12α-etiojervane-3β,20β-diol 3-acetate in cyclohexane in the presence of lead tetraacetate and iodine afforded a C-18 functional *C*-nor-*D*-homosteroid as a 18,20-epoxide which was oxidized to the corresponding γ-lactone with chromium trioxide. A mixture of the 17α-ethyl-12α-etiojervane-3β,20α-diol 3-acetate and its 20β isomer in contrast gave no 18-functional compounds upon irradiation under similar conditions.

Selective functionalization of inactive angular methyl groups by processes, which involve intramolecular free radical reactions[3] have been proven to be successful in steroids. There exists, however, no studies on the functionalization of inactive methyl groups by intramolecular radical processes in the field of *C*-nor-*D*-homosteroids. In this and subsequent papers the functionalization of the 13β-methyl group in the *C*-nor-*D*-homosteroid, derived from jerveratrum alkaloids by this process will be reported. These C-18 functional *C*-nor-*D*-homosteroids may be of value in further transformations of this important group of steroids.

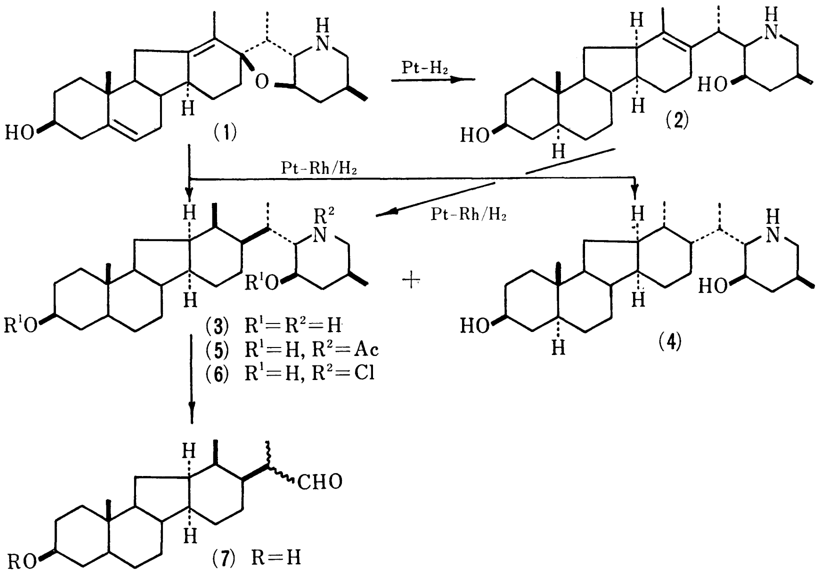
Results

Catalytic hydrogenation of tetrasubstituted double bonds in (22*S*,25*S*)-5α-veratr-13(17)-enine-3β,23β-diol (**2**), prepared by the platinum-catalyzed hydrogenation[4] of 11-deoxojervine (**1**),[5] was affected using a rhodium–platinum catalyst.[6] The perhydro derivative (**3**), mp 219—221 °C, was obtained in a 35% yield. The NMR spectrum of **3** exhibited a 3-H singlet at τ 9.20 due to the 19-H, and three 3-H doublets centered at τ 9.23 (*J*=*ca.* 6 Hz, a signal of the doublet coincided with 19-H), 9.11 (*J*=6.3 Hz) and 8.99 (*J*=6.3 Hz) due to the three secondary methyl groups. At lower field, after D_2O exchange, a broad 2-H multiplet at τ 6.47, attributable to the 3α-H and the 23-αH, a 1-H doublet at τ 7.52 (*J*=9.6) and a 1-H double doublet at τ 7.08 (*J*=12 and 4) presented themselves. Irradiation at τ 6.47 caused the doublet at τ 7.52 to collapse to a singlet and thus the doublet has been assigned to the 22β-H. The double doublet is then assignable to one of the 27-methylene protons. The stereochemistry was assumed to be (22*S*,25*S*)-5α-veratranine-3β,23β-diol (**3**) on the basis of the *cis* addition of hydrogen atoms to an isolated olefinic center from the less-hindered side of steroid molecules and confirmed by its transformation into 17β-acetyl-12α-etiojervan-3β-ol[7] (**10**) identical with a specimen derived from a *C*-nor-*D*-homosapogenin by Johns and Laos.[8] The configurations at C-12, C-13, and C-17 in the 3β-ol **10** were established by further transformations as described later in this paper.

It was subsequently found that the diol **3** could be directly obtained by the catalytic hydrogenation of 11-deoxojervine in the presence of a rhodium–platinum catalyst or a large amount of Adams' platinum catalyst in acetic acid. From the hydrogenation product using the rhodium–platinum catalyst, perhydro compound (**4**), mp 178—180 °C, isomeric with the diol **3** was isolated in a 4% yield. The NMR spectra of **4** and compound **3** were very similar exhibiting a 3-H singlet at τ 9.25 due to the 19-H, and 4 singlets due to the overlap of three doublets centered at τ 9.13 (*J*=6), 9.08 (*J*=6), and 9.00 (*J*=6) assignable to three secondary methyl groups. A broad 2-H multiplet at τ 6.47 attributable to an overlap of the 3α-H and the 23-αH, a 1-H doublet at τ 7.73 (*J*=9.9 Hz, 22-βH), and a 1-H double doublet after D_2O exchange at τ 7.03 (*J*=12 and 4, one of 27-CH_2) were also present further downfield in the spectrum. No evidence is available on the configurations at the C-13 and the C-17 centers, but the structure has been tentatively assigned as (22*S*,25*S*)-5α,13α,17α-veratranine-3β,23β-diol (**4**) resulting from *cis* addition of hydrogen atoms from a more-hindered side.

The heterocyclic ring of diol **3** was removed by the procedure devised by Frank and Johnson.[9,10] Treatment of the diol **3** in dry THF with *N*-chlorosuccinimide for 1 h in an atmosphere of nitrogen afforded a *N*-chloro derivative (**6**). This was treated *in situ* with sodium methoxide in methanol for *ca.* 24 h at 0—10 °C to afford an aldehyde (**7**), mp 109—110 °C, in a 95% yield. The NMR spectral data was in agreement with the structure assigned. The mass spectrum exhibited a base peak at *m*/*e* 274 resulting from a loss of the C-17-substituent from the molecular ion involving a McLafferty rearrangement of a γ-hydrogen.

