

TRITERPENES. XXX.*

STUDY FOR THE SYNTHESIS OF GLOCHIDIOL

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A way was devised for the preparation of triterpenic diols with hydroxy groups in positions 1β and 3α , or 1β and 3β from common triterpenic 3β -hydroxy derivatives. The study was carried out with the derivatives of $19\beta,28$ -epoxy- 18α -oleanane (XX) because of their easy availability. The work is a model study for the synthesis of glochidiol (I).

Glochidiol (I), $20(29)$ -lupene- $1\beta,3\alpha$ -diol, was the first isolated pentacyclic 1,3-dihydroxytriterpene¹. In past years a series of other 1,3-dihydroxytriterpenoids²⁻⁴ has been isolated. A general way for the preparation of $1\beta,3\alpha$ -dihydroxytriterpenes from current 3-hydroxy compounds has not yet been elaborated. The only described preparation of glochidiol is the reduction of glochidol (II) which is accessible only from natural material². In this paper we tried to find suitable procedures for the preparation of $1\beta,3\alpha$ -dihydroxy derivatives of pentacyclic triterpenes which would enable both the synthesis of glochidiol from lupeol, and the termination of the conformational study of triterpenic 1,3-dihydroxy compounds, carried out in our laboratory⁵. For this study we used derivatives of $19\beta,28$ -epoxy- 18α -oleanane (XX) because of their easy accessibility.

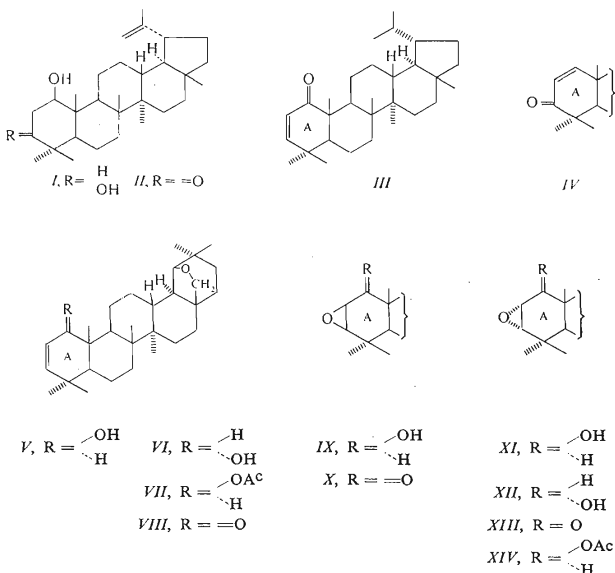
The preparation of 3-deoxy derivatives of pentacyclic triterpenoids substituted in position 1 with a hydroxy group or oxo group from 3-hydroxy derivatives has been the subject of a series of papers⁵⁻⁹. For our own work we could therefore start from $19\beta(28)$ -epoxy- 18α -olean-2-en- 1β -ol (V) (ref.⁸) which we described earlier. This compound on epoxidation with perbenzoic acid gave a chromatographically inseparable mixture of two isomeric epoxides IX and XI, which we separated successfully by fractional crystallisation. Both products differed substantially in the frequency of $\nu(\text{O}-\text{H})$. The hydroxy group of the first of them is not intramolecularly associated, as is evident from the comparison of the $\nu(\text{OH})$ of this substance with the corresponding values of substances XXI ($\Delta\nu(\text{OH})$ 3 cm^{-1}). In contrast to this the second isomer contains a hydroxy group bound internally ($\Delta\nu(\text{OH})$ 19 cm^{-1} , ϵ 119).

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Similar values of $\nu(\text{OH})$ were also found¹⁰ in epiepoxybufanamine (XXX) and epicrinamidine (XXIX) (Table I). Therefore we assign the structure of $2\alpha,3\alpha$ -epoxy derivative XI to the former and the structure of $2\beta,3\beta$ -epoxy derivative IX to the latter derivative.

