REVISED STRUCTURE OF THURBERINE. SYNTHESIS OF 3,12-LUPANEDIONE*

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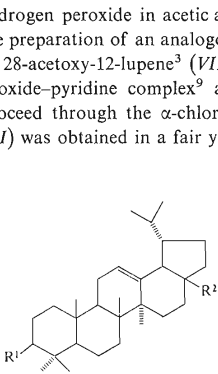
Received May 12th, 1976

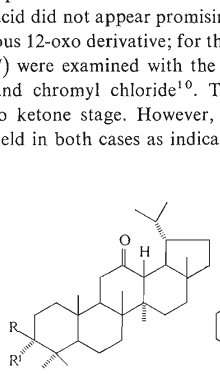
3,12-Lupanedione (*X*) was prepared by an unambiguous route from 3β,28-diacetoxy-12-lupene (*I*) and shown not be identical with a derivative of the naturally occurring triterpene thurberine to which to the structure of 20(29)-lupene-3β,12β-diol was assigned by the earlier investigators. On the basis of a comparison of physical data of the lupane derivatives *XII*–*XVII* substituted at positions 3 and 16 with those of analogous derivatives of thurberine and by means of mass spectra of 3,12-lupanedione (*X*), 3,16-lupanedione (*XVII*), and dihydrothurberinedione, thurberine has been now proposed the corrected structure of 20(29)-lupene-3β,16β-diol (*XII*). Different anisotropic effects of the oxo group at position 12 and 16 were demonstrated (^{1}H-NMR spectra); on the other hand, the Cotton effect cannot be used to differentiate between the 12- and 16-lupanone derivatives. Mass spectra of 16-lupanone derivatives were analysed.

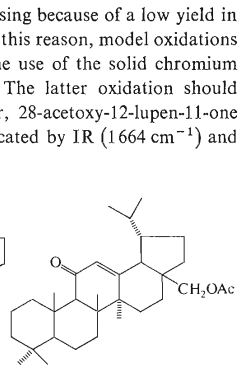
It has been claimed in an earlier paper[1] of this Series that the triterpenic pentacyclic diol thurberine[2] isolated from *Lemaireocereus thurberi* (Organ Pipe Cactus) cannot exhibit the proposed structure, namely, on the basis of the reported mass spectrum of its dioxo derivative which does not correspond to the characteristic fragmentation of 12-lupanone derivatives[1]. In order to confirm this idea we felt desirable to synthesize 3,12-lupanedione (*X*), *i.e.* the compound the structure of which had been proposed[2] for dihydrothurberinedione, and to compare properties of these two substances. A seven-step synthesis from 3β,28-diacetoxy-12-lupene[3] (*I*) was devised as the most advantageous route. Partial hydrolysis of compound *I* yielded the hydroxy derivative *II*; consequently, the double bond at position 12 participates in hydrolysis at position 28 similar to the participation of double bond at position 20(29) of the side chain[4]. The 17β-hydroxymethyl group of the monoacetate *II* was selectively oxidized with the use of pyridinium chlorochromate[5] as the oxidant. The resulting aldehyde *IV* was subjected to the Huang-Minlon[6] modification of the Wolff–Kishner reduction to afford after the reacetylation 3β-acetoxy-12-lupene (*V*) with the required methyl group at position 17β. The ^{1}H-NMR spectrum of compound *V* exhibits a signal of the new methyl group at position 17β which is markedly

* Part LIII in the series Triterpenes; Part LII: This Journal: *41*, 3452 (1976).

shifted into the higher magnetic field by the action of the shielding double bond cone at position 12 (by 0·15 ppm when compared with the saturated derivative[7]). The signals of other methyl groups and the signal of the double bond proton correspond to signals of 12-lupene derivatives[3,8]. The subsequent synthetic step consisted in transformation of compound *V* into the 12-oxo derivative. The oxidation with hydrogen peroxide in acetic acid did not appear promising because of a low yield in the preparation of an analogous 12-oxo derivative; for this reason, model oxidations of 28-acetoxy-12-lupene[3] (*VII*) were examined with the use of the solid chromium trioxide–pyridine complex[9] and chromyl chloride[10]. The latter oxidation should proceed through the α-chloro ketone stage. However, 28-acetoxy-12-lupen-11-one (*XI*) was obtained in a fair yield in both cases as indicated by IR (1664 cm^{-1}) and