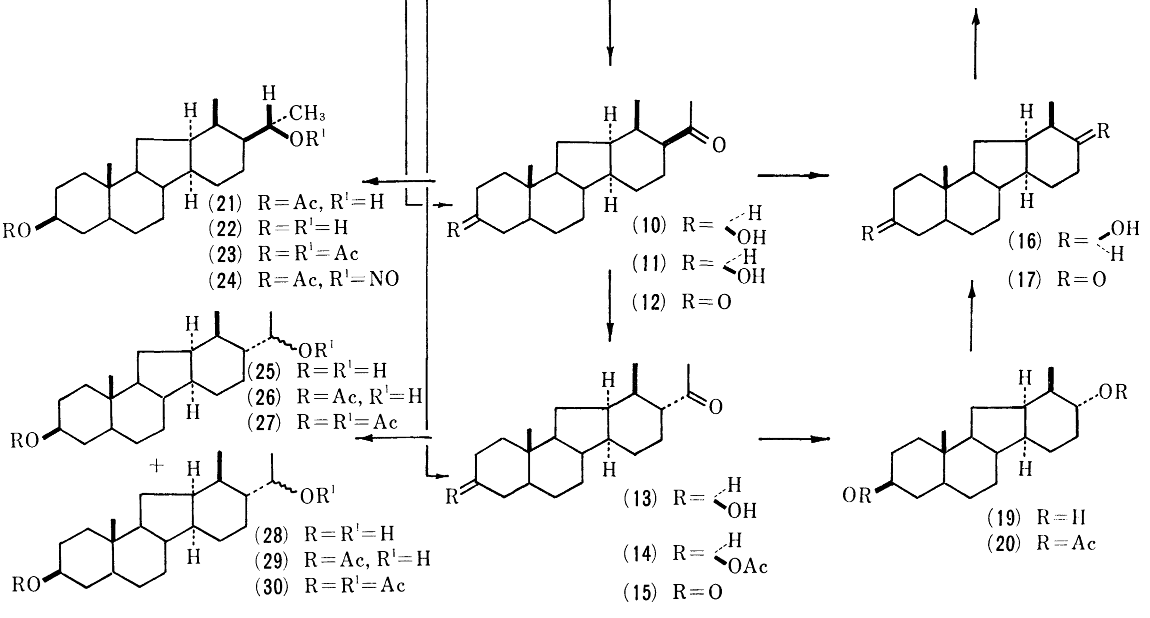
Treatment of the aldehyde **7** in THF with butyl nitrite in the presence of sodium methoxide afforded a ketone (**10**), mp 150—152 °C, in a 90% yield. Upon acetylation and oxidation with Jones reagent the 3-acetate (**11**), mp 116—118 °C, and a 3-one (**12**); mp 158—160 °C, were formed. The ketone **10** and acetate **11** were identical with the specimens[8] kindly provided by Dr. Johns. The corresponding oxime (**9**), mp 106—109 °C, which is characteristically obtained as the product in this reaction,[9] was isolated in only one experiment. Hydrolysis of the oxime with aq ethanolic HCl under reflux, however, gave an isomeric ketone which was identical with the ketone (**13**) obtained by treatment of the ketone **10** with base. It is assumed



Scheme 1.

to be epimeric with the ketone **10** at the C-17.

The configurations at C-12 and C-13 in methyl ketone **10** have been established by Johns and Laos by transformation into 12α-etiojervane-3,17-dione (**17**) by Baeyer-villiger oxidation, followed by hydrolysis and oxidation with Jones' reagent. Repetition of these experiments afforded a diol (**16**)[11] and a dione (**17**) which were identical with the specimens prepared by Johns and Laos from a *C*-nor-*D*-homosapogenin, by direct comparison. As described by Johns and Laos,[8] treatment of the dione **17** with methanolic 5% KOH for 1 h under reflux resulted in partial epimerization at C-13 and afforded an equilibrium mixture of 12α-etiojervane-3,20-dione **17** and 12α,13α-dione (**18**). Recrystallization of this mixture from aq acetone afforded a pure dione **18**, mp 136—140 °C, identical with a specimen obtained from *C*-nor-*D*-homosapogenin by Johns and Laos.[8] The configurations at the C-17



Scheme 2.

centers of methyl ketone **10** and consequently the diol **3**, and the aldehyde **7**, were confirmed as *β* on the basis of the following epimerization experiments.

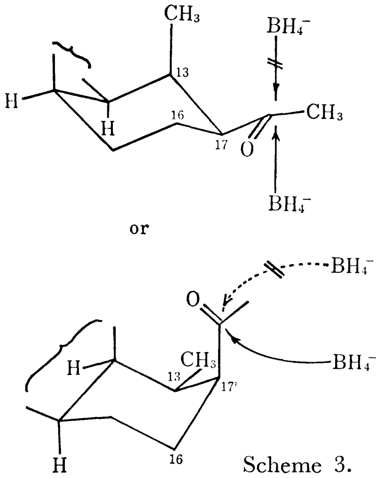
Treatment of the methyl ketone **10** with methanolic potassium hydroxide (2.5%) for 12 h at room temperature gave an isomeric ketone **13**, mp 140.0—141.5 °C, the acetate (**14**), mp 88.0—90.0 °C, of which was isomeric with methyl ketone acetate (**11**).

On Baeyer-Villiger oxidation, the isomeric ketone **13** afforded a new diol (**19**), mp 179.0—179.5 °C, which gave an acetate (**20**), mp 96—98 °C. The diol **19** was shown to be epimeric at C-17 with the diol **16** in that Jones' oxidation of the diol **19** afforded the dione **17** identical with the dione obtained by oxidation of the diol **16**. The D-ring of the ketones **10** and **13** is assumed to adopt one of four possible conformations, two *quasi* chair and two *quasi* boat forms. Regardless of these conformations, the 13*β*-methyl and the 17-acetyl substituents in the more stable ketone **13** will occupy more stable equatorial positions.

It follows that the 13*β*-methyl and the 17-acetyl substituents in the D-ring of the less stable ketone **10** and hence in the aldehyde **7** and the diol **3**, should be either in *β*-equatorial and *β*-axial or in *β*-axial and *β*-equatorial orientations. Thus, the isomerization of methyl ketone **10** into methyl ketone **13** demonstrates that the two substituents at C-13 and C-17 in the D-ring of compounds **3**, **7**, and **10** are oriented in the *cis* direction. The structures of the isomeric diols **16** and **19** have thus been assigned as 12α-etiojervane-3*β*,17*β*-diol and 12*α*-etiojervane-3*β*,17*α*-diol respectively.