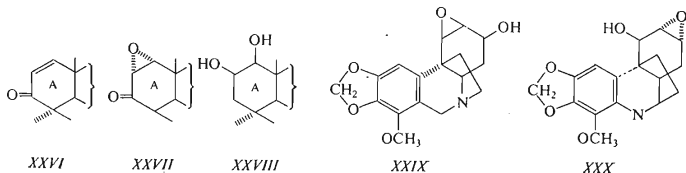
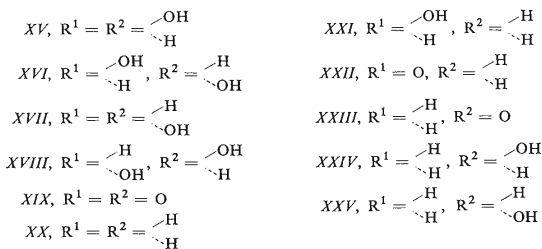
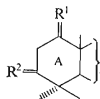
Although the mixture of both epoxides was formed during the reaction in all solvents used, its composition could still be influenced by their choice. Non-polar solvents (hexane, cyclohexane) furthered the formation of derivative IX, but the solvents with an acceptor character for the hydrogen bond proton (ether, dioxan) furthered the formation of derivative XI. In order to evaluate these effects quantitatively we carried out the epoxidation with 3-chloroperbenzoic acid and analysed the mixture of both epoxides formed quantitatively by infrared spectroscopy. When the reaction was carried out in hexane or cyclohexane the mixture of both epoxides contained 40% of substance IX and 60% of compound XI, while in ether the ratio was 28% of IX and 72% of XI and in dioxan 19% of IX and 81% of XI.

The effect of the allylic and homoallylic hydroxyl group on the course of epoxidation of the double bond has already been described by a number of authors¹²⁻¹⁵.



However, it has not yet been studied with unsaturated 1 β -hydroxy derivatives. The double bond of 19 β ,28-epoxy-18 α -olean-2-en-1 β -ol (V) is sterically more accessible from the α -side and therefore, for sterical reasons, the formation of epoxide XI can be expected. However, the hydroxy group forms an intermolecular hydrogen bond with the approaching peracid, thus furthering the formation of β -epoxide IX. If a solvent is used which abolishes the association of the hydroxy derivative with the peracid the orienting effect of the hydroxy group to epoxidation is suppressed and the sterical effects are furthered, which results in the formation of α -epoxide XI. During epoxidation of 19 β ,28-epoxy-18 α -oleanan-2-en-1 α -ol (VI) we obtained the previously described⁵ 2 α ,3 α :19 β ,28-diepoxy-18 α -oleanan-1 α -ol (XII). The nature of the solvent used does not manifest itself here because both the sterical effects and the hydroxyl group direct the approaching reagent in the same manner.

For further corroboration of the structure of the mentioned hydroxy epoxides IX, or XI, we oxidized them with chromium trioxide in pyridine to keto epoxides X or XIII, respectively. As we prepared compound XIII also by oxidation of 2 α ,3 α :19 β ,28-



-diepoxy-18 α -oleanan-1 α -ol (*XII*) it may be assumed that the assignment of the configuration of the epoxy group was correct. Both ketones, *X* and *XIII*, differ by the sign of the Cotton effect in the circular dichroism curves.

While substance *X* has a positive Cotton effect ($[\Theta]_{300} + 2667^\circ$), ketone *XIII* has a substantially stronger and negative Cotton effect ($[\Theta]_{323} - 3985$) which, in view of the reversed validity of the octant rule for α, β -epoxy ketones²¹ means a simultaneous confirmation of the epoxide cycles configuration.

