

REACTION OF 20-LUPANOL DERIVATES WITH LEAD TETRAACETATE*

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The reaction of 20-lupanol derivatives *I*, *VII* and *VIII* with lead tetraacetate gives derivatives *II*, *IX* and *X* as the main products; for sterical reasons, the transfer of 12βH on the oxygen radical takes place *via* a seven-membered cyclic transition state. The main reaction products of 20R noralcohol *III* with lead tetraacetate are 20,29,30-trinorlupane derivatives *IV* and *VI*. Oxidative opening of the ether ring of substance *X* gives keto acid *XI*. The structure of all substances prepared was determined by spectral methods (IR, ¹H-NMR and mass spectrometry).

In preceding papers¹⁻³ we proved that the photolysis of nitrites derived from 20S noralcohol *I*, tertiary alcohol *VII* and dinoralcohol *VIII* takes place under formation of 12 (*E*)-oximino-20-lupanol derivatives, while the nitrite derived from 20R noralcohol *III* does not give a product with an oxime group in this reactions. The different behaviour of nitrites derived from C₍₂₀₎-epimeric noralcohols *I* and *III* was then interpreted on the basis of sterical conditions for the formation of the transition state of Barton's reaction. Therefore we were interested in how the 20-O-radicals generated from alcohols *I*, *III*, *VII* and *VIII* in a different manner, *i.e.* with lead tetraacetate, would behave from this point of view. According to earlier experiences^{4,5} we made use of thermal initiation for this purpose. Using this procedure 20R noralcohol *III* afforded two dominant products, differing in polarity. The mass spectrum of the less polar substance with the molecular ion M⁺ 484 shows that a splitting off of acetaldehyde from noralcohol *III* took place by the known⁶ mechanism of β-elimination. The less polar product should, therefore, possess the structure of a 20,29,30-trinorlupane derivative with the double bond in the position 18,19 or 19, 21. As in its ¹H-NMR spectrum the signal of a single olefinic proton is present (5.25 p.p.m.), the position of the 19,21-double bond is excluded. The distinct change in chemical shifts of protons bound on C₍₂₈₎ (+0.18 and -0.12 p.p.m.) is indicative of the structure as in formula *IV*, with the double bond in 18,19, as well as the shifts of the methyl groups 10β,8β and 14α (+0.04, +0.03 and -0.13 p.p.m.), evaluated by using 3β,28-diacetoxy-20,29,30-trinorlupane⁷ (*XIII*) as standard. These changes are similar to those determined earlier^{5,8,9,10} in 28-acetoxy-18-lupene derivatives. For the chemi-