Reduction of methyl ketone **11** with $NaBH_4$ in a mixture of ethanol and ethyl acetate gave a single product (**21**), mp 126—129 °C, in greater than 95% yield. Under these conditions both the 3*β*-ol (**22**) and the 20*ξ*-epimer of **21** were not formed. Hydrolysis and acetylation of the 20*ξ*-ol afforded 3*β*,20*ξ*-diol, mp 252—254 °C, and the diacetate (**23**), mp 84.5—87.0 °C.

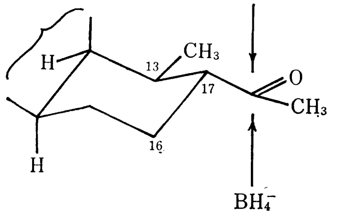
Reduction of isomeric 17*α*-acetyl-12*α*-etiojervan-3*β*-ol acetate with $NaBH_4$ under similar conditions afforded a mixture of 20*ξ*-ols (**26**)[4] and (**29**) which was hydrolyzed to a mixture of 3*β*,20*ξ*-diols. Separation by preparative TLC afforded 3*β*,20*ξ*-diol (**25**), mp 140.0—140.5 °C, and isomeric 3*β*,20*ξ*-diol (**28**), 187—189 °C, in 38 and 41% yields respectively.



Scheme 3.

No unambiguous spectral evidence with regard to the configurations of the hydroxyl group in the C-17 side chain of the etiojervanes (**21**, **26**, and **29**) was available. The stereochemistry can however be reasonably explained by considering the steric course of the reduction with complex metal hydrides. Examination of models of 17*β*-acetyletiojervane **11** indicates that regardless of the *quasi*-chair or *quasi*-boat conformation of the D-ring, the preferred conformation of the 17*β*-acetyl group would be such that the C=O bond eclipses the C-16–C-17 bond when the 13-methyl is axial and the 17*β*-acetyl is equatorial. Alternatively, with the 13-methyl equatorial and the 17*β*-acetyl group axial, the preferred conformation is for the carbonyl to lie orthogonal to the C-16–C-17 bond. In the former case, hydride ion attack would occur predominantly from the *α*-face due to the presence of the 13*β*-methyl group (steric approach control)[12] giving predominantly the *β*-ol **21** (Scheme 3). In the latter case, the hydride ion would attack predominantly from the front, and aided by the presence of the 13*β*-methyl and the predominant product would be the *β*-ol **21** (Scheme 3). In such cases, formation of the *α*-ol is unlikely.

The situation is analogous to the reduction of 20-oxopregnanes with complex metal hydrides where the predominant product is the 20*β*-isomer.[13]



Scheme 4.

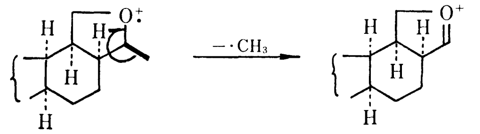
Examination of the model of 17*α*-etiojervane in which the 13*β*-methyl and the 17*α*-acetyl both occupy equatorial positions, shows that the preferred conformation of the 17*α*-acetyl group is when the C=O bond eclipses the C-13–C-18 bond in order to minimize the interaction between the skeletal part and the C-17 acetyl methyl. Thus, the hydride ion can approach the C=O bond equally from both the *α*- and *β*-sides affording a 1: 1 mixture of the observed *α*- and *β*-ols **26** and **29** (Scheme 4).

20*β*-ol **21** in pyridine readily afforded a crystalline nitrite (**24**), mp 102—106 °C, by treatment with nitrosyl chloride–pyridine.

Irradiation of the nitrite in benzene for 230 min under an atmosphere of nitrogen afforded a mixture of products. The product, hydrolyzed with methanolic 5% potassium hydroxide at room temperature and subjected to recrystallization and preparative TLC afforded 3*β*,20*β*-diol **22** (23%) and 17*β*-acetyl-3*β*-ol **10** (15%).

Examination of the NMR spectra of the other fractions from the preparative TLC failed to identify the 18-functionalized derivative. The failure in obtaining the 13*β*-methyl functionalized product contrasts with the results for the normal steroids.[14]

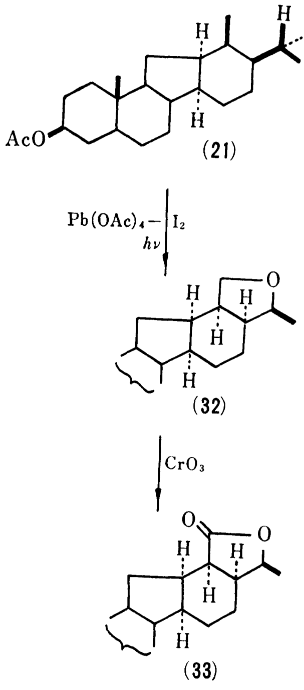
Functionalization of the 13*β*-methyl in the 20*β*-ol **21** was, however, achievable by the hypoiodide reaction (Scheme 5). Thus, 20β-ol **21** in cyclohexane containing iodine and lead tetraacetate was irradiated for 0.5 h with a 450 W high pressure Hg arc. Preparative TLC of the product afforded a crystalline 18,20-epoxide (**32**), mp 76—79 °C, resulting from intramolecular hydrogen abstraction, (16% yield) together with an amorphous substance (**31**). The NMR spectrum of the former exhibited two 3-H singlets at τ 9.22 and 7.98 which have been assigned 10β-methyl and OAc and a 3-H doublet (*J*=6.3 Hz) at τ 8.75 which has been assigned to the methyl attached to a carbon having an ether oxygen. The spectrum disclosed the absence of a signal attributable to the 13β-methyl and the presence of a multiplet due to the AB part of the ABX system from τ 5.88 to 6.91 ascribable to the 18-methylene protons. The mass spectrum was in full accordance with the epoxide structure (**32**). Thus, the prominent fragment ions (B) at *m/e* 345 (65%) and 285 (73%, $M^+-CH_3CO_2H-CH_3$) result from the expulsion of a methyl group from the molecular ion (A) and the molecular ion peak at *m/e* 360 (2%) and base peak at *m/e* 300 arise from the loss of acetic acid from the molecular ion. The amorphous substance **31** exhibited aromatic and cyclopropane protons in the NMR spectrum and contained iodine. No satisfactory structure has been evaluated for this compound.