TABLE II

Wavelengths and Molar Extinction Coefficients of $\pi \rightarrow \pi^*$ Transitions and $n \rightarrow \pi^*$ Transitions in the Ultraviolet Region and the Frequencies of $\nu(\text{C}=\text{O})$ in the Infrared Region of the Spectra

Compound	Position of carbonyl	$\pi \rightarrow \pi^*$ transition ^a λ_{max} , nm	ϵ^a	$n \rightarrow \pi^*$ transition ^b λ_{max} , nm	$\nu(\text{CO})^c$ cm^{-1}
<i>III</i>	1	220, 224	8 800, 7 870	337	1 683
<i>IV</i>	3	224, 229	9 600, 9 120	344	1 671
<i>VIII</i>	1	219, 224	8 300, 7 350	335.5	1 684
<i>XXVI</i>	3	224, 230	9 650, 9580	344	1 673
<i>XXII</i>	1	— —	—	294	1 703
<i>XXIII</i>	3	— —	— —	297	1 703

^a The first value for cyclohexane, the second for ethanol; ^b in tetrahydrofuran; ^c in chloroform.

TABLE I

Values of Frequencies and Molar Extinction Coefficients of $\nu(\text{O}-\text{H})$ Absorption

Substance	$\nu(\text{OH})$, (ϵ)	Substance	$\nu(\text{OH})$, (ϵ)
<i>IX</i>	3 602 (119)	<i>XXI</i>	3 621 (62) ^b
<i>XI</i>	3 618 (57)	<i>XXIV</i>	3 636 (43) ^b
<i>XII</i>	3 552 (67)	<i>XXV</i>	3 640 (56) ^b
<i>XV</i>	3 619.5 (92) ^a , 3 635 (51) ^a	<i>XXIX</i>	3 599 ^c
<i>XVI</i>	3 619.5 (81) ^a , 3 637 (65) ^a	<i>XXX</i>	3 614 ^c

^a The values after separation by computer; ^b ref.¹¹; ^c ref.¹⁰.

We also endeavoured to prepare ketone *XIII* by direct epoxidation of the unsaturated ketone *VIII* by hydrogen peroxide in alkaline medium under the conditions used for the preparation of $1\alpha,2\alpha:19\beta,28$ -diepoxy- 18α -oleanan-3-one (*XXVII*, ref.⁸). However, the reaction could not be performed. We were also unsuccessful in the case of the epoxidation of 2-lupene-1-one (*III*) although the epoxidation of 1-lupen-3-one (*IV*) (isomeric with the former) under the same conditions was easy^{1,5,16}. The difference in reactivities of unsaturated isomeric ketones, in agreement with spectral measurements in the UV region where a weak hypsochromic shift of the frequency corresponding to the $\pi-\pi^*$ transition was observed, the hypsochromic shift of the $n-\pi^*$ transition frequency, and the lower values of the molar extinction coefficients of unsaturated 1-oxo derivatives *III* and *VIII* might be explained – in view of the values found for their 3-oxo isomers *IV* and *XXVI* – by a partial distortion of the carbonyl group from the double bond plane. This supposition is also indicated by the comparison of the $\nu(\text{C}=\text{O})$ frequencies in the infrared region where the saturated 1-oxo derivatives *III* and *VIII* show absorption maxima at higher frequencies than their 3-oxo isomers *IV* and *XXVI* (Table II). The corresponding saturated 1-oxo derivative, *i.e.* $19\beta,28$ -epoxy- 18α -oleanan-1-one (*XXII*), displays an absorption maximum of $\nu(\text{C}=\text{O})$ at the same frequency as the isomeric $19\beta,28$ -epoxy- 18α -oleanan-3-one (*XXIII*), at 1703 cm^{-1} (Table II).

On reduction of $2\beta,3\beta:19\beta,28$ -diepoxy- 18α -oleanan- 1β -ol (*IX*) with lithium aluminum hydride a diol was obtained which did not display the absorption of the intramolecular hydrogen bond in the infrared spectrum. We assigned it the structure of $1\beta,3\beta$ -diol *XV*. The opening of the epoxide cycle takes place in this case as in the case of other $2\beta,3\beta$ -epoxides¹⁷ against the Fürst-Plattner rule according to which the formation of $1\beta,2\beta$ -diol *XXVIII* with the hydroxyl groups intramolecularly associated by a hydrogen bond would be expected. Reduction of $2\alpha,3\alpha:19\beta,28$ -diepoxy- 18α -oleanan- 1β -ol (*XI*) gave a diol which according to its IR absorption does not form an intramolecular hydrogen bond. As $2\alpha,3\alpha$ -epoxides are reduced with hydrides in accordance with the Fürst-Plattner rule^{18,19} we assigned the substance the structure of $1\beta,3\alpha$ -diol *XVI*.

