PREPARATION OF ISOMERIC 2-METHYL-1-OXOTRITERPENOIDS OF THE 18α-OLEANANE SERIES; CONFORMATION OF RING A*

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Received January 18th, 1986

2β-Methyl-1α-hydroxy (*XV*) and two isomeric 2-methyl-1-oxo derivatives (*XVI* and *XVII*) of 19β,28-epoxy-18α-oleanane were prepared from 19β,28-epoxy-2-methyl-18α-olean-1-en-3-one (*XI*) *via* 3β-chloro derivative *XIII* and unsaturated 1α-hydroxy derivative *XIV*. Allylic oxidation of 2-methyl-2-ene *VI* was studied as an alternative approach to compound *XIV*. Oxidation with selenium dioxide led to diol *VII*, aldehyde *VIII* and alcohol *IV*, oxidation with tert-butyl chromate gave epoxy ketone *X*. According to ^{1}H NMR and CD data, ring A in the 2β-methyl derivatives *XV* and *XVI* exists in a boat conformation. The 2α-methyl ketone *XVII* (chair form) is more stable than its 2β-epimer *XVI* (boat form): only 9 ± 3% of *XVI* exists at equilibrium. Conformation of ring A in the unsubstituted 1-ketone *I* and differences in stability of the boat form in 1,2- and 2,3-disubstituted triterpenoids are discussed.

In our recent study[1] on conformation of the ring A in 1-oxotriterpenoids we have used the epimeric 2-methyl derivatives of 19β,28-epoxy-18α-oleanan-1-one *XVI* and *XVII* as model compounds for the boat and chair form of the ring A, respectively. Conformation of the ring A in these ketones has been derived from vicinal interproton coupling constants. In the present communication we describe the preparation of the 2-methyl ketones *XVI* and *XVII* and bring further evidence on the conformation of ring A in these ketones and some other compounds.

We tried three methods for preparation of the 2-methyl ketones *XVI* and *XVII*. The first, successfully used by us[2,3] in the synthesis of analogous 2-methyl-3-oxo-triterpenoids, consists in Claisen condensation of 3-ketones leading to hydroxymethylene ketones, or in Mannich reaction affording methylene ketones, and subsequent hydrogenation. However, attempted application of this method to the known[4,5] 19β,28-epoxy-18α-oleanan-1-one (*I*) was unsuccessful. We failed to obtain the hydroxymethylene ketone *II* by Claisen condensation of *I* with ethyl formate in the presence of sodium hydride or triphenylmethyl sodium. Attempts to prepare the methylene ketone *III* by Manich reaction of *I* with paraformaldehyde and di-

* Part LXXIX in the series Triterpenes; Part LXXVIII: This Journal *51*, 2029 (1986).