(A)

(B) *m/e*345 and 285

Oxidation of (20*S*)-18,20-epoxy-17β-ethyl-12α-etiojervane-3β,20β-diol 3-acetate (**32**) with chromium trioxide afforded the corresponding γ-lactone (**33**), mp 89—90 °C, characterized by IR and NMR spectra [10β-methyl at τ 9.15 and 20ξ-methyl at τ 8.60 (*J*=6.0



Scheme 5.

TABLE 1. NMR PARAMETERS FOR ETIOJERVANE DERIVATIVES IN $CDCl_3$ SOLUTION
(Chemical shifts (τ) and splittings (Hz; in parentheses))

Compound	18-H	19-H	21-H	OAc	Other
7	8.97(d, 7.2)	9.20(s)	9.19(d, 7.2)	—	CHO, 0.42(d, 3.8)
8	8.96(d, 6.6)	9.16(s)	9.19(d, 6.6)	7.97(s)	CHO, 0.43(d, 3.8)
9	9.21(d, 6)	9.20(s)	8.12(s)	—	
10	9.20(d, 6.8)	9.20(s)	7.85(s)	—	
11[a]	9.28(d, 7)	9.24(s)	7.93(s)	8.04(s)	
12	9.16(d, 6.6)	8.99(s)	7.84(s)	—	
13[a]	9.21(d, 5.4)	9.21(s)	7.87(s)	—	
14[a]	9.30(d, 6)	9.26(s)	7.93(s)	8.05(s)	
15	9.15(d, 6.0)	8.98(s)	7.86(s)	—	
16	9.03(d, 6.6)	9.20(s)	—	—	
17	9.01(d, 6.0)	9.09(s)	—	—	
18	9.00(d, 6.2)	9.00(s)	—	—	
19	8.96(d, 6.6)	9.21(s)	—	—	
20	9.04(d, 7.8)	9.19(s)	—	7.92 and 7.92(s)	
21[a]	9.14(d, 7)	9.19(s)	8.81(d, 6.0)	7.99(s)	20-H 6.39(m)
23	9.22(d, 7.8)	9.18(s)	8.80(d, 6.0)	7.96 and 7.96(s)	
24	9.21(d, 6)	9.20(s)	8.63(d, 6.6)	7.98(s)	
25	9.08(d, 6.0)	9.20(s)	8.82(d, 6.0)	—	
27	9.13(d, 6)	9.19(s)	8.81(d, 6.0)	7.98 and 7.98(s)	
28	9.10(d, 5.3)	9.18(s)	8.86(d, 6.6)	—	
30	9.07(d, 4.5)	9.20(s)	8.85(d, 6.6)	7.99 and 7.99(s)	
32[a]	13β-methylene, 6.05 (bt, 8), 6.57 (bt, 8)	9.25(s)	8.78(d, 6.0)	8.00(s)	20α-H, 6.37(m)
33	—	9.15(s)	8.60(d, 6.0)	7.97(s)	

a) Measured by 100 MHz instrument.

Hz)], in 19% yield.

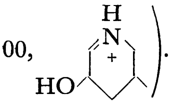
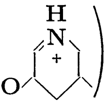
A mixture of the isomeric 20ξ-ols (**26**) and (**29**) was subjected to the hypoiodite reaction but no 18-functional compound resulting from intramolecular hydrogen abstraction was obtained.

The foregoing results demonstrate that the functionalization of the 13β-methyl group in *C*-nor-*D*-homosteroids may be achieved by intramolecular hydrogen abstraction of the 20β-oxyl radical attached to the C-17β alkyl but not by 20α and 20β-oxyl radicals attached to the C-17 α-alkyl group.

Experimental

All melting points were determined with a hot-plate (Yanagimoto micro melting point) apparatus and are uncorrected. Unless stated otherwise, IR spectra were determined in Nujol with a JASCO DS-402G or JASCO model IR-E spectrophotometer. Unless stated otherwise, NMR spectra were determined with a JEOL 3H-60 high resolution spectrometer in deuteriochloroform solution using TMS as an internal reference. The course of reaction and column chromatography were followed by thin layer chromatography with Wakogel B-5. Mass spectra were determined with a RMU-6E spectrometer with the exception of the MS of compound **21** which was determined with a Hitachi JMS-D 300 spectrometer.

*Catalytic Hydrogenation of (22*S*,25*S*)-5α-Veratr-13(17)-enine-3β,23β-diol (2).* The diol **2** (1 g) in acetic acid (30 ml) containing a rhodium–platinum oxide catalyst (2 g) was hydrogenated with stirring. The theoretical amount of hydrogen was absorbed in 22 h. After the removal of the catalyst, the filtrate was made alkaline by the addition of aq 10% sodium carbonate solution. To the solution was added chloroform and the chloroform complex obtained was recrystallized from acetone to yield (22*S*,25*S*)-5α-veratratranine-3β,23β-diol (**3**), identical with the diol obtained by catalytic hydrogenation of 11-deoxojervine.

Catalytic Hydrogenation of 11-Deoxojervine (1). (a) Rhodium–Platinum Catalyst: 11-Deoxojervine (8 g) in glacial acetic acid (130 ml) containing rhodium–platinum oxide[6] (2.69 g) was hydrogenated with stirring. The absorption of hydrogen practically ceased after 69 h. The catalyst was removed by filtration and washed with hot methanol. The filtrate and methanol washings were combined and the solution concentrated. To this solution methanol was added followed by methanolic potassium hydroxide and finally a small volume of water to afford crude crystals of diol **3**. The total weight of crystals obtained (5 crops) was recrystallized to afford the pure diol (2.88 g). Specimens for analysis were obtained by recrystallization from methanol, mp 219—221 °C. IR: 3274 and 3338 (OH and NH), 1038, and 968 cm^{-1} NMR, see text. Found: C, 77.78; H, 11.25; N, 3.42%. Calcd for $C_{27}H_{47}O_2N$, C, 77.64; H, 11.34; N, 3.35%; MS (80 eV), *m/e* (rel. intensity) 417 (0.2, M$^+$), 402 (0.3, M$^+ - CH_3$), 399 (0.4, M$^+ - H_2O$), 384 (0.8, M$^+ - CH_3 - H_2O$), and 114 (100, ). The residue from the filtrate was dissolved in acetone and to this solution a small volume of methanol was added to afford the crystals on standing. Recrystallization from aq methanol gave (22*S*,25*S*)-5α,13α,17α-veratranine-3β,23β-diol (**4**) (0.36 g). Specimens for analysis were obtained by recrystallization from acetone. Mp 178—180 °C: IR: 3112—3432 (OH and NH), 1040, and 883 cm^{-1}; NMR, see text. Found: C, 78.11; H, 11.27; N, 3.33%. Calcd for $C_{27}H_{47}O_2N$, C, 77.64; H, 11.34; N, 3.35%; MS (80 eV), *m/e* (rel. intensity), 417 (0.3, M$^+$), 402 (0.4, M$^+ - CH_3$), 399 (0.5, M$^+ - H_2O$), 384 (1.1, M$^+ - CH_3 - H_2O$), and 114 (). The yields of diol **3** from of hydrogenation conducted under different ratios of substrate and catalyst and under different concentrations, are tabulated below.