The diol *XVI* was also prepared by another method. Use was made of the fact that the epoxidation of 1β -acetoxy- $19\beta,28$ -epoxy- 18α -olean-2-ene²⁰ (*VII*) must take place under steric control (the starting material does not contain a hydroxy group in the position 1β). Thus we prepared epoxy acetate *XIV* which on reduction with lithium aluminum hydride gave diol *XVI*. The preparation of diol *XVI* by reduction of epoxy ketone *XIII* during which diol *XVI* was formed only in 25% yield in addition to 75% of diol¹¹ *XVII* was found less suitable.

The structure of diols *XV* and *XVI* was confirmed by the comparison of its $\nu(\text{O}-\text{H})$ frequencies with the values for corresponding monohydroxy derivatives¹¹ (Table I) and also by chemical means. Oxidation according to Jones of the two diols led to an identical diketone, *XIX*, which we also prepared from the diols *XVII* and

XVIII described earlier¹¹. The diketone formed displayed a number of characteristic properties of β -diketones. In the infrared spectrum the shifts of frequencies in the $1600\text{--}1750\text{ cm}^{-1}$ region could be followed in dependence on solvent (Fig. 1). A strong absorption at 1728 cm^{-1} and 1708 cm^{-1} in chloroform shows that diketone *XIX* is present predominantly in its keto form in this solvent. After addition of 10% of ethanol a relatively strong absorption maximum at 1616 cm^{-1} also appears, due to the solvated enol form. When the spectrum was measured in tetrahydrofuran still stronger maxima of the solvated enol form appeared at 1626 and 1663 cm^{-1} . In triethylamine the enol form with the maximum at 1617 cm^{-1} prevails. The structure of diketone *XIX* is also indicated by the bathochromic absorption maximum shift in the UV spectrum after alkalization of the sample solution in ethanol. The maximum shifted from 258 nm to 287 nm (enolisation of diketone).

Reduction of diketone *XIX* with sodium in 1-propanol led to diol *XV* as the main product. This is in contrast to the reduction with hydrides (lithium aluminum hydride and sodium borohydride) which afforded the earlier described¹¹ diol *XVIII* as the main product. As during the reduction of 1,3-dioxo derivatives of pentacyclic triterpenes with sodium in 1-propanol the formation of diequatorial 1,3-diols¹ may be expected the mentioned reaction may be considered, on the basis of analogy, as an additional proof of the structure of diol *XV*.

From this study it follows that diol *XVI* has the same configuration of the hydroxy groups as in glochidiol (*I*) isolated from natural material and therefore our work indicates the way for the preparation of compounds of this type.

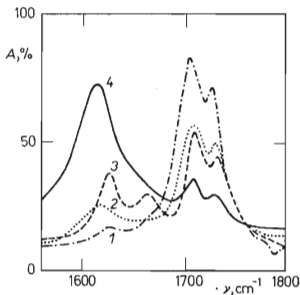


FIG. 1

Absorption of $19\beta,28$ -Epoxyoleanane-1,3-dione (*XIX*) in the Infrared Spectra in the 1550 to 1750 cm^{-1} Region Measured in Various Solvents

1 Chloroform, 2 chloroform-ethanol 9 : 1, 3 tetrahydrofuran, 4 triethylamine.

EXPERIMENTAL

Melting points were measured on a Kofler block and they are not corrected. Optical rotations were measured in chloroform with a $\pm 2^\circ$ accuracy with a ETL-NPL polarimeter of Bendix-Ericsson with objective indication. For the identification of compounds the IR spectra were measured in 5–8% solutions in chloroform on a UR 20 apparatus. For the study of hydrogen bonds and the ν (OH) frequencies in the infrared region, and for the recording of spectra in the UV region the Unicam SP 700 apparatus was used. The measurements in the infrared region 3400 to 3650 cm^{-1} were carried out at 25°C in tetrachloromethane (conc. 1 to 4 $\cdot 10^{-3}$ M). For UV measurements cyclohexane or ethanol (conc. 10^{-3} M) were employed at 25°C. CD curves were recorded on a Roussel-Jouan 185 dichrograph at the concentration 1–3 $\cdot 10^{-3}$ M in dioxan. Samples for analysis were dried at 100°C and 0.1 Torr over phosphorus pentoxide for 16–24 hours.