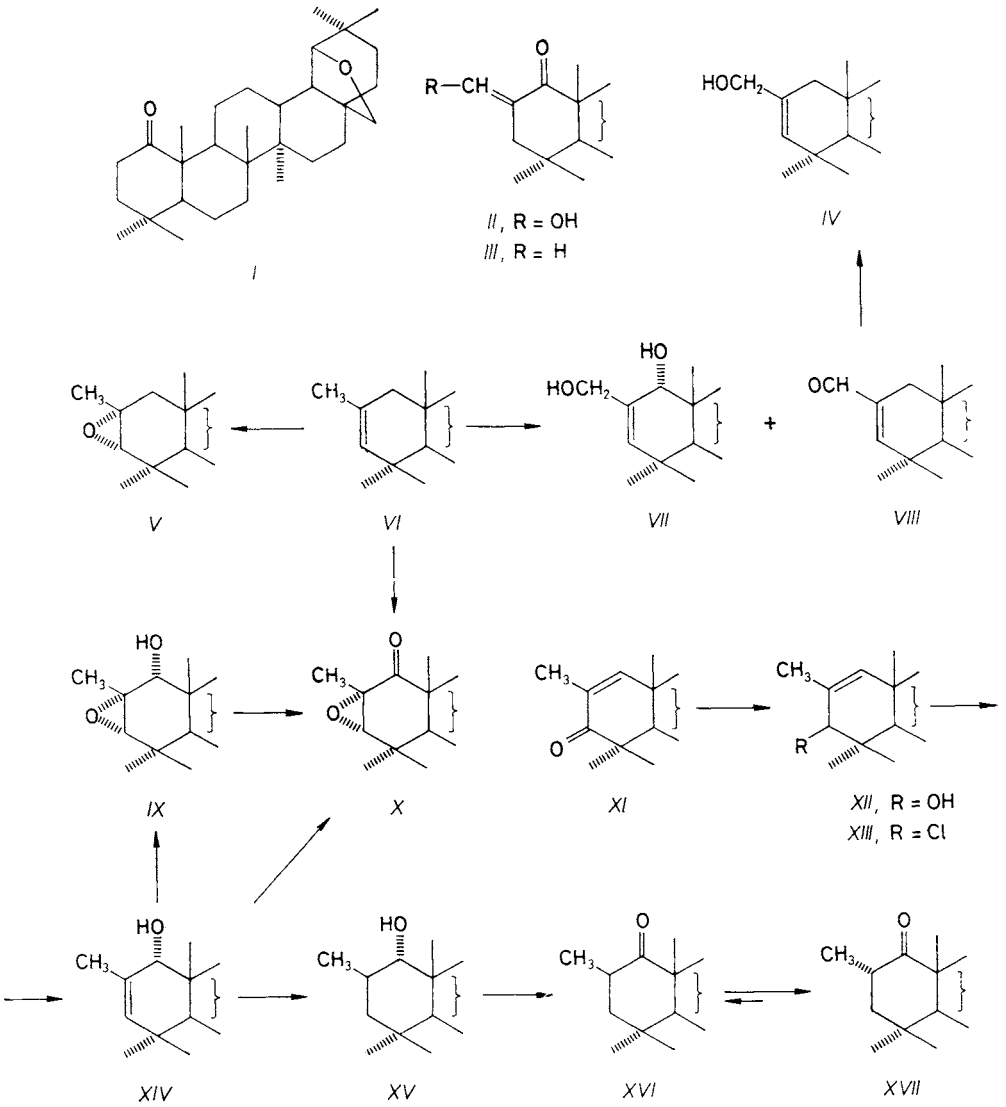
methylamine hydrochloride in boiling dioxane resulted in quantitative recovery of *I* even after refluxing for 100 hours, whereas the analogous 3-oxo derivatives reacted completely already within 10 hours (see refs[2,3]).

The second possible way to 2-methyl-1-oxo derivatives consists in introduction of an oxygen functionality (such as hydroxyl or carbonyl group) into the position 1 by allylic oxidation of the 2-methyl-2-ene derivative *VI* (for preparation see ref.[2]), followed by hydrogenation of the 2(3)-double bond. Selenium dioxide or Cr(VI)--compounds are currently employed for the allylic oxidation of analogous triterpenoid olefins without methyl at $C_{(2)}$ (see refs[4,6] and references therein). Unfortunately, oxidation of the olefin *VI* led to products unsuitable for the planned synthesis of 2-methyl-1-oxo derivatives: reaction with selenium dioxide in dioxane afforded diol *VII* together with the α,β-unsaturated aldehyde *VIII* and a small amount of 2-hydroxymethyl compound *IV*, but no 1α-hydroxy derivative *XIV* or the corresponding α,β-unsaturated ketone. For comparison, we prepared the compound *IV* by reduction of aldehyde *VIII* with sodium borohydride. Obviously, the methyl group in position 2 of olefin *VI* is oxidized faster than the methylene in position 1. This fact is at variance with the Guillemonat's rules[7] and results probably from steric hindrance of the methylene group. Oxidation of the olefin *VI* with Cr(VI)-derivatives led to complex mixtures containing also products in which the ether bridge in the ring E had been oxidized to a lactone grouping. Oxidation with tert-butyl chromate afforded epoxy ketone *X* as the principal product.

The third, successful, method was based on introduction of the 1α-hydroxy group by substitution of the 3β-chlorine atom in *XIII*, combined with allylic rearrangement (for an analogy see ref.[8]). The starting 19β,28-epoxy-2-methyl-18α-olean-1-en-3-one (*XI*), obtained according to ref.[2], was reduced with lithium aluminium hydride to the hydroxy derivative *XII* which on treatment with phosphorus pentachloride in acetic acid gave the chloro derivative *XIII*. This was converted with potassium hydroxide in aqueous dioxane into the unsaturated 1α-alcohol *XIV* in an almost quantitative yield. Catalytic hydrogenation of *XIV* led to the 2β-methyl-1α-ol *XV* which on oxidation with sodium dichromate furnished the 2β-methyl ketone *XVI*. The isomeric 2α-methyl ketone *XVII* was obtained by base-catalysed isomerization of the 2β-isomer *XVI* and separated chromatographically.