Weight ratio between deoxojervine and the catalyst	Concentration of deoxojervine (g/100 ml)	Yield of diol **3** (%)
1:0.3	5.0	39
1:0.33	6.2	36
1:0.66	5.0	42
1:1	3.3	46
1:1.4	2.5	46

(b) Platinum Catalyst: 11-Deoxojervine (2.0 g) in glacial acetic acid (20 ml) containing Adams platinum oxide (0.68 g) was hydrogenated for 60 h under atmospheric pressure with stirring. The solution was worked up as described in procedure (a). The diol **3** obtained, was recrystallized from methanol (0.613 g).

Preparation of N*-Acetyl-(22*S*,25*S*)-5α-veratranine-3β,23β-diol (5).* The diol **3** was acetylated with acetic anhydride and pyridine at 60—70 °C for 3 h. After the usual work-up, an amorphous 3-*O*,23-*O*,*N*-triacetyl derivative of diol **3** [NMR τ 9.20 (3-H, s, 19-H), 7.84 and 7.95 (3-H and 6-H, s, N-Ac, and OAc)] was obtained. This triacetyl derivative was hydrolyzed with methanolic 2.5% potassium hydroxide at room temperature overnight. The usual work-up afforded the *N*-acetyl derivative **5** which was recrystallized from aq acetone. Mp 227—229 °C: IR: 3153 and 3429 (OH), 1602 cm^{-1} (NAc), 1025, and 986 cm^{-1}. Found: C, 75.76; H, 10.69; N, 2.84%. for $C_{29}H_{49}O_3N$; C, 75.77; H, 10.74; N, 3.05%.

N*-Chloro-(22*S*,25*S*)-5α-veratranine-3β,23β-diol (6).* The diol **3** (50 mg) and *N*-chlorosuccinimide (22 mg) in dry THF (8 ml) were stirred for 1 h under dry nitrogen atmosphere. After the addition of water, the resultant precipitate was collected by filtration. The crude *N*-chloro derivative was dissolved in chloroform, the solution filtered and the residue recrystallized from acetone to yield the pure *N*-chloro derivative, mp over 290 °C, in an almost quantitative yield. IR: 3399 cm^{-1} (OH), 1036, and 1019 cm^{-1}. Found: N, 2.97%. Calcd for $C_{27}H_{46}O_2NCl$, N, 3.10%.

Degradation of Diol 3 to 20-Formyl-17β-ethyletiojervan-3β-ol (7). The diol **3** (1.4 g) and *N*-chlorosuccinimide (0.63 g) in dry THF (250 ml) were stirred for 1 h under an atmosphere of nitrogen. The reaction mixture was cooled to −20—−40 °C and to this solution a mixture of sodium (4.0 g) in dry methanol (70 ml) was added within a period of 0.5 h. The mixture was allowed to stand at −2——10 °C for 15 h and then at 0 °C for 9 h. This procedure was conducted under an atmosphere of nitrogen. The solution was concentrated (<35 °C) and water (300 ml) added to the solution. The mixture was neutralized with 6 M-hydrochloric acid (50 ml) at *ca.* −7——4 °C and then stirred for 2.5 h at room temperature. The reaction mixture was extracted three times with chloroform and the combined chloroform solution were washed with water, dried and evaporated to afford crude aldehyde **7**. The products from other two identical procedures were combined (3.1 g, 95%). The crude aldehyde **7** was recrystallized from aq ethanol. Mp 109—111 °C: IR: 3363 (broad, OH), 1708 and 2703 (CHO), and 1024 cm^{-1}. Found: C, 79.22; H, 10.72%. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.92%; MS, (80 eV), *m/e* (rel. intensity), 332 (2.0, M$^+$), 317 (0.7, M$^+$−CH$_3$), 314 (1.6, M$^+$−H$_2$O), 274 (100, M$^+$−H−C-17-substituent), 259 (20.5, M$^+$−H−C-17-substituent−CH$_3$), 257 (19.6, M$^+$−C-17-substituent−H$_2$O), 149 (44.2), 148 (49.5), and 107 (35.3). The acetyl derivative **8** was prepared by the usual method. Mp 114—116 °C (methanol): IR: 1720 and 1735 cm^{-1} (CHO), 1242, and 1028 cm^{-1}. Found: C, 76.48; H, 9.98%. Calcd for $C_{24}H_{38}O_3$: C, 76.96; H, 10.23%; MS (80 eV), *m/e* (rel. intensity) 374 (1.1, M$^+$), 316 (100, M$^+$−C-17-substituent−H), 257 (30.9, M$^+$−C-17-substituent−CH$_3$CO$_2$H), 256 (42.4, M$^+$−C-17-substituent−H−CH$_3$CO$_2$H), 149 (57.4), 148 (62.3), 107 (56.0), and 93 (56.0).

*Preparation of 17β-Acetyl-12α-etiojervan-3β-ol (**10**) and the 3-Acetate.* To a solution of the aldehyde **7** (1.3 g) and butyl nitrite (5 ml) in THF (10 ml) was added sodium (460 mg) in dry methanol (10 ml) under an atmosphere of nitrogen at −20 °C over 20 min. The mixture was set aside 25 h at 2—3 °C and neutralized by the addition of hydrochloric acid (3 ml) at 0—−4 °C. The solution was concentrated (<35 °C) and extracted with chloroform. The chloroform solution was washed with water, dried and evaporated and the viscous residue subjected to silica gel column chromatography (Mallincrodt, 100 mesh). The column was successively eluted with hexane, benzene, chloroform, and diethyl ether. The chloroform and diethyl ether fractions afforded a ketone **10**, mp 145—150 °C (1.14 g, 90%). Specimens for analysis were obtained by recrystallization from aq ethanol; mp 150—152 °C (lit,[8] 154—156 °C); IR: 1699 (acetyl), 3523 (OH), 1193, and 1063 cm^{-1}. The acetyl derivative **11** was obtained in the usual manner and recrystallized from aq methanol. Mp 116—118 °C (lit,[8] 131—133 °C); IR: 1692 (Ac), and 1720 cm^{-1} (OAc), 1241, and 1030 cm^{-1}. Methyl ketone **10** and its acetate **11** were identical with specimens prepared by Johns and Laos[8] by direct comparison.