The reaction mixture was worked up in the following manner, unless stated otherwise: The reaction mixture was poured into ether, the solution was washed with water, dilute hydrochloric acid (1 : 4), 5% sodium carbonate, and again with water. The ethereal solution was dried over sodium sulfate and the solvents were distilled off. For chromatography neutral alumina (Reanal) of activity II (according to Brockmann) was used. For thin layer chromatography silica gel G was used and detection was carried out under UV light after spraying with morin reagent (0.02% in methanol). The identity of samples, unless stated otherwise, were proved by comparison of their IR spectra, thin-layer chromatography, and mixture melting point. Quantitative analysis by infrared spectroscopy was performed using Fidort's method²².

2 β ,3 β :19 β ,28-Diepoxy-18 α -oleanan-1 β -ol (*IX*) and 2 α ,3 α :
:19 β ,28-diepoxy-18 α -oleanan-1 β -ol (*XI*)

a) To 300 mg of 19 β ,28-epoxy-18 α -olean-2-en-1 β -ol⁸ (*V*) in 10 ml of chloroform 100 ml of 0.1M perbenzoic acid solution in hexane were added and the reaction mixture allowed to stand at +3°C for 3 days. Crystals separated out gradually on standing which were then filtered off (120 mg, m.p. 276°C), dissolved in chloroform and the solution filtered through a layer of alumina. The residue after evaporation (substance *IX*) was crystallised twice from chloroform-ethanol, m.p. 290–291°C (needles), $[\alpha]_D +37^\circ$ (*c* 0.56); ν (O—H) 3602 cm^{-1} (ϵ 112). For $\text{C}_{30}\text{H}_{48}\text{O}_3$ (456.7) calculated: 78.89% C, 10.59% H; found: 78.88% C, 10.51% H. The filtrate was poured into ether and the mixture was washed with water, sodium carbonate and water, dried over sodium sulfate and the solvents were distilled off. The residue was dissolved in chloroform, filtered through a layer of alumina and the residue was submitted to fractional crystallisation from chloroform-methanol. In addition to fractions which represented a mixture of substances *IX* and *XI* pure substance *XI* was also obtained, m.p. 294–295°C (plates), $[\alpha]_D +32.5^\circ$ (*c* 0.66); ν (O—H) 3617 cm^{-1} (ϵ 57). Similar results were obtained also on epoxidation of substance *V* with perbenzoic acid in a mixture of cyclohexane and hexane 1 : 1.

b) To a solution of 310 mg of substance *V* in 100 ml of ether 20 ml of a 0.34M perbenzoic acid solution in ether were added at +8°C and the mixture was allowed to stand at +3°C for 10 days. After washing with sodium carbonate and water the solution was dried over sodium sulfate and the solvents were distilled off. The residue was chromatographed on 15 g of alumina. Benzene (100 ml) eluted 55 mg of substance, m.p. 326–328°C (chloroform-methanol), identical with an unsaturated ketone *VIII*; next 100 ml of benzene and 25 ml of benzene-ether mixture (9 : 1) eluted 125 mg of the starting compound *V*, m.p. 260°C (chloroform-light petroleum). At 254°C the substance partly melted and changed its crystal structure; $[\alpha]_D +44.5^\circ$ (*c* 0.68). Benzene-ether mixture (4 : 1; 150 ml) eluted 135 mg of a mixture of both epoxides *IX* and *XI* from which on fractional crystallisation a fraction of pure substance *XI* was obtained in addition

to mixed fractions. M.p. 300°C (chloroform-methanol), $[\alpha]_D + 31^\circ$ (*c* 0.72); $\nu(\text{O—H})$ 3618 cm^{-1} (ϵ 57). For $\text{C}_{30}\text{H}_{48}\text{O}_3$ (456.67) calculated: 78.89% C, 10.59% H; found: 78.88% C, 10.89% H. Similar results were obtained when working in dioxan-ether mixture 1 : 1.