Attempts to oxidize the 1α-hydroxy derivative *XIV* to the α,β-unsaturated ketone with Cr(VI)-compounds failed: oxidation with chromium trioxide in acetic acid afforded the epoxy ketone *X*, whereas oxidation with sodium dichromate in a buffered medium (acetic acid–sodium acetate) afforded the 2α,3α-epoxy-1α-ol *IX*. Compound *IX* was also prepared from *XIV* by treatment with 3-chloroperoxybenzoic acid. Oxidation of *IX* with chromium trioxide gave the epoxy ketone *X*. The mentioned reactions show that the 1α-hydroxy derivative *XIV* behaves anomalously: epoxidation of the 2(3) double bond is faster than oxidation of the hydroxy group to the ketone. Contrariwise, analogous 2(3)-unsaturated 1α-hydroxytriterpenoids

without methyl group at $C_{(2)}$ (such as *XVIII*) on reaction with chromium trioxide and related reagents generally give α,β-unsaturated ketones[4,8].



Structure of the prepared compounds was confirmed by IR and ^{1}H NMR spectra (Table I). For comparison, Table I includes also data for the starting olefin *VI*, the epoxide *V* (prepared from *VI* by treatment with 3-chloroperoxybenzoic acid) and the unsaturated alcohol *XVIII* (described in ref.[8]). Configuration of substituents

on the ring A was assigned using the α-attack rule (in epoxidations, hydrogenation, allylic oxidation and substitution combined with allylic rearrangement) and analogies [4,6,8,9]. The α-configuration of the hydroxyl at $C_{(1)}$ in compounds *VII*, *IX*, *XIV*, and *XV* follows also from the ^{1}H NMR spectra of unsaturated alcohols *VII* and *XIV*: the $C_{(1)}H$ signal appears as a sharp singlet and decoupling experiments revealed neither $C_{(1)}H$–$C_{(3)}H$ allylic coupling nor long-range coupling between $C_{(1)}H$ and 10β-CH_3. This fact is in accord with the pseudoequatorial position of the 1β-hydrogen atom. Similarly, no allylic coupling was found for the model compound *XVIII* for

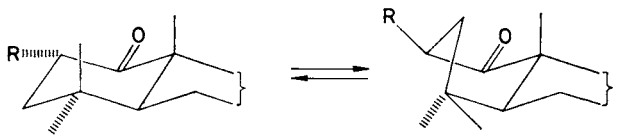
TABLE I
Proton NMR parameters, $\delta(J)$

Compound[a]	$C_{(1)}H$	$C_{(2)}CH_n$[b]	$C_{(3)}H$	Skeletal CH_3[c]
IV	2·01 d[d] (16·5)	3·94 s	5·36 bs	0·81, 0·85, 0·89, 0·93, 0·94, 0·97, 1·01
V	1·83 d[d] (14)	1·31 s	2·61 s	0·80, 0·84 d (0·6), 0·88, 0·935, 0·945, 0·99, 1·06
VI	1·82 d[d] (16·5)	1·60 d (1·2)	5·07 bs	0·80, 0·84, 0·85, 0·92, 0·92, 0·94, 1·00
VII	3·71 s	4·14 s	5·47 s	0·79, 0·80, 0·88, 0·94, 0·98, 1·01, 1·03
VIII	2·51 d[d] (16·9)	9·44 s	6·45 d (2·2)	0·78, 0·81, 0·92, 0·94, 1·01, 1·02, 1·10
IX	3·40 s	1·44 s	2·87 s	0·76, 0·79, 0·93, 0·93, 0·97, 0·98, 1·04
X	—	1·44 s	2·90 s	0·81, 0·94, 0·94, 1·00, 1·09, 1·13, 1·16
XIV	3·41 s	1·78 d (1·4)	5·19 q (1·4)	0·79, 0·79, 0·85, 0·94, 0·95, 0·98, 1·02
XV	3·04 d (6·3)	1·08 d (5·8)	[e]	0·80, 0·85, 0·89, 0·93, 0·94, 0·96, 1·01
XVI	—	1·01 d (6·7)	[f]	0·79, 0·90, 0·92, 0·93, 1·02, 1·04, 1·10
XVII	—	0·93 d (6·2)	[f]	0·81, 0·87, 0·93, 0·96, 1·02, 1·10, 1·29
XVIII	3·65 d (5)	[g]	5·52 d (10)	0·80, 0·84, 0·89, 0·94, 0·98, 0·98, 1·03