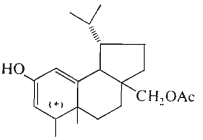
I, R^1 = OAc, R^2 = CH_2OAc
II, R^1 = Oac, R^2 = CH_2OH
III, R^1 = OH, R^2 = CH_2OH
IV, R^1 = OAc, R^2 = CHO
V, R^1 = OAc, R^2 = CH_3
VI, R^1 = OH, R^2 = CH_3
VII, R^1 = H, R^2 = CH_2OAc

VIII, R = OAc, R^1 = H
IX, R = OH, R^1 = H
X, R + R^1 = O

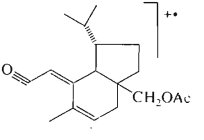
XI

UV (235 nm, ε 13400) absorption. The markedly negative Cotton effect of the $n \rightarrow \pi^*$ transition, $\lambda_{max}(\Delta\varepsilon)$ 354 nm (−2·7) and 339 nm (−2·8), is indicative of the unchanged 18α-configuration of the skeleton. The allyl position was therefore involved in both oxidations. The ^{1}H-NMR spectrum of compound *XI* exhibits a downfiled shift of 10β and 14α methyl group signals ($\Delta\delta$ −0·215 and −0·2 ppm, resp., referred to the 12-lupene ring system), the double bond proton signal is changed to a singlet (5·54 ppm), and a new signal of the 9α hydrogen may be observed as a broad singlet (2·185 ppm). The proposed structure is also confirmed by the mass spectrum. The base peak is represented by the *a* ion, *m/e* 331 from which the *m/e* 271 ion is formed by loss of one molecule of acetic acid. The *b* ion, *m/e* 290 is also characteristic. This fragmentation is analogous to that of 11-oxo-12-oleanene and ursene derivatives[11]. Consequently, the above mentioned oxidation with hydrogen peroxide in acetic acid[3] had

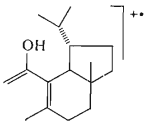
to be used also in the case of the olefin *V*. Contrary to expectations, the 12-oxo derivative *VIII* was obtained in a good yield while the usual by-product of this reaction, the 13β-hydroxy ketone was formed in a trace amount only. The mass spectrum of compound *VIII* exhibits significant ions *c*, *m/e* 234, *d*, *m/e* 221, and *e*, *m/e* 219, characteristic of 12-lupanone derivatives[1]. The mild alkaline hydrolysis of compound