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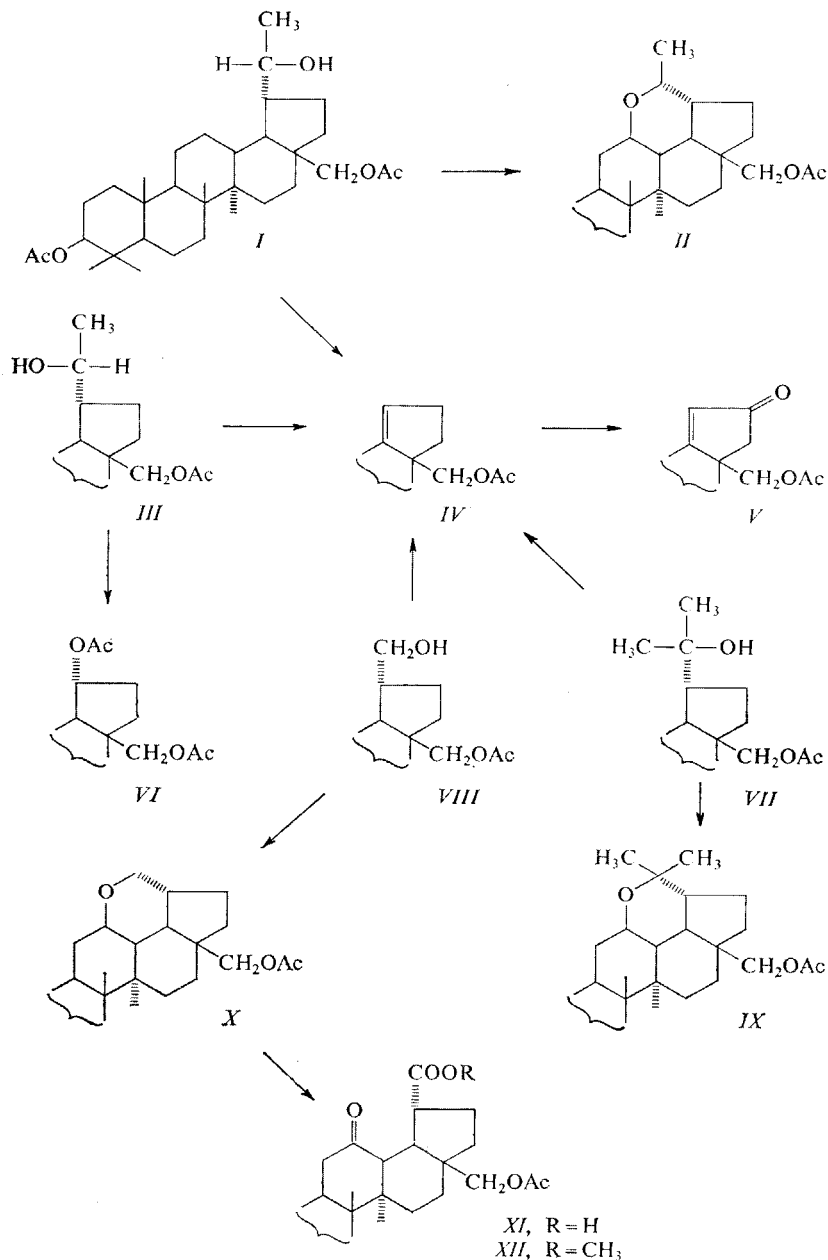
cal confirmation of structure *IV* we submitted this product to allylic oxidation with the complex of chromium trioxide with pyridine in dichloromethane¹¹. Thus α,β -unsaturated ketone of *s-trans* configuration was formed in 65% yield. In its ¹H-NMR spectrum the signal of one hydrogen (19-H) is again evident, this time as a doublet of very small coupling constant; a decoupling experiment proved that this splitting is caused by the allylic interaction with 13 β -H. Further an isolated AB system of two protons bound on C₍₂₂₎ is again very prominent in the spectrum. On the basis of these facts we consider that the structure *V* for the product of allylic oxidation is proved.

The second dominant product (*VI*) of the reaction of noralcohol *III* with lead tetraacetate contains more than two acetoxyl groups according to its IR spectrum. In its ¹H-NMR spectrum the signal of another acetoxyl group (singlet 1.98 p.p.m.) appears in addition to the signals of the acetoxyl groups in the positions 3 β and 28. On the basis of the known⁶ reaction course of alcohols with lead tetraacetate we proposed for this compound the structure of trinoracetate *VI*. From the form of the signal of 19-H (multiplet $W \approx 28$ Hz) it is not possible to determinate the configuration of the acetoxyl group; for both possibilities a study of Dreiding models gives practically equal values for the sums of the vicinal coupling constants. As the values of the chemical shifts of protons bound to C₍₂₈₎ practically do not differ from the values found for unsubstituted trinorlupane derivative *XIII* we consider the structure with the 19 α orientation of the acetoxyl group as more probable.

On reaction of 20*S* noralcohol *I* with lead tetraacetate substance *II* (50%) is formed as the main product in addition to trinorolefin *IV*. The IR spectrum of substance *II* does not contain any characteristic vibrations except those for two acetoxyl groups. On the basis of the mass spectrum (loss of 2 mass units) we considered 3 possible structures for this substance; closing of the ether ring between C₍₂₀₎ and C₍₁₂₎ or C₍₁₈₎ or C₍₂₁₎. The presence of the multiplet (3.11 p.p.m.) belonging to the two protons in α -positions to the ethereal oxygen excludes the 18 $\alpha,20$ -epoxy structure. The agreement of the chemical shifts of both α -hydrogens indicates the structure in which these hydrogens are located symmetrically with respect to the closest oxygen substituents, *i.e.* the ether oxygen and the 28-acetoxyl group. As is evident from the Dreiding models this requirement is satisfied by the structure 12 $\beta,20$ -epoxy (*II*) better than by the alternative 20,21 α -epoxy structure. The changes in the shifts of the methyl groups bound to the B and C rings, *i.e.* 8 $\beta,10\beta$ and 14 α show that the ethereal ring is closed to C₍₁₂₎.