[a] All spectra exhibit a singlet at δ 3·54–3·55 ($C_{(19)}H$), together with a doublet at δ 3·43–3·45 and a broad doublet at δ 3·77–3·79 (J = 7·8 Hz, $C_{(28)}H_2$); [b] n = 1, 2 or 3, according to the structure; [c] singlets, unless stated otherwise; [d] signal of one of the $C_{(1)}$ protons, signal of the other proton is overlapped; [e] signal not found; [f] see ref.[1]; [g] $C_{(2)}H$: 5·73 dd ($J \sim$ 10 and $J \sim$ 5 Hz).

which the configuration of the hydroxyl had been determined previously in a chemical way[4,6,8,9]. Spectra of all the unsaturated alcohols *VII*, *XIV*, and *XVIII* contain a broad doublet of doublets at δ 2·22 ($J \sim 11$ and ~ 4 Hz), obviously due to an axial hydrogen close to the 1α-hydroxy group (probably 9α-H). The *cis*-relation of the hydroxyl and the epoxide oxygen in *IX* is confirmed by the presence of an intramolecularly hydrogen-bonded hydroxyl band in the infrared spectrum (ν(OH) = = 3 543 cm^{-1}; in CCl_4). A similar value of ν(OH) was found[9] for the analogous 1α-hydroxy-2α,3α-epoxide without methyl group at $C_{(2)}$ (3 552 cm^{-1}) whereas the second possible *cis*-derivative (1β-hydroxy-2β,3β-epoxide) showed a completely different value[9] (3 602 cm^{-1}).

The ring A in 2β-methyl-1α-ol *XV* exists in a boat form as follows from the vicinal coupling constant $J_{1\beta,2\alpha} = 6{\cdot}3$ Hz, similar to that for the analogous 2β-bromo-1α-ol and its acetate (6·0 Hz), for which the boat form has been proved also by other methods[10]. The chair form in 1α,2β-disubstituted triterpenoids is characterized by the value of $J_{1\beta,2\alpha} = 2{\cdot}5-3$ Hz (see ref.[10]). The boat form *B** in the 2β-methyl ketone *XVI* and the chair conformation *C* in the 2α-methyl ketone *XVII* were derived from the coupling constants already earlier[1]; the conformation of the ring A in these ketones agrees with that of the corresponding 2-bromo-1-oxo derivatives *XIX* and *XX* (see ref.[10]). Also the CD spectra (Table II) are in accord with the mentioned conformations. The chair form of the 2α-isomers (*C*) is characterized by a weak positive Cotton effect, whereas the boat in the 2β-isomers (*B*) by a strong negative



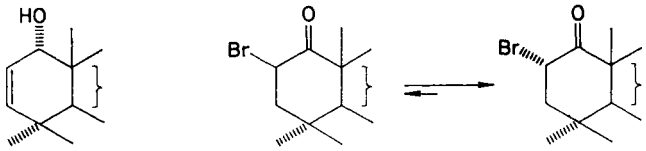
C (2α-isomers) ⇌ *B* (2β-isomers)

R = Br or CH_3

Cotton effect (see also refs[10,13]). For the 2α-isomers *XVII* and *XX*, where the substituent at $C_{(2)}$ is equatorial and lies close to the carbonyl nodal plane, the $\Delta\varepsilon$ values agree well. The difference in the $\Delta\varepsilon$ values for the 2β-isomers *XVI* and *XIX* may be caused by a less equatorial character of the substituent R in the boat form (in the extreme case the $C_{(2)}$—R bond may be bisectional): the substituent is farther from the nodal plane and thus the effect of Br and CH_3 on the dichroic absorption