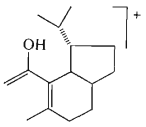
a, *m/e* 331



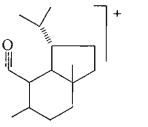
b, *m/e* 290



c, *m/e* 234



e, *m/e* 219

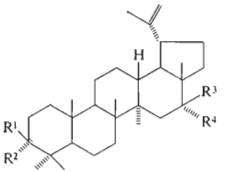


d, *m/e* 221

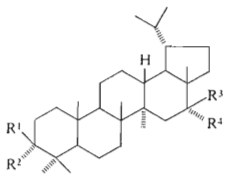
VIII yielded the hydroxy derivative *IX* which was without isolation oxidized to 3,12-lupanedione (*X*) with the use of pyridinium chlorochromate[5]. Overall yield of the synthesis was 11% (referred to the starting olefin *I*). The IR spectrum of the diketone *X* exhibits absorption of two keto groups on six-membered rings (1697 cm^{-1}) As suggested by ^{1}H-NMR spectrum, the 12-oxo group of compound *X* markedly supports the nonequivalence of methyl groups on the isopropyl chain and brings about a strong downfield shift of the 8β-methyl group signal by −0·26 ppm with respect to 3-lupanone[7] (*XVIII*). A similar shift of the methyl group at position 8β has been observed earlier[1,3]. The effect of the 12-oxo group on methyl groups at positions 17β and 14α is less pronounced ($\Delta\delta$ −0·17 and 0·06 ppm, resp.). Since the coupling constant of the doublet corresponding to the hydrogen on the $C_{(13)}$ carbon atom (2·8 ppm) is 10 Hz (this is possible in that case only when hydrogens on $C_{(13)}$ and $C_{(18)}$ exhibit the trans diaxial position), the configuration β must be ascribed to the $C_{(13)}$-hydrogen atom. The mass spectrum of compound *X* is characteristic of 12-oxolupane derivatives[1] (significant *c*, *d*, and *e* ions). In addition to mass spectra, the authentic 3,12-lupanedione (*X*) and dihydrothurberinedione[2] also differ in melting

point and optical rotation values (*X*: m.p. 183–185°C, $[\alpha]_D$ +28°; dihydrothurberinedione[2]: m.p. 263–266°C, $[\alpha]_D$ −32°); consequently, the two substances are assumed not to be identical.

An interesting observation has been made on comparison of the properties of thurberine[2] and its derivatives with those of analogous derivatives of lupane bearing along with the substituent at position 3 an additional substituent at another position. Thus, the melting point and optical rotation data of 20(29)-lupene-3β,16β-diol[12] (*XII*) and some derivatives are strikingly similar to those of thurberin and analogous derivatives (Table I). Since the mass spectra of diketones *XIV* and *XVII* have not been reported, the saturated diol *XV* was oxidized with the Jones agent analogously to ref.[12] to afford 3,16-lupanedione (*XVII*), in the mass spectrum of which the same main fragments were found as reported[2] for dihydrothurberinedione, namely, *m/e* 247, 229, 219, and 205. As indicated by ^{1}H-NMR spectrum of compound *XVII*,



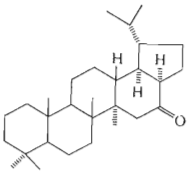
XII, $R^1 = R^3 = OH$, $R^2 = R^4 = H$
XIII, $R^1 = R^3 = OAc$, $R^2 = R^4 = H$
XIV, $R^1 + R^2 = R^3 + R^4 = O$



XV, $R^1 = R^3 = OH$, $R^2 = R^4 = H$
XVI, $R^1 = R^3 = OAc$, $R^2 = R^4 = H$
XVII, $R^1 + R^2 = R^3 + R^4 = O$
XVIII, $R^1 + R^2 = O$, $R^3 = R^4 = H$

the 16-oxo group does not affect (contrary to the 12-oxo group) signals of methyl groups on the isopropyl chain and signals of other angular methyl groups except for the signal of the 17β-methyl group which exhibits a strong downfield shift ($\Delta\delta$ +0·4 ppm). Methyl group signals of derivatives *X* and *XVII* are compared with those of 3-lupanone (*XVIII*) in Table II. Concerning the chiroptical properties, the sign of the Cotton effect cannot be used in differentiation of 12- and 16-lupanone derivatives. Contribution of the Cotton effect of the 12-oxo group is negative in all known cases[1,3,15,16] similarly to 16-lupanone derivative such as dihydrothurberinedione[2], 16-hopanone derivatives[17], and 28-nor-17α-lupan-16-one[3] (*XIX*). It may be thus inferred from data of Table I and from comparison of mass spectra that 20(29)-lupene-3β,16β-diol (*XII*) and thurberine are identical (see also ref.[18,19]).