The reaction of alcohol *VII* with lead tetraacetate also led to a substance the mass spectrum of which indicates the loss of two mass units; this main product (50%) was obtained in addition to norolefin *IV* (34%). The chemical shifts of the methyl signals practically coincide with those of the methyl signals of norether *III*. The proposed structure *IX* is confirmed by the finding of the signal 12 α H in the shape of a multiplet (3.26 p.p.m., $W \approx 26$ Hz) and two singlets of the methyls on C₍₂₀₎ (1.17 and

1.09 p.p.m.). The chemical shift of the downfield methyl is in agreement with the chemical shift of the 20 β methyl in the spectrum of norether *II*; this methyl has,



therefore, configuration 20β , while the upfield methyl has the configuration 20α . Similar differences as between the signals $20\alpha\text{CH}_3$ and $20\beta\text{CH}_3$ also occur in the spectrum of dinorether *X* between the signals $20\alpha\text{H}$ and $20\beta\text{H}$.

On reaction of dinoralcohol *VIII* with lead tetraacetate a very small amount (4%) of trinorolefin *IV* is formed; as the main product (50%) a substance was isolated the IR spectrum of which does not contain any characteristic vibrations except for the bands of the acetoxyl groups, and its mass spectrum indicates the loss of two mass units. On the basis of agreement between the chemical shifts of methyls in the $^1\text{H-NMR}$ spectrum with the shifts of methyl signals in the spectra of norether *II* and ether *IX* we proposed the structure of dinorether *X* for this compound. Further proofs of the structure *X* follow from the analysis of the signals of the protons in α -positions with respect to the ethereal oxygen. The signals $12\alpha\text{H}$ and $20\alpha\text{H}$ again overlap, which indicates their symmetrical arrangement with respect to the ethereal oxygen and 28-OAc . The value $J_{19,20} \approx 3$ Hz, which was read from the splitting of the signal of $20\beta\text{H}$ (4.09 dd p.p.m.) corresponds to the dihedral angle between $19\beta\text{H}$ and $20\beta\text{H}$ of about 60° ; this angle is in very good agreement with the angle found on Dreiding models.

To check the proposed structure we submitted dinorether *X* to oxidation with chromium trioxide in acetic acid. From the reaction mixture we isolated keto acid *XI* instead of the expected δ -lactone. Its reaction with diazomethane gave methyl ester *XII*. In its $^1\text{H-NMR}$ spectrum the signals characteristic of 12-lupanone derivatives^{1,2,4} were found, a downfield shift of the signal $8\beta\text{CH}_3$ (+0.22 p.p.m.) and an up-

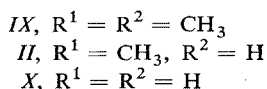
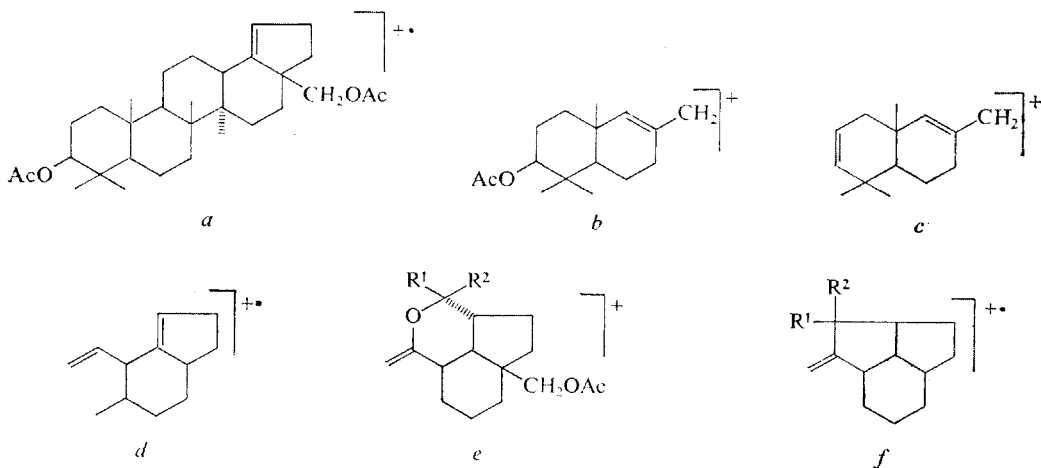