* For sake of simplicity, formula *B* depicts only one of the possible classical boat forms of the ring A. In actual fact, the boat is somewhat twisted[1,10,11], its geometry roughly corresponding to the $T_1(B^3)$ form, considered by Tsuda and Kiuchi[12] for 3-oxotriterpenoids.

may be different. Another possible explanation is that the boat forms in the 2β--bromo ketone *XIX* and in the 2β-methyl ketone *XVI* differ somewhat in geometry; since in these structures the Cotton effect is determined mainly by chirality of the boat form of the ring A, even small changes in geometry may considerably influence the value of Δε. The fact that in the 2β-methyl derivatives *XV* and *XVI* as well as in the corresponding 2β-bromo compounds the ring A exists in a boat conformation shows that in 1,2-disubstituted triterpenoids the 2β-methyl group destabilizes the chair form approximately to the same extent as does the 2β-bromo substituent. The same conclusion was obtained by us already earlier for the analogous 2,3-disubstituted triterpenoids[2].



XVIII *XIX* *XX*

Compared with 2-methyl-3-oxotriterpenoids, the 2-methyl-1-oxo derivatives *XVI* and *XVII* are much more stable. They do not isomerize under acidic conditions effecting rapid isomerization of 2-methyl-3-oxotriterpenoids[2,3]. The higher stability of the ketones *XVI* and *XVII* can be obviously ascribed to a more difficult enolization of 1-oxo derivatives than of 3-oxo compounds (see also ref.[13]). In an alkaline medium, the ketones *XVI* and *XVII* give an equilibrium mixture containing (according to optical rotation) 9 ± 3% of the 2β-isomer *XVI*. For 2-methyl-3-oxo derivatives of 19β,28-epoxy-18α-oleanane we found[2] 52 ± 4%, and for analogous 28-lupanenitrile derivatives 47 ± 3% of the 2β-isomer[3]. Since the ring A in all 2β-isomers exists in the boat conformation whereas in all 2α-isomers it adopts the chair form,

TABLE II
CD data for 1-oxo derivatives (in dioxane)

Ketone	*I*[a]		*XVI*	*XVII*	*XIX*[a]	*XX*[a]
Substituent on $C_{(2)}$	–		β-CH_3	α-CH_3	β-Br	α-Br
λ_{max}, nm	311	~275	306	292	300	286
Δε	−0·43	+0·09	−2·8	+0·8	−1·5	+0·77

[a] See also refs[4,10].

the mentioned values agree with the general rule[5,10] that in 1,2-disubstituted triterpenoids and 4,4-dimethylsteroids the boat is less preferred than in the corresponding 2,3-disubstituted compounds.

The composition of the equilibrium mixture of 2-methyl ketones *XVI* and *XVII* agrees with that found[5] for the 2-bromo ketones *XIX* and *XX* (9 ± 2% of the 2β--isomer *XIX*). As follows from the above-mentioned considerations on the conformation of ring A in the ketones *XVI*, *XVII*, *XIX*, and *XX*, the isomerization equilibrium between the 2α- and 2β-isomers (*XVII* ⇄ *XVI*, *XX* ⇄ *XIX*) can in principle be regarded as an equilibrium between the forms *C* and *B*. The same position of the equilibrium *C* ⇄ *B* for R = Br and CH_3 indicates that the equilibrium is determined by energy difference between the chair and boat form of ring A in the 1-oxo compound rather than by the character of the substituent R (this question is discussed in more detail for the analogous 3-ketones in ref.[11]). We can thus expect that in unsubstituted ketone *I* the chair form *C* (R = H) will highly predominate over the boat conformation *B* (R = H). The same conclusion was obtained from the vicinal coupling constants $J_{H2,H3}$ (ref.[1]). Minor amounts of boat form in the conformational equilibrium may be responsible for the weak negative maximum at 311 nm in the CD spectrum of ketone *I* (Table II).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotation was measured on an automatic polarimeter ETL-NPL (Bendix–Ericsson) in chloroform (*c* 0·3—1·0); accuracy ±2°. Infrared spectra were recorded on a UR-10 (Zeiss, Jena) spectrometer in chloroform, unless stated otherwise. Ultraviolet spectra were taken on a Unicam SP700 spectrometer and CD spectra on a Roussel–Jouan Dichrographe II. ^{1}H NMR spectra were measured on Varian HA 100 or Varian XL 200 spectrometer in deuteriochloroform with tetramethylsilane as internal standard. The coupling constants were obtained by first order analysis. Column chromatography was performed on silica gel Silpearl (Kavalier, Votice), thin-layer chromatography (TLC) on silica gel G according to Stahl (Merck). The "usual work-up procedure" means dilution of the reaction mixture with water, extraction with ether, washing with water (or saturated solution of sodium hydrogen carbonate or dilute hydrochloric acid and water), drying over sodium sulfate and evaporation of the solvent. Analytical samples were dried over phosphorus pentoxide under diminished pressure at 100°C.