Since the mass spectra of 16-lupanone derivatives have not been so far examined, it appeared of interest to analyse in this respect the 16-oxo derivatives *XVII* and *XIX*



XIX

TABLE I

Physical Constants of Thurberine and Derivatives in Comparison with those of 3,16-Disubstituted Derivatives of Lupane

Compound[a]	M.p., °C	$[\alpha]_D$	Compound[a]	M.p., °C	$[\alpha]_D$
20(29)-lupene-3β,16β-diol (*XII*)	218–219	+23°	thurberine	206–208	+12°
3β,16β-diacetoxy-20(29)--lupene (*XIII*)	200–201	+42°	thurberine diacetate	191–192	+47°
3β,16β-lupane-diol (*XV*)	273–274	− 9°	dihydrothurberine	259–261	−62°
3β,16β-diacetoxylupane (*XVI*)	242–244	+ 4°	dihydrothurberine diacetate	241–243	+ 9°
20(29)-lupene-3,16-dione (*XIV*)	187–188	+ 4°	thurberinedione	182–183	+22°
16-lupanedione (*XVII*)	270–272	−30°	dihydrothurberinedione	263–266	−32°

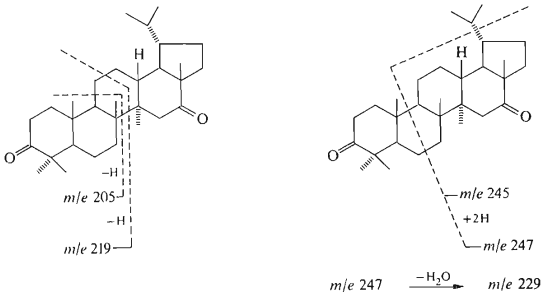
[a] Constants of 3,16-disubstituted derivatives of lupane are taken from ref.[12]; constants of thurberine derivatives originate from ref.[2]. Optical rotation was measured under various conditions and allows thus a rough correlation only.

TABLE II

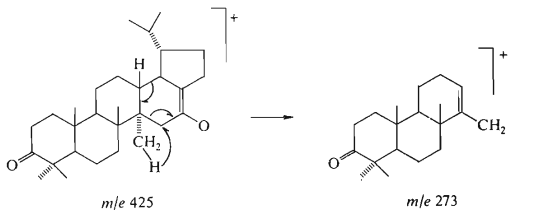
^{1}H-NMR Spectra of Dioxo Derivatives *X* and *XVII* and of 3-Lupanone (*XVIII*), ref.[7]

Compound	8β-CH_3	14α-CH_3	17β-CH_3	$(CH_3)_2CH$
XVIII	1·08	0·95	0·77	0·77 d + 0·84 d
X	1·34	0·83	0·78	0·79 d + 0·93 d
XVII	1·09	0·91	1·17	0·75 d + 0·87 d

(ref.[3]). The oxo group at position 16 does not affect fragmentation of the pentacyclic ring system to such an extent as in the case of 12-oxo derivatives[1]. Most ionic species of the *m/e* 200–300 region are due to cleavage of rings B and C accompanied by hydrogen transfer. In the case of 3,16-lupanedione (*XVII*), the fragmentation may be illustrated by Scheme 1. The *m/e* 273 ionic species are formed from the $(M - CH_3)^+$ ions by cleavage of ring D (Scheme 2).



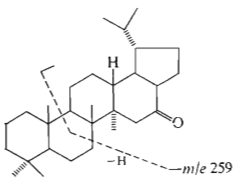
SCHEME 1

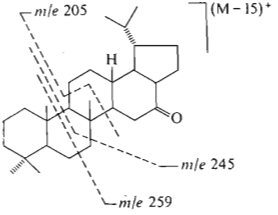


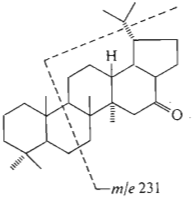
SCHEME 2

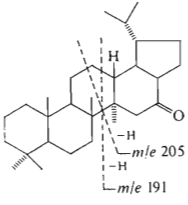
The fragmentations of the model 28-nor-17α-lupan-16-one (*XIX*) have also been examined. Similar to 3,16-lupanedione (*XVII*), the B and C rings are mainly cleaved with the formation of ions at *m/e* 259 ($C_{18}H_{27}O$), 245 ($C_{17}H_{25}O$), 231 ($C_{16}H_{23}O$), 205 ($C_{14}H_{21}O$), and 191 ($C_{13}H_{19}O$); this cleavage is independent of the D/E ring junction (Scheme 3).