*Preparation of 17β-Acetyl-12α-etiojervan-3β-ol Oxime (**9**) and the Acid-catalyzed Hydrolysis to 17α-Acetyl-12α-etiojervan-3β-ol (**13**).*

The oxime **9** was obtained only from this precedure. To a solution of the aldehyde **7** (50 mg) and butyl nitrite (0.5 ml) in methanol (1.5 ml) was added sodium metal (62 mg) in dry methanol (1.5 ml) over 3 min in an atmosphere of dry nitrogen at −20 °C. The mixture was set aside for 27.5 h at 0 °C. The pH of the mixture was adjusted to 4 by the addition of hydrochloric acid (*ca.* 6 drops) at −20 °C. After removal of the solvent, the residue was extracted with chloroform. After the usual work-up, the residue (42 mg) was purified by preparative TLC to afford a crude oxime (36 mg). The oxime was recrystallized from acetone to yield the pure oxime, mp 106—109 °C. IR: no carbonyl band, 3336 cm^{-1} (OH), 1040, and 879 cm^{-1}. The oxime (*ca.* 20 mg) in ethanol (10 ml) containing hydrochloric acid (1 ml) was refluxed for 2 h for 40 min. The reaction mixture was concentrated and extracted with diethyl ether and water. The organic layer was worked up to afford a residue (17 mg). After recrystallization from aq methanol it was shown to be identical with 17α-ethyl-12α-etiojervan-3β,20ξ-ol (**13**), obtained by the isomerization of 17β-ketone **10**.

*Oxidation of 17β-Acetyl-12α-etiojervan-3β-ol (**10**) with Chromium Trioxide.* To the 3β-ol **10** (105 mg) in acetone (5 ml), cooled in an ice-water bath, was added Jones' reagent (7 drops) and the mixture stirred for 1 h. After the usual work-up, the residue (120 mg) was recrystallized from acetone to afford the 3,20-dione **12** in 95% yield. Specimens for analysis were obtained by recrystallization from acetone. Mp 158—160 °C. Found: C, 79.58; H, 10.07%. Calcd for $C_{21}H_{32}O_2$: C, 79.90; H, 10.19%: MS (80 eV), *m/e* (rel. intensity); 316 (65, M$^+$), 301 (19, M$^+$−CH$_3$), 232 (42), 231 (44), 203 (30), 163 (55), 107 (58), 95 (86), 85 (100), 55 (87), and 43 (91).

*Preparation of 12α-Etiojervane-3β,17β-diol (**16**) by the Baeyer-Villiger Oxidation of 17β-Acetyl-12α-etiojervan-3β-ol.* A solution of the 20-one **10** (178 mg) and perbenzoic acid (90% purity, 105 mg) in chloroform (0.75 ml) were allowed to stand for 7 days at room temperature. The excess of perbenzoic acid was decomposed by the addition of 10% aq sodium hydrogen sulfite and the reaction mixture extracted with chloroform and water. The organic layer was washed with 10% aq sodium carbonate and water successively and dried. After evaporation of the solvent the residue (150 mg) was dissolved in methanolic 5% potassium hydroxide solution (10 ml) and allowed to stand for 3 h at room temperature. The usual work-up of the solution afforded a residue which was subjected to preparative TLC with a 1 : 1 mixture of chloroform and diethyl ether. The starting material (20 mg) and 13β-etiojervane-3β,17β-diol **16** (49 mg) were obtained. Recrystallization from acetone–cyclohexane, gave **16** which melted at 167—169 °C (lit,[8] mp 169—170 °C). The diol was proved to be identical with a specimen prepared by Johns and Laos[8] by direct comparison. IR: 3339 (OH), 1036, and 1069 cm^{-1}.

*Oxidation of 12α-Etiojervane-3β,17β-diol (**16**) with Chromium Trioxide.* To the diol **16** (50 mg) in acetone (10 ml) cooled by ice-water, was added Jones' reagent (3 drops). The reaction mixture was stirred for 1 h. After the excess chromium trioxide was decomposed by the addition of 10% aq sodium hydrogen sulfite, the solvent was evaporated and the reaction mixture worked up in the usual manner. The dione **17** was recrystallized from acetone (42 mg). Specimens for direct comparison were obtained by recrystallization from diethyl ether. Mp 169—170 °C (lit,[8] 169—170 °C). This specimen was identical with dione **17** prepared by Johns and Laos by a direct comparison. IR 1700 and 1713 cm^{-1} (carbonyl).

*Isomerization of 12α-Etiojervane-3,17-dione (**17**) with Base.*

The dione (20 mg) in methanolic 5% potassium hydroxide solution (10 ml) was refluxed for 1 h under an atmosphere of nitrogen. The solution was concentrated and the residue extracted with diethyl ether and water. After the usual work-up, the residue was recrystallized from aq acetone to yield crystals (18 mg); mp 115—125 °C which were largely an isomer **18**, epimeric at the C-13 and contaminated with a small amount of the starting ketone as evidenced by a weak singlet at τ 9.09 due to 19-H of **17** in the NMR spectrum. The mixture was recrystallized twice to afford pure 12α,13α-etiojervane-3,17-dione (1 mg), mp 136—140 °C (lit,[8] mp 143—145 °C). This compound was identical with the specimen prepared by Johns and Laos[8] by a direct comparison.

*Base-catalyzed Epimerization of 17β-Acetyl-12α-etiojervan-3β-ol (**10**).* The 3β-ol **10** (100 mg) in methanolic 2.5% potassium hydroxide (10 ml) was allowed to stand for 12 h under an atmosphere of nitrogen. The solution was neutralized by the addition of dilute hydrochloric acid and extracted with chloroform. The organic layer was washed with water, dried and evaporated. The residue was recrystallized from a diethyl ether–hexane mixture to yield 17α-acetyl-12α-etiojervan-3β-ol (**13**) (78 mg). Specimens (57 mg) for analysis were obtained by recrystallization from aq methanol. Mp 140.0—141.5 °C: IR: 3450 (OH), 1695 (acetyl), 1166, 1069, and 1045 cm^{-1}. Found: C, 78.54; H, 10.49%. Calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76%. The acetate (**14**) was prepared in usual way and was recrystallized from aq methanol. Mp 88—90 °C: IR: 1723 and 1701 cm^{-1}, (carbonyl and OAc), 1240, and 1030 cm^{-1}. Found: C, 76.67; H, 9.97%. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07%.