19β,28-Epoxy-2-hydroxymethyl-18α-olean-2-ene (*IV*)

Sodium borohydride (0·25 g) in methanol (25 ml) was added to a solution of aldehyde *VIII* (0·14 g) in benzene (25 ml). After standing for 10 h at room temperature, the excess hydride was destroyed with saturated solution of ammonium chloride and the benzene layer was separated, washed with water and dried over sodium sulfate. Evaporation of the solvent gave hydroxy derivative *IV* (0·1 g), m.p. 242—243°C (ether–methanol); $[\alpha]_D$ +71°. IR spectrum: 1 032 (C—O—C), 3 610 cm^{-1} (OH). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 81·67% C, 11·02% H.

2α,3α; 19β,28-Diepoxy-2β-methyl-18α-oleanane (*V*)

A solution of 19β,28-epoxy-2-methyl-18α-olean-2-ene (*VI*; 0·15 g; see ref.[2]) and 3-chloroperoxybenzoic acid (0·15 g) in dichloromethane was allowed to stand overnight at 0°C, diluted with chloroform, washed with 10% potassium bisulfite and water and dried over sodium sulfate. Yield 0·12 g; m.p. 234–236°C (chloroform–methanol); $[\alpha]_D$ +43°. IR spectrum: 1 030 cm^{-1} (C—O—C). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 81·99% C, 10·98% H.

19β,28-Epoxy-2-hydroxymethyl-18α-olean-2-en-1α-ol (*VII*)
and 19β,28-Epoxy-2-formyl-18α-olean-2-ene (*VIII*)

Selenium dioxide (0·35 g) was added to a solution of olefin[2] *VI* (0·35 g) in dioxane (100 ml). After reflux for 30 min, the mixture was cooled, diluted with water to three times of the original volume and extracted with ether. The ethereal solution was mixed with 1 mol l^{-1} potassium hydroxide solution, followed immediately with 5% silver nitrate solution. The mixture was briefly shaken and the aqueous layer, containing the precipitated silver oxide and selenide, was separated. The ethereal layer was washed with a solution of potassium bisulfite and water and dried over sodium sulfate. The solvent was evaporated and the residue (0·33 g) chromatographed on silica gel (10 g) in light petroleum–ether (8 : 1). Aldehyde *VIII* (0·13 g) was eluted first; m.p. 276–285°C (decomposition) (dichloromethane–methanol); $[\alpha]_D$ +85°. IR spectrum: 1 030 (C—O—C), 1 649 (C=C), 1 680, 2 722, 2 824 cm^{-1} (CHO). UV spectrum (in cyclohexane): λ_{max} = 228 nm (ε 14 300). For $C_{31}H_{48}O_2$ (452·7) calculated: 82·24% C, 10·69% H; found: 82·11% C, 10·71% H. Further fractions contained hydroxy derivative *IV* (1 mg), m.p. 241–243°C, identical (TLC) with the authentic sample prepared above. The most polar compound eluted was diol *VII* (0·15 g), m.p. 274–276°C (ether–methanol); $[\alpha]_D$ +117°. IR spectrum: 1 033 (C—O—C), 3 614 cm^{-1} (OH). For $C_{31}H_{50}O_3$ (470·7) calculated: 79·10% C, 10·71% H; found: 78·98% C, 10·64% H.