The ionic species $C_{19}H_{31}$ (*m/e* 259), $C_{18}H_{29}$ (*m/e* 245), $C_{17}H_{27}$ (*m/e* 231), $C_{15}H_{25}$ (*m/e* 205), and $C_{14}H_{23}$ (*m/e* 191) are formed analogously by cleavage of rings C and D. However, their abundance is lower than that of oxygen analogues with the

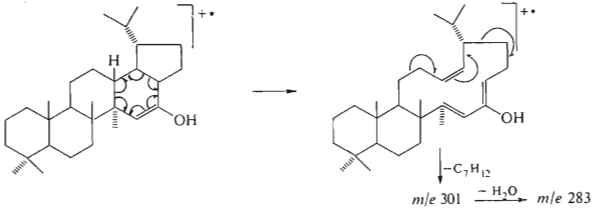


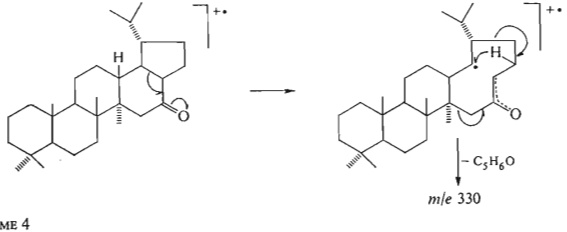






SCHEME 3





SCHEME 4

same nominal masses. In addition to the above fragmentation paths usual with pentacyclic triterpenes[11,13], 28-nor-17α-lupan-16-one (*XIX*) exhibits a fragmentation due to the presence of the oxo group at position 16. Formation of the ions at *m/e* 330, 301, and 283 may be expressed by Scheme 4.

EXPERIMENTAL

Melting points were taken on a heated microscope stage (Kofler block) and were not corrected. Optical rotation was measured in chloroform on an automatic ETL-NPL (Bendix-Ericson) polarimeter (accuracy, ±2°). The IR spectra were recorded in chloroform on a UR 10 (Carl Zeiss, Jena) apparatus. The ^{1}H-NMR spectra were measured in deuteriochloroform on a Varian HA 100 apparatus (tetramethylsilane as internal standard, chemical shifts in ppm, δ scale). The CD curves were measured in dioxane on a Roussel-Jouan Dichrographe 180 apparatus. Mass spectra were recorded on a Varian MAT 311 apparatus (ionizing potential 70 eV, ionizing current 1 mA ion source temperature 200°C, direct inlet system temperature 130—160°C). The above mentioned fragmentation paths were established by the Direct Analysis of Daughter Ions[14] technique; the stated composition of ions was obtained by the high resolution technique. Analytical samples were dried over phosphorus pentoxide at 100°C/0·1 Torr for 12 h. Reaction mixtures were processed as follows. The mixture was evaporated under diminished pressure to dryness, the residue extracted with ether, the ethereal solution washed with dilute (1 : 4) hydrochloric acid, 5% aqueous sodium carbonate, and several portions of water, dried over anhydrous sodium sulfate, filtered, and the filtrate evaporated under diminished pressure to dryness. Column chromatography was performed on neutral alumina of Brockmann activity II (Reanal, Budapest, Hungary).

Partial Hydrolysis of 3β,28-diacetoxy-12-lupene (*I*)