TABLE I
Characteristic Parameters of $^1\text{H-NMR}$ Spectra^a

Com- pounds ^a	$4\alpha\text{CH}_3^b$ $4\beta\text{CH}_3$	$10\beta\text{CH}_3^b$	$8\beta\text{CH}_3^b$	$14\alpha\text{CH}_3^b$	28-H_2^c	Other signals ^d
<i>I</i> ^e	0.84	0.86	1.05	0.92	3.79 d	1.09 d, $J_{20,29} = 6.3$ (20- CH_3); 4.09 dq; $J_{19,20} = 4.2$ (20-H)
<i>II</i> ^e	0.85	(0.92)	(1.06)	(0.99)	3.75 d	1.17 d, $J_{20,29} = 6.2$ (20 βCH_3); 3.11 m, $W \approx 30$ (overlapped 12 αH and 20 αH)
<i>IV</i> ^g	0.85	0.90	1.06	0.80	3.91	4.07 ^{f,g} s, $W = 8$ (19-H)
<i>V</i> ^e	0.85	0.93	1.14	0.85	4.10 d	2.10 and 2.55 ^g , $J_{\text{gem}} = -18$ (22- H_2); 2.67 m (13 βH); 5.83 d, $J_{13,19} = 1.5$ (19-H)
<i>VI</i> ^h	0.83	(0.83)	(1.00)	(0.95)	3.70 d	1.98 s (19 αCOCH_3); 4.91 m, $W \approx 28$ (19 βH)
<i>IX</i> ^h	0.85	(0.90)	(1.05)	(1.01)	3.75 d	1.09 s (20 αCH_3); 1.17 s (20 βCH_3); 3.26 m, $W \approx 26$ (12 αH)
<i>X</i> ^h	0.84	(0.90)	(1.05)	(0.99)	3.73 d	3.02 m, $W \approx 40$ (overlapped 12 αH and 20 αH); 4.09 dd, $J_{\text{gem}} \approx -10.5$, $J_{19,20} \approx 3$ (20 βH)
<i>XII</i> ^h	0.84	0.89	1.24	0.84	3.59 d	2.56 d, $J_{13,18} \approx 10$ (13 βH); 3.73 s (COO CH_3)
<i>XIII</i> ^{c,i}	0.84	0.86	1.03	0.93	3.73 d	4.19 d
<i>XIV</i> ^{c,i}	0.84	0.84	1.02	0.97	3.69 d	2.44 m (19 βH); 3.63 s (COO CH_3)

^a The spectra were measured in deuteriochloroform with tetramethylsilane as internal reference. Chemical shifts are given in δ -scale (p.p.m.); coupling constants (J) and widths of multiplets (W) are given in Hz. ^b Singlets. The values given in parentheses are assigned tentatively and may be mutually interchanged. ^c $J_{\text{gem}} = -11$ Hz. ^d In the spectra of all substances the signal of 3 αH appears as a multiplet at 4.43—4.51, $W = 17$, and the signals of 3 $\beta\text{-OCOCH}_3$ and 28- OCOCH_3 as singlets at 2.00—2.06. ^e Measured on a Varian HA-100 (100 MHz) instrument. ^f $J_{\text{gem}} = -10.5$ Hz. ^g AB system; the chemical shift values were obtained by computation. ^h Measured with a Tesla 80-MHz instrument. ⁱ Compounds *XIII* and *XIV* were measured as models: 3 β ,28-diacetoxy-20,29,30-trinorlupan (*XIII*), methyl 3 β ,28-diacetoxy-29,30-dinorlupan-20-oate (*XIV*).