c) To a solution of 100 mg of substance *V* in 500 ml hexane 200 mg of solid 85% 3-chloroperbenzoic acid were added. The mixture was allowed to stand for 4 days at +3°C, it was washed with sodium carbonate and water, and dried over sodium sulfate. After evaporation of the solvents the residue was chromatographed on a thin-layer of silica gel G (development in benzene-ether 5 : 1). Some starting material *V* (30 mg) and 70 mg of a mixture of epoxides *IX* and *XI* were obtained. Quantitative analysis of the mixture of epoxides by infrared spectroscopy demonstrated that the mixture contained 40% of substance *IX* and 60% of substance *XI*. The same results were obtained when working in cyclohexane at room temperature.

d) To 60 mg of compound *V* in 50 ml of ether 80 mg of solid 85% 3-chloroperbenzoic acid were added and the mixture was allowed to stand at 3°C for four weeks. After working up as in the above experiment 25 mg of a mixture of epoxides *IX* and *XI* was obtained (containing 28% of compound *IX* and 72% of compound *XI*) along with 20 mg of the starting material *V*.

e) A mixture of 140 mg of compound *V* and 150 mg of 85% 3-chloroperbenzoic acid in 50 ml of dioxan was allowed to stand at room temperature for 4 weeks. After pouring the mixture into ether and working up as above a mixture of epoxides was obtained (70 mg) containing 19% of *IX* and 81% of *XI*.

$2\alpha,3\alpha:19\beta,28$ -Diepoxy-18 α -oleanan-1 α -ol (*XII*)

To a solution of 300 mg of 19 $\beta,28$ -epoxy-18 α -olean-2-en-1 α -ol (*VI*) (ref.^{7,9}) in 90 ml of an ether-dioxan mixture (14 : 1) 40 ml of a 0.34M perbenzoic acid solution in ether were added and the mixture allowed to stand at +3°C for 10 days. After washing with ether and drying over sodium sulfate the solvents were evaporated and the residue chromatographed on 15 g of alumina. Elution with benzene gave 240 mg of epoxide⁵ *XII*, m.p. 313–315°C (chloroform-methanol); $[\alpha]_D + 71^\circ$ (*c* 0.66); $\nu(\text{O—H})$ 3552 cm^{-1} (ϵ 67). The mother liquors were evaporated. In the 3500 to 3650 region of the IR spectrum the residue absorbed only at 3552 cm^{-1} . The same result was obtained on epoxidation in hexane.

$2\beta,3\beta:19\beta,28$ -Diepoxy-18 α -oleanan-1-one (*X*)

A solution of 80 mg of hydroxy epoxide *IX* in 40 ml of pyridine was added with 120 mg of chromium trioxide and the mixture was allowed to stand under occasional shaking at room temperature for one week. After working up the residue was crystallised from chloroform-methanol. Yield 70 mg, m.p. 321–322°C, $[\alpha]_D + 152.5^\circ$ (*c* 0.67); CD: $[\theta]_{300} + 2667^\circ$. For $\text{C}_{30}\text{H}_{46}\text{O}_3$ (454.7) calculated: 79.24% C, 10.20% H; found: 79.24% C, 10.39% H.