To the olefin *I* (1 g) in benzene (20 ml), a solution of potassium hydroxide (300 mg) in 80% aqueous ethanol (20 ml) was added dropwise, the mixture stirred at room temperature for 12 h (the course of the reaction was checked by thin-layer chromatography), and processed as usual. Chromatography on alumina (70 g) with the use of light petroleum as eluant yielded 750 mg of 3β-acetoxy-28-hydroxy-12-lupene (*II*), m.p. 187—189°C (ether), $[\alpha]_D$ +2·5° (*c* 0·79). IR spectrum: 1035, 1255, 1712 (CH_3COO), 3600 (OH) cm^{-1}. Mass spectrum: M^+ 484 ($C_{32}H_{52}O_3$, 5%) 469 (M − CH_3, 6%), 466 (M − H_2O, 2%), 453 (M − CH_2OH, 5%), 424 (M − CH_3COOH, 5%), 409 (M − CH_3COOH—CH_3, 6%), 234 (20%), 203 (100%), 189 (58%), 175 (28%). Elution with 9 : 1 light petroleum–ether yielded 120 mg of 3β,28-dihydroxy-12-lupene (*III*), m.p. 265—266° (ether), $[\alpha]_D$ +8^0 (*c* 0·17). IR spectrum: 3610 cm^{-1} (OH).

3β-Acetoxy-28-oxo-12-lupene (*IV*)

A solution of the monoacetate *II* (600 mg) in dichloromethane (5 ml) was gradually added to a stirred suspension of pyridinium chlorochromate[5] (1·2 g) and anhydrous sodium acetate (100 mg) in dichloromethane (5 ml). The resulting mixture was stirred at room temperature for 2 h, diluted with ether, and decanted. The inorganic residue was washed with two portions of hot ether. The organic solutions were combined and passed through a small column of alumina; the effluent was processed as usual. Crystallisation from a mixture of light petroleum and ether yielded 590 mg of the aldehyde *IV*, m.p. 185—190°C (decomp.), $[\alpha]_D$ −6·5° (*c* 0·75). IR spectrum: 1028,

1257, 1710 (CH_3COO), 1710, 2715, 2820 (CHO) cm^{-1}. Mass spectrum: M^+ 482 ($C_{32}H_{50}O_3$, 10·5%), 467 (M — CH_3, 3%), 452 (M — 2 CH_3, 5%), 439 (5%), 422 (M — CH_3COOH, 10%), 379 (20%), 249 (19%), 232 (32%), 203 (63%), 189 (100%), 175 (58%).

3β-Acetoxy-12-lupene (*V*)

To a solution of the aldehyde *IV* (550 mg) in benzene (15 ml) and ethanol (5 ml), hydrazine hydrate (99%, 1 ml) was added, the mixture refluxed on a steam bath for 4 h, and evaporated under diminished pressure. The residue was treated with additional hydrazine hydrate (1 ml), diethylene glycol (15 ml), and potassium hydroxide (1 g), the whole slowly heated up to 230°C, and maintained at this temperature for 2 h. Usual work-up and chromatography on a column of alumina (20 g; elution with 9 : 1 light petroleum–ether) yielded 280 mg of the amorphous alcohol *VI* (IR: 3600 cm^{-1}, OH). The material was dissolved in pyridine (15 ml) and acetic anhydride (15 ml), the solution kept at room temperature for 12 h, and processed as usual. Yield, 280 mg of the acetate *V*, m.p. 160—162°C (ether). ^{1}H-NMR spectrum: 0·62 (17β-CH_3), 0·76 d + 0·88 d, J = 6·7 Hz ($CH(CH_3)_2$), 0·88 (4α-CH_3, 4β-CH_3), 1·00 (10β-CH_3), 1·02 (8β-CH_3), 1·12 (14α-CH_3) 2·055 (3β-CH_3COO), 4·51 m ($C_{3\alpha}$—H), 5·14 μm, $W^1/2$ = 9 Hz (C_{12}—H) p.p.m. Mass spectrum: M^+ 468 ($C_{32}H_{52}O_2$, 17%), 453 (M — CH_3, 19%), 425 (3%), 408 (M — CH_3COOH, 5%), 393 (M — CH_3COOH—CH_3, 12·5%), 365 (4%) 218 (75%), 203 (100%), 189 (50%), 175 (35%).