field shift of the signal $14\alpha\text{CH}_3$ (-0.13 p.p.m.), and the signal of $13\beta\text{H}$ appears as a doublet (2.56 p.p.m.) with a coupling constant $J_{13,18} \approx 10$ Hz (Table I). The mass spectrum of methyl ester *XII* contains fragments characteristic of 12-lupanone derivatives¹². The oxidative opening of the ether ring of dinorether *X* represents a preparatively advantageous method for the preparation of 12-lupanone derivatives. The yield of keto acid *XI* is about 25% (calculated per starting dinoralcohol *VIII*); Barton's reaction, described earlier^{1,2}, and subsequent deoxygenation give 12-lupanone derivatives in about 6–12% yield (calculated per starting alcohols).

Further confirmation of the structure of homologous 12 β ,20-epoxy derivatives *IX*, *II* and *X* follows from their mass spectra. It was found that their fragmentation is dependent of the substitution at $\text{C}_{(20)}$ and that it takes place in two ways. The first of them is the elimination of acetone (in ether *IX*), acetaldehyde (in ether *II*), and ormaldehyde (in ether *X*) under formation of the double bond 18 (19). In all mentioned ethers the ion *a* of m/e 484 (or *a* – 60) is thus formed which is simultaneously the molecular ion of olefin *IV*. On further fragmentation of this ion the ions *b*, *c* and *d* are formed. In another way ions *e* (or *e* – 15) are formed by the fragmentation of the molecular ion of ethers. They splitt off a molecule of water and the radical $\text{CH}_2\text{OCOCH}_3$ under formation of a new five-membered ring (ions *f*). In addition to characteristic ions which are listed in Table II the spectra of all substances measured contain the ions $\text{M}-15$, $\text{M}-60$ and $\text{M}-73$. Analogous fragmentation of the ring C, considered for the formation of ions *b*, *c* and *d*, are

TABLE II
Characteristic Fragments of the Mass Spectra^a

Compounds	M^+	<i>a</i>	<i>a</i> – 60	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>e</i> – 15	<i>f</i>
<i>IX</i>	542 (1.2)	484 (3)	424 (24)	249 (6)	189 (37)	161 (44)	292 (1.5)	277 (6.5)	201 (12.5)
<i>II</i>	528 (2.5)	484 (2.5)	424 (6)	249 (6)	189 (14)	161 (13)	278 (13)	263 (44)	187 (15)
<i>X</i>	514 (2.6)	484 (0)	424 (3)	249 (45)	189 (17)	161 (24)	264 (10)	249 (45)	173 (12)
<i>IV</i>	484 (2)	484 (2)	424 (22)	249 (3.3)	189 (17)	161 (32)	—	—	—

^a The values are given in m/e ; those in parentheses express the relative abundance, referred to the base peak, which in all cases was the ion m/e 43 ($\text{C}_2\text{H}_3\text{O}$). The composition of all ions discussed was checked by the HR method, with an error less than 5 p.p.m. The spectra were measured on a Varian MAT 311 instrument, energy of ionizing electrons: 70 eV, ionizing current: 1 mA, ion source temperature: 200°C, temperature of direct inlet system: 120–180°C.

known¹³ from the mass spectra of 20(29)-lupene derivatives. The formation of the ions of type *f* with a new five-membered ring is evidently typical of 12 β ,20-epoxy derivatives *II*, *IX* and *X* and its general occurrence has been proved¹⁴ in the fragmentation of substituted tetrahydropyrane derivatives.

From the mechanistical point of view the comparison of the reaction of 20-lupanol derivatives with lead tetraacetate and in Barton's reaction¹⁻³ leads to the following conclusion: In both cases the C₍₂₀₎-O radical is formed in the first phase. This radical is unable – even when the steric interaction of substituents on C₍₂₀₎ (*i.e.* in dinoranol *VIII*) are minimized – to undergo a 1,4-transfer of hydrogen from C₍₂₁₎; the shortest distance at which 21 α H can approach (about 2 Å) is evidently too long for this transfer. For sterical reasons the usual 1,5-hydrogen transfer¹⁵ does not take place either, but the unusual 1,6-transfer of hydrogen *via* a seven-membered cycle transition state is favoured.