Oxidation of 17α-Acetyl-12α-etiojervan-3β-ol with Chromium Trioxide. To 17α-acetyl-12α-etiojervan-3β-ol (70 mg) in acetone (4 ml) cooled by ice–water, was added Jones' reagent and the solution stirred for 1 h. After the excess reagent was decomposed by the addition of 10% aq sodium hydrogen sulfite, the solution was worked up. The product (73 ml) was recrystallized from aq methanol to afford 17α-acetyl-12β-etiojervan-3-one, mp 87—88 °C, (48 mg). IR: 1700 cm^{-1} (broad, carbonyl). Found: C, 79.59; H, 10.12%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

Preparation of 12α-Etiojervane-3β,17α-diol (19) by Baeyer-Villiger Oxidation of 17α-Acetyl-12α-etiojervan-3β-ol. The reaction was conducted as described for the oxidation of the 17β-isomer **10**. The 20-one **13** (178 mg) afforded a crude product (200 mg) which was hydrolyzed in a manner similar to that for the 17β-isomer. The crude product was subjected to preparative TLC with a 5: 1 mixture of chloroform and acetone to afford the starting material (41 mg) and etiojervane-3β,17α-diol (83 mg). Specimens of the latter for analysis were obtained by recrystallization from aq methanol. Mp 179.0—179.5 °C; IR: 3240—3372 (OH) and 1034 cm^{-1}. Found: C, 78.05; H, 10.93%. Calcd for $C_{29}H_{32}O_2$: C, 78.03; H, 11.03%. Diacetate **20**, mp 96—98 °C, was prepared by the usual method. IR ($CHCl_3$), 1722 (broad, OAc), 1250, 1028, and 978 cm^{-1}. Found: C, 73.30, H, 9.82%; Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64%.

Reduction of 17β-Acetyl-12α-etiojervan-3β-ol Acetate (11) with NaBH$_4$. 17β-Acetyl-12α-etiojervan-3β-ol acetate (300 mg) and $NaBH_4$ (160 mg) in absolute ethanol (26 ml) containing ethyl acetate (0.75 ml) were stirred for 2.5 h. After the excess reagent was decomposed by the addition of acetic acid, the solvent was removed to afford a residue which was extracted with chloroform. After the usual work-up, the product (310 mg) was examined by TLC which indicated the formation of virtually a single product. The product was recrystallized from a diethyl ether–hexane mixture to yield pure 17β-ethyl-12α-ethiojervane-3β,20ξ-diol 3-acetate (**21**), in greater than 95% yield. Specimens for analysis were obtained by recrystallization from aq methanol. Mp 126—129 °C: IR: ($CHCl_3$), 1719 (OAc), 3519 and 3401 (OH), 1457, 1393, 1269, and 1027 cm^{-1}. Found: C, 75.62; H, 10.45%. Calcd for $C_{23}H_{38}O_3$: C, 76.19; H, 10.57%. MS (70 eV) *m/e* (relative intensity), 344 (56.3, M^+-H_2O), 329 ($M^+-H_2O-CH_3$), 315 (18.4), 302 (22.5, M^+-AcOH), 274 (47.5), 269 (26.6), 257 (88.3, M^+-C-17-side chain$-$AcOH), 147 (56.1), 107 (100), 95 (82.2), 93 (91.9), 81 (78.0), and 43 (74.3).

Hydrolysis of 17β-Ethyl-12α-etiojervane-3β,20ξ-diol 3-Acetate (21). The 3-acetate (60 mg) in methanolic 2.5% potassium hydroxide (15 ml) was allowed to stand for 3 h at room temperature under an atmosphere of nitrogen. The solution was concentrated and extracted with chloroform. The usual work-up afforded a residue which was recrystallized to afford 3β,20ξ-diol **22** (53 mg). Specimens for analysis were obtained by further recrystallization from aq methanol. Mp 252—254 °C; IR: 3247 (OH), 1064, 1048, 1027, and 1010 cm^{-1}. Found: C, 78.06; H, 11.13%. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32 %; MS (80 eV), *m/e* (relative intensity), 302 (59, M^+-H_2O), 287 (18), 273 (21), 257 (77, M^+-H_2O-C-17 substituent), 147 (65), 107 (99), 95 (100), 81 (91), 67 (79), and 55 (86).

Acetylation of 17β-Ethyl-12α-etiojervane-3β,20ξ-diol 3-Acetate (21). The 3-acetate (43 mg) and acetic anhydride (0.5 ml) in pyridine (0.5 ml) were allowed to stand for 3 h at room temperature. The usual work-up afforded the diacetate **23** (35 mg). Recrystallization from aq methanol gave the pure product, mp 84.5—87.0 °C. IR: 1718 cm^{-1} (OAc), 1239, 1051, and 1024 cm^{-1}. Found: C, 74.36; H, 9.70%. Calcd for $C_{25}H_{40}O_4$: C, 74.21; H, 9.97%.

Reduction of 17α-Acetyl-12α-etiojervan-3β-ol Acetate(14) with NaBH$_4$. 17α-Acetyl-12α-etiojervan-3β-ol acetate (**14**) (300 mg) and $NaBH_4$ (160 mg) in absolute ethanol (26 ml) containing ethyl acetate (0.75 ml) were stirred for 3 h at room temperature. The addition of acetic acid to the reaction mixture and extraction with chloroform afforded a product (332 mg). A portion of the product (178 mg) was treated with methanolic 5% potassium hydroxide solution and allowed to stand for 1 h. The usual work-up afforded products which were subjected to preparative TLC with a 5: 1 mixture of chloroform and acetone to afford two fractions. The more mobile fraction (63 mg) was recrystallized from aq methanol to afford 3β,20ξ-diol **25** (55 mg), mp 140.0—140.5 °C. IR: 3170—3310 (OH), 1038, 1009, and 895 cm^{-1}. Found: C, 78.50; H, 11.31%. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32%. The less mobile fraction (70 mg) was recrystallized from aq methanol to afford 3β,20ξ-diol **28** (59 mg), mp 187—189 °C. IR: 3336 (OH), 1063, 1038, and 895 cm^{-1}. Found: C, 78.87; H, 11.42%. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32%. The diacetates **27** and **30** of the diols **25** and **28** were prepared by standard methods. The diacetate **27** from diol **25**, mp 131—132 °C (aq methanol). IR: ($CHCl_3$), 1739, 1241, 1042, and 1030 cm^{-1}. Found: C, 74.63; H, 9.84%. Calcd for $C_{25}H_{40}O_4$: C, 74.21; H, 9.97%. The diacetate **30** from diol **28** was amorphous. IR: ($CHCl_3$), 1725 (OAc), 1255, and 1028 cm^{-1}.