3β-Acetoxy-12-lupanone (*VIII*)

Hydrogen peroxide (30%, 3 ml) in acetic acid (3 ml) was added dropwise at 100°C to a solution of 3β-acetoxy-12-lupene (*V*; 270 mg) in glacial acetic acid (10 ml). The mixture was heated on a steam bath for 2 h, cooled down, diluted with water, extracted with ether, and the extract processed as usual. Preparative thin-layer chromatography on silica gel (4 : 1 light petroleum–ether as eluant) yielded 150 mg of the 12-oxo derivative *VIII*, m.p. 282—284°C (ether). Mass spectrum: M^+ 484 ($C_{32}H_{52}O_3$, 55%), 469 (M — CH_3, 23%), 451 (5%), 441 (3%), 424 (M — CH_3COOH, 10%), 409 (M — CH_3COOH—CH_3, 5%), 249 (17%), 234 (68%), 221 (30%), 219 (64%), 149 (100%).

3,12-Lupanedione (*X*)

Potassium hydroxide (300 mg) in 80% aqueous ethanol (10 ml) was added into a solution of the acetate *VIII* (120 mg) in benzene (20 ml), the mixture refluxed for 2 h, and processed as usual to afford 110 mg of the alcohol *IX* which was dissolved in dichloromethane (10 ml). The solution was added dropwise to pyridinium chlorochromate (300 mg) in dichloromethane (10 ml). The mixture was stirred at room temperature for 2 h, diluted with ether, the organic solution decanted, and the residual inorganic material washed with two portions of hot ether. The organic solutions were combined, passed through a small column of alumina, and evaporated. Crystallisation of the residue from ether yielded 90 mg of 3,12-lupanedione (*X*), m.p. 183—185°C, $[\alpha]_D$ +28° (*c* 0·28). IR spectrum: 1697 cm^{-1} (C=O). ^{1}H-NMR spectrum: 0·79 d + 0·93 d, J = 6·6 Hz ($CH(CH_3)_2$), 0·78 (17β-CH_3), 0·83 (14α-CH_3), 1·01 (10β-CH_3), 1·055 (4β-CH_3), 1·10 (4α-CH_3), 1·34 (8β-CH_3), 2·3 m (2-H_2, 11-H_2), 2·8 d, J = 10 Hz (13-H) p.p.m. Mass spectrum: M^+ 440 ($C_{30}H_{48}O_2$, 28%), 425 (M — CH_3, 24%), 422 (M — H_2O, 10%), 407 (9%), 397 (6%), 234 (50%), 221 (25%), 219 (60%), 205 (58%), 123 (100%). CD spectrum (dioxane): λ_{max}, nm ($\Delta\varepsilon$) 232 (0), 243 (+0·1), 256 (0), 298 (—1·18), 380 (0).

Oxidation of 28-Acetoxy-12-lupene with the Chromium Trioxide–Pyridine Complex

The olefin *VII* (100 mg) and the crystalline chromium trioxide–pyridine complex[9] (700 mg) were dissolved in dichloromethane (40 ml) and the solution was stirred under nitrogen at room temperature for 15 h. Further 200 mg of the complex were then added and the stirring continued for 9 h. The clear solution was decanted and the residual inorganic material washed with ether. The organic solutions were combined and processed as usual. Column chromatography on 5 g alumina (light petroleum as eluant) yielded 80 mg of the amorphous oxo derivative *XI*, $[\alpha]_D + 13°$ (*c* 0·62). IR spectrum: 1036, 1247, 1737 (CH_3COO), 1664 (C=C–C=O) cm^{-1}. UV spectrum (cyclohexane): λ_{max} (ε) 235 nm (13400). CD spectrum (dioxane): λ_{max}, nm (Δε) 288 (0), 339 (−2·8), 354 (−2·7), 370 (−1·2), 385 (0). ^{1}H-NMR spectrum: 0·74 d + 0·88 d (J = 6·9 Hz, $CH(CH_3)_2$), 0·84 (4β-CH_3), 0·87 (4α-CH_3), 1·17 (10β-CH_3), 1·21 (8β-CH_3), 1·35 (14α-CH_3), 2·04 ($OCOCH_3$), 2·185 bs (9-H), 3·74 d + 3·89 d, J = 12 Hz (28-H_2), 5·54 s (12-H) p.p.m. Mass spectrum: M^+ 482 ($C_{32}H_{50}O_3$, 7%), 467 (M − CH_3, 5%), 331 (100%), 290 (11%), 271 (16%). For $C_{32}H_{50}O_3$ (482·7) calculated 79·62% C, 10·44% H; found: 79·56% C, 10·32% H.