$2\alpha,3\alpha:19\beta,28$ -Diepoxy-18 α -oleanan-1-one (*XIII*)

a) To a solution of 300 mg of hydroxy epoxide *XII* in 75 ml of pyridine 300 mg of chromium trioxide were added and the mixture allowed to stand at room temperature for 12 days. (After 5 days it still contained about 20% of the starting material). After the usual work-up 240 mg of a substance were obtained, m.p. 325–326°C (chloroform-methanol). For analysis a sample was recrystallised from chloroform-methanol; m.p. 327°C, $[\alpha]_D + 53.5^\circ$ (*c* 0.67); CD: $[\theta]_{323} - 3985^\circ$. For $\text{C}_{30}\text{H}_{46}\text{O}_3$ (454.7) calculated: 79.24% C, 10.20% H; found: 79.28% C, 10.43% H.

b) A solution of 80 mg of hydroxy epoxide *XI* in 40 ml of pyridine was added with 120 mg of chromium trioxide and the mixture allowed to stand at room temperature for 12 days. The residue after the conventional working up was crystallised from chloroform-methanol, yielding 60 mg of substance, m.p. 323–324°C. After a double recrystallisation the melting point raised to 327°C. The substance was identical with that prepared as under *a*.

19 β ,28-Epoxy-18 α -oleanane-1 β ,3 β -diol (*XV*)

a) 100 mg of hydroxy epoxide *IX* in 100 ml of ether were refluxed with 300 mg of lithium aluminum hydride for 4 h. The mixture was poured into ethyl acetate. After the usual working up the residue was crystallised from ethyl acetate. Yield 80 mg, m.p. 290–292°C. After two additional crystallisations from ethanol-hexane 60 mg of product were obtained, m.p. 304–305°C, $[\alpha]_D +35^\circ$ (*c* 0.67); $\nu(\text{O—H})$ 3619.5 cm^{-1} (ϵ 92), 3635 cm^{-1} (ϵ 51), separated by computer. For $\text{C}_{30}\text{H}_{50}\text{O}_3$ (458.7) calculated: 78.55% C, 10.99% H; found: 78.16% C, 10.98% H.

b) To 50 mg of diketone *XIX* in 15 ml of 1-propanol 750 mg of sodium were added in small portions over 10 minutes and the mixture was refluxed for 40 minutes. After working up the residue (50 mg) was chromatographed on a thin layer plate (development in benzene-ether 1 : 1). Yield 22 mg of the most polar substance, diol *XV*, m.p. 289–292°C (ethyl acetate), 14 mg of diol *XVIII* (identity proved by IR spectroscopy and TLC), 4 mg of diol *XVII* (identity proved by thin layer chromatography), and 10 mg of unidentified substances.

19 β ,28-Epoxy-18 α -oleanane-1 β ,3 α -diol (*XVI*)

a) Hydroxy epoxide *XI* (250 mg) in 100 ml of ether was refluxed with 500 mg of lithium aluminum hydride for 3 h and then allowed to stand overnight. The mixture was poured into ethyl acetate and worked up. The residue was crystallised from ether-hexane yielding 130 mg of product melting at 272–281°C, $[\alpha]_D +28^\circ$ (*c* 0.62); $\nu(\text{O—H})$ 3619.5 cm^{-1} (ϵ 81), 3637 cm^{-1} (ϵ 65), separated with a computer. For $\text{C}_{30}\text{H}_{50}\text{O}_3$ (458.7) calculated: 78.55% C, 10.99% H; found: 78.26% C, 10.97% H.

b) Acetoxy epoxide *XIV* (50 mg) in 10 ml of ether was refluxed with 40 ml of lithium aluminum hydride for 5 h. The mixture was allowed to stand overnight, then poured into ethyl acetate and worked up in the conventional manner. The residue (40 mg) was crystallised from a mixture of ether and hexane. Yield 30 mg, m.p. of substance 277–279°C, identical with that prepared under *a*).

c) Oxo epoxide *XIII* (60 mg) was extracted into a solution of 500 mg of lithium aluminum hydride in 100 ml of ether for 1 h. The mixture was then refluxed for 4 h, cooled and poured into ethyl acetate and worked up as usual. The residue was chromatographed on a thin-layer plate in benzene-ether 2 : 1. Yield 15 mg of compound *XVI* (identity proved by IR spectra and thin-layer chromatography), and 45 mg of compound *XVII*, m.p. 277–278°C, identical with the product described in literature^{5,11}.