Both investigated types of reactions show an unusual position of the 20R-noranol *III*. Its methyl group on C₍₂₀₎ should assume the unfavourable² antiperiplanar conformation with respect to 19H during the transfer of 12 β H into the oxygen radical. Therefore no oximino derivative is formed in Barton's reaction, and in the reaction with lead tetraacetate the products of β -fragmentation are formed. Hence, both reactions have the same transition states the sterical requirements of which are almost identical. The extent of β -fragmentation, observed in the reaction with lead tetraacetate indicates that in this reaction the mechanism with a developed radical character of the transition state is preferred.

EXPERIMENTAL

The melting points were determined on a Kofler block. Optical rotations were measured in chloroform on an automatic polarimeter ETL-NPL (Bendix-Ericsson) with a 1–2° accuracy. The infrared spectra were measured in chloroform on a UR-10 or UR-20 (Zeiss, Jena GDR) spectrophotometer; the ultraviolet spectra were measured on a Unicam SP-700 apparatus. ¹H-NMR spectra were measured with a Varian HA-100 and a Tesla 80-MHz instrument. The mass spectra were recorded with a Varian MAT-311 spectrometer. For column chromatography neutral alumina (Reanal act. II) and silica gel according to Pitra (80–120 μ) were used. For thin-layer chromatography silica gel G (Merck) was used. Solutions of reaction products were dried over sodium sulfate. Samples for analysis were dried over phosphorus pentoxide at 80°C and 0.1–1 Torr for 8–12 hours. The identity of the samples prepared by different procedures was checked by mixture melting point determination, thin-layer chromatography and infrared spectra measurements.

Reaction of Noranol *I* with Lead Tetraacetate

Lead tetraacetate (600 mg) was added to solution of noranol *I* (600 mg) (ref.¹⁶) in benzene (60 ml) and the mixture was refluxed under stirring for three hours. Another 500 mg of lead tetraacetate were added and the mixture refluxed for an additional 6.5 hours. This was repeated again and the mixture was poured into water and the product extracted with ether. The organic phase

was washed with a saturated solution of sodium hydrogen carbonate (3 times) and water. The residue was chromatographed on a column of alumina (60 g). Benzene eluted 40 mg of trinorolefin *IV*, m.p. 191–194°C (ether), $[\alpha]_D -4^\circ$ (*c* 0.50). Further elution with benzene gave 300 mg of norether *II*, m.p. 218–221°C, $[\alpha]_D 0^\circ$ (*c* 1.11). IR spectrum: 1728, 1260 1035 (CH₃COO) cm⁻¹. For C₃₃H₅₂O₅ (528.7) calculated: 74.96% C, 9.91% H; found: 74.54% C, 10.04% H.

Reaction of Noralcohol *III* with Lead Tetraacetate

The reaction was carried out with 600 mg of noralcohol *III* (ref.¹⁶) in the same manner as in the case of noralcohol *I*. The residue was chromatographed on a column of alumina (60 g) with benzene. Yield, 270 mg of trinorolefin *IV*, m.p. 194–197°C (ether), $[\alpha]_D -4.8^\circ$ (*c* 1.26); IR spectrum: 1730, 1262, 1033 (CH₃COO) cm⁻¹. For C₃₁H₄₈O₄ (484.7) calculated: 76.81% C, 9.98% H, found 76.94% C, 10.14% H. Further elution with benzene gave 120 mg of amorphous acetate *VI*, $[\alpha]_D 0^\circ$ (*c* 0.91). IR spectrum: 1728, 1250, 1040 (CH₃COO) cm⁻¹. For C₃₃H₅₂O₆ (544.7) calculated: 72.75% C, 9.62% H; found: 72.98% C, 9.85% H.