17β-Ethyl-12α-etiojervane-3β,20ξ-diol 3-Acetate 20-Nitrite (24). 20ξ-Ol **21** (290 mg) in pyridine (2 ml) was nitrosated with nitrosyl chloride in pyridine at −20 to −30 °C by the standard method. The crude nitrite **24** was recrystallized from methanol. Mp 102—106 °C: IR: 1734 (OAc), 1631, 794, 774, (ONO), 1242, and 1031 cm^{-1}.

Photolysis of Nitrite 24. The nitrite (200 mg) in dry benzene (10 ml) in a Pyrex vessel was irradiated with a 100 W high pressure Hg arc for 3 h and 50 min under an atmosphere of nitrogen. After evaporation of the solvent, the residue was examined by TLC which indicated at least 6 spots. The product was dissolved in chloroform and the solution washed with water, dried and evaporated. The residue was hydrolyzed with methanolic 5% potassium hydroxide solution (5 ml) at room temperature and under an atmosphere of nitrogen for 3 h. The usual work-up afforded a residue which was dissolved in acetone to yield crystals (38 mg) of 17β-ethyl-12α-etiojervane-3β,20ξ-diol (**22**). The residue from the filtrate was subjected to preparative TLC with chloroform. The plates were developed three times and the major three fractions, A (13 mg), B (48 mg), and C (60 mg) were obtained. The NMR spectra of fraction A showed the absence of a C-18 functionalized product. The amorphous fraction B was recrystallized from acetone to afford 17α-acetyl-12α-etiojervan-3β-ol (**13**) (25 mg). Fraction C exhibited three spots on TLC examination and this was subjected again to preparative TLC with a 40: 1 mixture of diethyl ether–methanol to afford two major fractions C-1 (35 mg) and C-2 (18 mg). The more mobile fraction C-1 was a mixture and fraction C-2 showed a single spot on the TLC. The NMR spectra of both fractions, however, showed the absence of a C-18 functionalized product.

The Hypoiodite Reaction of 17β-Ethyl-12α-etiojervane-3β,20ξ-diol 3-Acetate. Freshly prepared lead tetraacetate (600 mg) and sodium carbonate (200 mg) in cyclohexane (18 ml) were refluxed for 1 h and the solution brought to room temperature. To this solution, were added 17β-ethyl-12α-etiojervane-3β,20ξ-diol 3-acetate (180 mg) and iodine (160 mg) and the solution irradiated under reflux for 0.5 h with a 450 W high pressure Hg arc. The insoluble material was removed by filtration and washed with hot cyclohexane. The filtrate and washings were combined and the solution washed with 10% aq sodium hydrogen sulfite and water successively. The organic layer was dried and evaporated to afford a brownish residue (0.2 g) which was dissolved in methanolic 2.5% potassium hydroxide solution (10 ml). The solution was allowed to stand for 3 h under an atmosphere of nitrogen, concentrated under reduced pressure and extracted with chloroform and water. The usual work-up of the organic layer gave a residue which showed two major and a very minor spot on TLC. The residue was subjected to preparative TLC with chloroform. The TLC plates were developed three times to afford three fractions. The most mobile amorphous fraction (79 mg) could not however crystallize but gave a positive Beilstein test and the chloroform solution developed an yellow color by the addition of tetranitromethane. UV λ_{max} (ethanol) 262 nm; NMR τ 2.99 (2H, q, possibly ortho aromatic protons), 8.92 (s, 19-H), 7.97 (s, OAc), 7.68 (s, possibly the methyl group attached to the aromatic ring), 8.01 (s), 9.38 (1H, d, $J=1.7$ Hz, the proton possibly attached to the cyclopropane ring). IR ($CHCl_3$) no carbonyl or hydroxyl groups. The second mobile fraction (4 mg) was an unidentified gum. The least mobile amorphous fraction (48 mg) was a deacetylated product of a 18,20-epoxide **32**. This fraction was acetylated with acetic anhydride (2 ml) and pyridine (2 ml). After the usual work-up, the product was recrystallized from aq methanol to yield a 18,20-epoxide (**32**) (29 mg), amorphous. IR: 1732 (OAc), 1024, and 1237 cm^{-1}. Found: C, 76.50; H, 9.92%. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07%; MS (80 eV), *m/e* (rel. intensity) 360 (2.4 M^+), 345 (65.0, M^+-CH_3), 316 (16.7), 300 (100, $M^+-CH_3CO_2H$), 285 (73.4, $M^+-CH_3CO_2H-CH_3$), 149 (92.2), 148 (92.2), and 141 (98.4).

Oxidation of 18,20-Epoxide (32) with Chromium Trioxide. To the 18,20-epoxide (25 mg) in glacial acetic acid, was added dropwise chromium trioxide (50 mg) in aq acetic acid (90%) (2 ml) a period over 0.5 h while the solution refluxed. The reaction mixture was further refluxed for 0.5 h and the solvent removed under reduced pressure. The residue was extracted with chloroform and water and the organic layer washed with water and dried (Na_2SO_4). The residue (23 mg) from the solution was dissolved in methanolic hydrochloric acid (10 ml) to hydrolyze the 3β-acetoxyl group and allowed to stand overningt. After removal of the solvent, the residue was dissolved in chloroform. The chloroform solution was worked up in the usual way to afford the crude lactone (20 mg). The lactone was subjected to preparative TLC with a 1 : 20 mixture of benzene and chloroform to afford 6 fractions. The third mobile fraction (4 mg) was the major product. The product in pyridine was subjected to acetylation in the usual way. The usual work-up of the reaction mixture afforded a crystalline lactone **33** (5 mg) which was recrystallized from diethyl ether. Mp 89—90 °C; IR: 1752 (γ-lactone), 1726 (OAc), 1238, and 1029 cm^{-1}. Found: C, 73.64; H, 9.21%. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64%.

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