2α,3α; 19β,28-Diepoxy-2β-methyl-18α-oleanan-1α-ol (*IX*)

A) Sodium acetate trihydrate (0·6 g), hydroxy derivative *XIV* (0·15 g) and sodium dichromate dihydrate (0·3 g) were dissolved in acetic acid (25 ml) in the given order. After standing at room temperature for 2 h, the mixture was worked up in the usual manner and the crude product was chromatographed on silica gel (10 g). Benzene with 2% ether eluted epoxyalcohol *IX* (0·1 g), m.p. 260–261°C (chloroform–ether); $[\alpha]_D$ +60°. IR spectrum: 1 029 (C—O—C), 3 530 cm^{-1} (OH); ν(OH) = 3 543 cm^{-1}, $\Delta\nu_{1/2}$ = 37 cm^{-1}, ε = 73 (in tetrachloromethane, $c = 2 \cdot 10^{-3}$ mol $\cdot l^{-1}$, Unicam SP 700). For $C_{31}H_{50}O_3$ (470·7) calculated: 79·10% C, 10·71% H; found: 79·26% C, 10·75% H.

B) A solution of *XIV* (90 mg) and 3-chloroperoxybenzoic acid (0·1 g) in dichloromethane (2 ml) was allowed to stand for 24 h at 0°C, diluted with dichloromethane, shaken with solid sodium hydrogen carbonate and filtered through alumina. Removal of the solvent and crystallization from dichloromethane–methanol afforded *IX* (80 mg), m.p. 258–260°C; $[\alpha]_D$ +62°, identical (IR spectra and TLC) with the sample obtained according to procedure *A*.

2α,3α; 19β,28-Diepoxy-2β-methyl-18α-oleanan-1-one (*X*)

A) To a solution of olefin[2] *VI* (0·1 g) in a mixture of acetic acid (10 ml), tetrachloromethane (10 ml) and acetic anhydride (1 ml) was added a solution of tert-butyl chromate (5 ml; prepared by dissolving 7 g of chromium trioxide in 15 g of tert-butyl alcohol and adding 50 ml of acetic acid, 60 ml of tetrachloromethane and 20 ml of acetic anhydride). The mixture was heated to

80°C for 4 h, cooled, diluted with chloroform (20 ml), washed with water, saturated solution of oxalic acid, solution of sodium hydrogen carbonate, water, and dried over sodium sulfate. The solvent was distilled off and the residue chromatographed on silica gel (10 g). Light petroleum–ether (6 : 1) eluted successively the unreacted olefin *VI* (6 mg), a mixture of unidentified compounds (20 mg), and then the epoxy ketone *X* (50 mg), m.p. 278–280°C (chloroform–methanol); $[\alpha]_D$ +55°, IR spectrum: 1 030 (C—O—C), 1 711 cm^{-1} (C=O). For $C_{31}H_{48}O_3$ (468·7) calculated: 79·43% C, 10·32% H; found: 79·47% C, 10·33% H.

B) Chromium trioxide (0·1 g) in acetic acid (5 ml) was added to a solution of *XIV* (0·16 g) in acetic acid (20 ml). After standing for 1·5 h at room temperature, the mixture was worked up as usual. Crystallization from chloroform–methanol afforded epoxy ketone *X* (0·13 g), m.p. 275–278°C, identical (TLC and IR spectrum) with the sample obtained by procedure *A*.

C) The title compound *X* was obtained by oxidation of epoxy alcohol *IX* (50 mg) with chromium trioxide or Jones reagent in acetic acid for 0·5 h followed by the usual work-up. The yield was 40 mg and 35 mg, respectively.

19β,28-Epoxy-2-methyl-18α-olean-1-en-3β-ol (*XII*)

19β,28-Epoxy-2-methyl-18α-olean-1-en-3-one (*XI*, ref.[2]; 3·0 g) was dissolved in boiling ether (150 ml), lithium aluminium hydride (3·0 g) was added to the cold solution and the mixture was refluxed for 1 h. The excess hydride was destroyed with ethyl acetate and saturated solution of sodium sulfate, the organic layer was washed with water and dried over sodium sulfate. The solvent was distilled off and the residue crystallized from chloroform–heptane to give *XII*, m.p. 218–220°C; $[\alpha]_D$ +73·5°. IR spectrum: 1 028 (C—O—C), 3 440, 3 610 and 3 630 cm^{-1} (OH). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 81·87% C, 11·11% H.