3β,28-Diacetoxy-20,29,30-trinorlup-18-ene-21-one (*V*)

200 mg of the chromium tioxide–pyridine complex¹¹ were added to a solution of 94.7 mg of trinorolefin *IV* in 7 ml of dichloromethane and the reaction mixture was stirred for 18 hours. It was then poured into water and the product extracted with ether and the extract washed with water, 5% sodium carbonate solution (3 times) and again with water. The residue (94 mg) gave on crystallization from light petroleum 70 mg of unsaturated ketone *V*, m.p. 216–219°C, $[\alpha]_D -55^\circ$ (*c* 0.62). IR spectrum: 1726, 1250, 1037 (CH₃COO), 1690, 1615 (C=C–C=O) cm⁻¹. UV spectrum (cyclohexane): λ_{\max} 226 nm, log ϵ 4.31 CD (dioxan): $\Delta_\epsilon -1.47$. For C₃₁H₄₆O₅ (498.7) calculated: 74.66% C, 9.30% H; found: 74.38% C, 9.52% H.

Reaction of Alcohol *VII* with Lead Tetraacetate

Lead tetraacetate (1000 mg) and dried calcium carbonate (1000 mg) were added to a solution of alcohol *VII* (500 mg; ref.^{3,17}) in 100 ml of benzene and the mixture refluxed under stirring for 9 hours. After cooling and filtration the residue on the filter was washed with ether; the combined organic fractions were washed with saturated sodium carbonate solution (twice) and water. The residue was chromatographed on a column of alumina (45 g). Light petroleum eluted 150 mg of trinorolefin *IV*, m.p. 196–198°C, $[\alpha]_D -3^\circ$ (*c* 0.61). A light petroleum–ether mixture (9 : 1) eluted 250 mg of ether *IX*, m.p. 261–264°C (ether–light petroleum), $[\alpha]_D +16^\circ$ (*c* 0.63). IR spectrum: 1734, 1260, 1032 (CH₃COO) cm⁻¹. For C₃₄H₅₄O₅ (542.8) calculated: 75.23% C, 10.03% H; found: 75.56% C, 9.97% H.

Reaction of Dinoralcohol *VIII* with Lead Tetraacetate

A suspension of lead tetraacetate (1.2 g) in a solution of dinoralcohol *VIII* (520 mg; ref.²) in benzene (50 ml) was refluxed under stirring for 7 hours. The reaction mixture was worked up in the same manner as in the case of noralcohol *I*. The residue was chromatographed on a column of silica gel (50 g). Elution with light petroleum–ether (9 : 1) gave 15 mg of trinorolefin *IV*, m.p. 193–195°C (ether), $[\alpha]_D -1^\circ$ (*c* 0.67). Further elution with the same solvent mixture afforded 260 mg of dinorether *X*, m.p. 203–205°C (light petroleum), $[\alpha]_D -4.1^\circ$ (*c* 1.45). IR spectrum: 1725, 1256, 1035 (CH₃COO) cm⁻¹. For C₃₂H₅₀O₅ (514.7) calculated: 74.67% C, 9.79% H; found: 74.45% C, 9.65% H.

Methyl Ester of 3 β ,28-Diacetoxy-12-oxo-29,30-dinorlupan-20-oic Acid (XII)

A solution of dinorether *X* (100 mg) and chromium trioxide (100 mg) in acetic acid (6 ml) was heated at 45°C for 48 hours. Excess oxidation reagent was decomposed with 1 ml of methanol and the mixture was poured into water. The product was extracted with dichloromethane, the organic phase was washed with a solution of sodium hydrogen carbonate (5 times) and water. The residue (70 mg) was chromatographed on a preparative thin-layer plate with silica gel (20 \times 20 cm) in benzene-acetone (4 : 1). Yield 45 mg of amorphous acid *XI*, $[\alpha]_D + 8.8$ (*c* 1.03). IR spectrum: 1735, 1260, 1033 (CH₃COO), 3500, 3300–2700, 1715 (COOH), 1715, 1435 (—COCH₂) cm⁻¹. On reaction with diazomethane oily methyl ester *XII* was prepared, $[\alpha]_D - 4.8^\circ$ (*c* 0.83). IR spectrum: 1728, 1257, 1034 (CH₃COO), 1728, 1442 (COOCH₃), 1710 inflexion (CO) cm⁻¹. For C₃₃H₅₀O₇ (558.7) calculated: 70.93% C, 9.02% H; found: 70.99% C, 8.98% H.

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