1 β -Acetoxy-2 α ,3 α :19 β ,28-diepoxy-18 α -oleanane (*XIV*)

To 400 mg of acetate *VII* (ref.²⁰) 20 ml of a perbenzoic acid solution in chloroform (30 mg of peracid in 1 ml of the solution) were added and the mixture allowed to stand at –5°C for a fortnight. It was then washed with sodium carbonate, water, and filtered through a layer of alumina and evaporated. The residue (400 mg) was chromatographed on 150 g of alumina. Elution with benzene (300 ml) and benzene-ether 99 : 1 (500 ml) yielded 110 mg of the starting substance

VII. Elution with benzene-ether 19 : 1 mixture (300 ml) gave 230 mg of a product, m.p. 233 to 238°C (chloroform-methanol). A sample for analysis was recrystallised from a mixture of chloroform and methanol, m.p. 239-242°C, $[\alpha]_D +34^\circ$ (c 0.52). For $C_{32}H_{50}O_4$ (498.7) calculated: 77.06% C, 10.11% H; found: 76.61% C, 10.18% H.

19 β ,28-Epoxy-18 α -oleanane-1,3-dione (XIX)

a) A solution of diol XV (40 mg) in 100 ml of acetone was added, under stirring, with 0.15 ml of Jones reagent (1 ml contained 260 mg of CrO_3) and the solution was allowed to stand at room temperature for 2 min. Concentrated aqueous oxalic acid solution (20 ml) was added and the mixture worked up in the usual manner. The residue (30 mg) was chromatographed on a thin-layer plate (with benzene-ether 9 : 1). Yield 25 mg of diketone XIX, m.p. 338-342°C (chloroform-hexane), $[\alpha]_D +131^\circ$ (c 0.59). For $C_{30}H_{46}O_3$ (454.6) calculated: 79.24% C, 10.20% H; found: 79.15% C, 10.22% H.

b) To 30 mg of diol XVI in 50 ml acetone 0.15 ml of Jones reagent were added under stirring at room temperature. After two minutes the mixture was worked up as above. Yield 20 mg of diketone XIX, m.p. 338-342°C (chloroform-hexane).

c) To 100 mg of diol XVII in 80 ml of acetone 0.45 ml of Jones reagent were added under stirring and the mixture allowed to stand for 2.5 min. Saturated oxalic acid solution (100 ml) was then added and the mixture worked up as in the preceding case. Yield 63 mg of product XIX, m.p. 338-342°C (chloroform-hexane).

d) To 230 mg of diol XVIII in 300 ml of acetone 1.15 ml of Jones reagent were added under stirring and allowed to stand for 2.5 min. The mixture was worked up as above. Yield 170 mg of diketone XIX, m.p. 338-342°C (chloroform-hexane).

19 β ,28-Epoxy-18 α -oleanane-1 α ,3 β -diol (XVIII)

a) Diketone XIX (30 mg) in 60 ml of ether was mixed with 60 mg of lithium aluminum hydride and refluxed for 10 h. After 12 hours standing at room temperature the reaction mixture was added in several portions with 15 ml of ethyl acetate and worked up in the usual manner. The residue (20 mg) was submitted to thin-layer chromatography (double development with benzene-ether 2 : 1). Yield 10 mg of diol¹¹ XVIII, m.p. 281-284°C (chloroform-ethanol) and 2 mg of diol XVII, m.p. 277-279°C (chloroform-ethanol). Identity was proved by comparison with authentic samples¹¹.

b) Diketone XIX (30 mg) was refluxed with 20 mg sodium borohydride for 10 h. The residue obtained after the conventional working up was chromatographed on a preparative thin layer (double development in benzene-ether 2 : 1). Yield 15 mg of diol XVIII, m.p. 283-285°C (chloroform-ethanol), 4 mg of diol XV, m.p. 288-291°C (ethyl acetate), and 2.5 mg of diol XVII, m.p. 276-278°C (chloroform-ethanol). Identity was proved by comparison with authentic samples¹¹.

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