3β-Chloro-19β,28-epoxy-2-methyl-18α-olean-1-ene (*XIII*)

Phosphorus pentachloride (4·0 g) was added in portions during 10 min to a solution of *XII* (2·3 g) in acetic acid (200 ml). After standing at room temperature for 10 min, the mixture was worked up in the usual manner. Crystallization from benzene–ethanol afforded *XIII* (1·6 g) m.p. 192–194°C, $[\alpha]_D$ +168°. IR spectrum: 1 032 (C—O—C) cm^{-1}. For $C_{31}H_{49}ClO$ (473·2) calculated: 78·69% C, 10·44% H; found: 78·97% C, 10·53% H.

19β,28-Epoxy-2-methyl-18α-olean-2-en-1α-ol (*XIV*)

Potassium hydroxide (3·0 g) in water (75 ml) was added to a solution of *XIII* (1·5 g) in dioxane (500 ml). Water was added with stirring until the mixture was homogeneous. After refluxing for 4 h, the mixture was cooled and processed in the usual way. The residue (1·3 g) was chromatographed on silica gel (300 g) in benzene–ether (7 : 1) to afford *XIV* (1·0 g), m.p. 236–237°C (chloroform–light petroleum); $[\alpha]_D$ +103°. IR spectrum: 1 030 (C—O—C), 3 430, 3 600 cm^{-1} (OH). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 81·93% C, 11·18% H.

19β,28-Epoxy-2β-methyl-18α-oleanan-1α-ol (*XV*)

Unsaturated alcohol *XIV* (0·60 g) was hydrogenated for 32 h in acetic acid (65 ml) over Adams platinum oxide catalyst (0·4 g). The catalyst was filtered off, the filtrate diluted with water and the product collected and crystallized from chloroform-methanol and chloroform–light petroleum, yield 0·46 g of *XV*, m.p. 261–262°C; $[\alpha]_D$ +84°. IR spectrum: 1 030 (C—O—C), 3 620 cm^{-1} (OH). For $C_{31}H_{52}O_2$ (456·7) calculated: 81·52% C, 11·48% H; found: 81·80% C, 11·30% H.

19β,28-Epoxy-2β-methyl-18α-oleanan-1-one (*XVI*)

A mixture of *XV* (0·11 g), anhydrous sodium acetate (0·17 g), sodium dichromate dihydrate (0·17 g) and acetic acid (40 ml) was stirred at room temperature for 1 h. After standing for 4·5 h, it was worked up as usual and the residue crystallized from chloroform–methanol to give 80 mg of *XVI*, m.p. 212–214°C; $[\alpha]_D$ −5·5°. IR spectrum: 1 035 (C—O—C)), 1 699 cm^{-1} (C=O). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 81·69% C, 11·29% H.

19β,28-Epoxy-2α-methyl-18α-oleanan-1-one (*XVII*)

A mixture of *XVI* (0·12 g), potassium hydroxide (0·5 g), benzene (2 ml) and ethanol (10 ml) was refluxed for 6 h. After the usual work-up the residue was chromatographed on a column of silica gel (15 g) in light petroleum–ether (9 : 1) to afford 80 mg of *XVII*, m.p. 260–261°C (chloroform–methanol), $[\alpha]_D$ +108·5°. IR spectrum: 1 035 (C—O—C), 1 697 cm^{-1} (C=O). For $C_{31}H_{50}O_2$ (454·7) calculated: 81·88% C, 11·08% H; found: 82·01% C, 11·19% H. Further elution with the same solvent mixture afforded a mixture of ketones *XVI* and *XVII* (40 mg).

Equilibration of Methyl Ketones *XVI* and *XVII*

Potassium hydroxide in ethanol (5%; 10 ml) was added to a solution of *XVI* or *XVII* (0·02 to 0·10 g) in benzene (2 ml). After reflux for 6 h the mixture was worked up in the usual manner and the residue set to crystals on addition of several drops of methanol. The thus-obtained equilibrium mixtures of *XVI* and *XVII* were dried at 100°C for 3 h and had $[\alpha]_D$ +98 ± 2° (mean of six independent measurements).

The authors are indebted to Dr S. Hilgard, Charles University, Prague, for measurement of the IR *spectra and to Dr S. Vašíčková, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, for* CD *spectral measurements.*

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Translated by M. Tichý.