Oxidation of 28-Acetoxy-12-lupene (*VII*) with Chromyl Chloride

Chromyl chloride (360 mg) was added dropwise at −70°C to a stirred solution of the olefin *VII* (170 mg) in acetone (20 ml). The stirring was continued for 1 h with cooling and for 1 h at room temperature, the mixture diluted with acetic acid (8 ml) and treated with excess zinc powder. The whole was stirred at room temperature for 3 h, filtered, and the filtrate processed as usual. Preparative thin-layer chromatography yielded 120 mg of the amorphous 1-oxo derivative *XI* which was in every respect identical with the substance obtained in the preceding paragraph.

3,16-Lupanedione (*XVII*)

The Jones reagent (5 drops) was added into a solution of the diol *XV* (20 mg) in 2 : 1 chloroform–acetone (10 ml). After 30 min at room temperature, ethanol (5 ml) was added and the mixture processed as usual. Preparative thin-layer chromatography (7 : 3 light petroleum–ether as eluant) yielded 15 mg of the diketone *XVII*, m.p. 270–273°C (light petroleum–methanol). ^{1}H-NMR spectrum: 0·75 d + 0·87 d, J = 6·8 Hz ($CH(CH_3)_2$), 0·91 (CH_3), 0·96 (CH_3), 1·04 (CH_3), 1·09 (2 CH_3), 1·17 (CH_3), 1·79 d + 2·71 d, J = 14 Hz ($C_{(15)}H_2$), 2·45 m ($C_{(2)}H_2$) p.p.m. Mass spectrum: M^+ 440 ($C_{30}H_{48}O_2$, 25%), 425 ($C_{29}H_{45}O_2$, 9%), 407 ($C_{29}H_{43}O$, 6%), 397 ($C_{27}H_{41}O_2$, 12%), 379 ($C_{27}H_{39}O$, 6%), 273 ($C_{19}H_{29}O$, 6%), 247 ($C_{17}H_{27}O$, 12%), 245 ($C_{17}H_{25}O$, 7%), 229 ($C_{17}H_{25}$, 13%), 219 ($C_{15}H_{23}O$, 22%), 205 ($C_{14}H_{21}O$, 82%), 81 (100%).

17-Nor-17α-lupan-16-one (*XIX*)

Mass spectrum: M^+ 412 ($C_{29}H_{48}O$, 16%), 397 ($C_{28}H_{45}O$, 12%), 379 (8%), 369 ($C_{26}H_{41}O$, 2·5%), 351 ($C_{26}H_{39}$, 1·5%), 330 (4%), 301 (3%), 283 (4%), 259 (d $C_{18}H_{27}O$, $C_{19}H_{31}$ (4 : 1), 6%), 245 (d $C_{17}H_{25}O$, $C_{18}H_{29}$ (2 : 1), 5%), 231 (d $C_{16}H_{23}O$, $C_{17}H_{27}$ (3 : 1), 5%), 218 (12%), 205 (d $C_{14}H_{21}O$, $C_{15}H_{25}$ (6 : 1), 15%), 191 (100%).

The authors wish to thank Professor P. R. Jefferies, The University of Western Australia, for the gift of authentic 20(29)-*lupene*-3β,16β-*diol* (XV), *Dr M. Buděšínský, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague, for measurement of* ^{1}H-NMR *spectra, Dr I. Frič of the same Institute for measurement of* CD *curves, and Dr S. Hilgard, Department of Organic Chemistry, Charles University, Prague, for measurement of UV spectra.*

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Translated by J. Pliml.