

1032. Dehydrogenation with Mercuric Acetate in the Lupane Series. Part II.¹ Lupeol and its Derivatives.

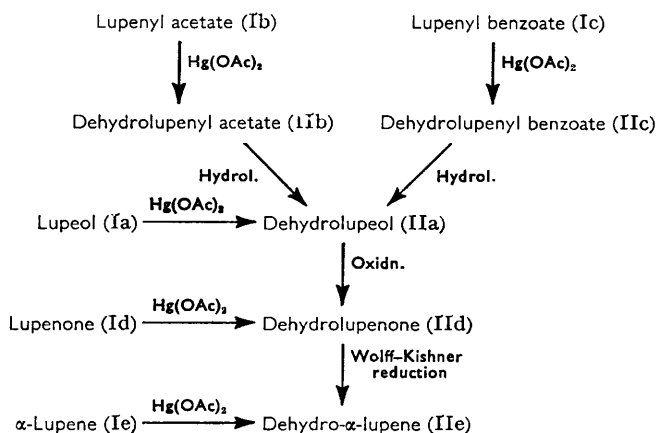
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Lupeol, lupenone, α -lupene and lupenyl esters are shown to react with mercuric acetate to give the corresponding dehydro-compounds containing the additional double bond at the 12,13-position.

DEHYDROGENATION of betulin diacetate and of methyl acetylbetulinate with mercuric acetate results in the formation of 3 β ,28-diacetoxylupa-12,20(30)-diene and of methyl 3 β -acetoxylupa-12,20(30)-diene-28-oate respectively.¹ In the present communication we show that lupeol (Ia), lupenyl acetate (Ib), lupenyl benzoate (Ic), lupenone (Id), and α -lupene (Ie) undergo analogous dehydrogenation at position 12, 13.

The dehydrogenation is effected in all cases in chloroform-acetic acid at room temperature for 14 days or at 100° for 5 hr. Lupenyl acetate (Ib) and lupenyl benzoate (Ic) give the corresponding dehydro-esters (IIb and IIc), each giving on hydrolysis lupa-12,20(30)-dien-3 β -ol (IIa). Since the latter is also obtained by dehydrogenation of lupeol (Ia) with mercuric acetate, the same change is occurring with lupeol and its esters during the dehydrogenation.

The dehydrogenation products resulting from lupenone, α -lupene, and lupeol have been interrelated as shown in the scheme. It follows that in the five compounds (Ia—e) the unsaturated linkage is introduced at the same position.



We established the location of this olefinic linkage by reference to the reactions of dehydrolupeol (IIa) and its acetate (IIb).

That the dehydro-compounds (IIa—c) contain two non-conjugated olefinic linkages is evident from ultraviolet absorption and from the reaction of dehydrolupenyl acetate with perbenzoic acid wherein two atoms of oxygen are consumed with formation of 3 β -acetoxylupa-12,13:20,30-diepoxyilupane (III), which does not give a colour with tetranitromethane or show selective ultraviolet absorption. This was confirmed when the dehydro-acetate (IIb), on reaction with osmium tetroxide and then lithium aluminium hydride, gave a resinous lupanepentaol (IVa) which afforded a diacetate (IVb); this compound is transparent to ultraviolet light and does not give a colour with tetranitromethane.

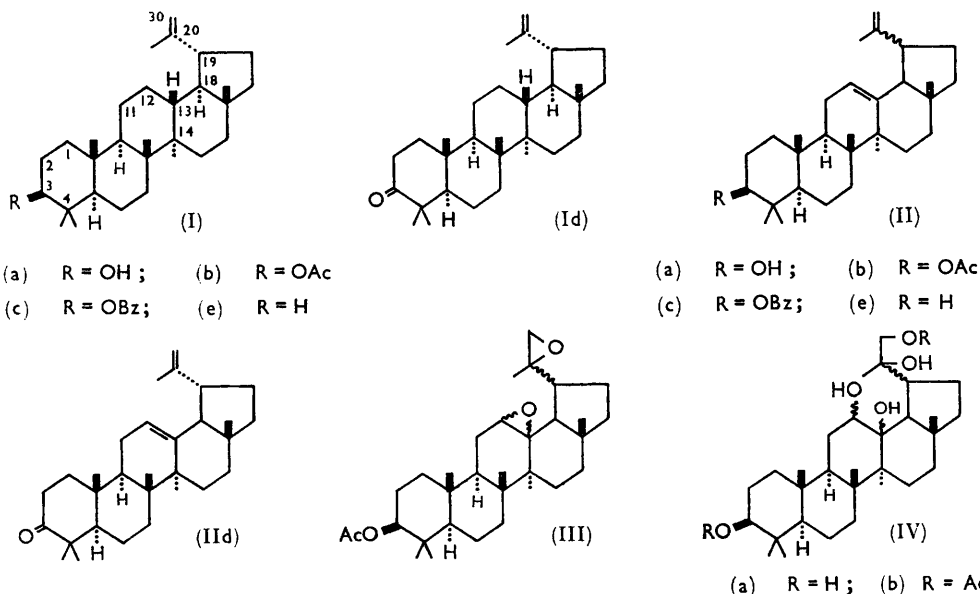
One of the olefinic bonds in the dehydro-compounds is of the vinylidene type showing infrared absorption bands at 1631 and 891 cm.⁻¹. Further cleavage of the resinous lupanepentaol with lead tetra-acetate gave formaldehyde. In our previous communication¹ we

¹ Part I, *J.*, 1961, 3353.

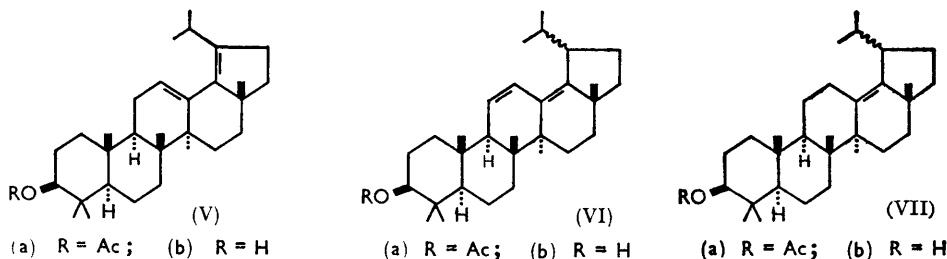
showed that rearrangement of the lupene skeleton does not occur during the reaction with mercuric acetate and hence we can assume that the vinylidene group in the dehydro-compounds (IIa—e) occupies the same position as in lupeol.

The new double bond which is introduced on dehydrogenation of the lupene derivatives (Ia—e) might be expected to occupy position 12,13 by analogy with the products formed from betulin diacetate and methyl acetylbetulinat,¹ and the evidence which follows confirms this.

Isomerisation of the non-conjugated dienyl acetate (IIb) with hydrochloric acid in acetic acid gave the conjugated diene (Va), λ_{\max} 234 m μ (ϵ 9500) being consistent with a *cisoid* heteroannular diene.² A second product was 3 β -acetoxy-lupa-11,13(18)-diene (VIa)



whose ultraviolet absorption (λ_{\max} 244, 252, and 260 m μ , ϵ 23,000, 27,000, 19,400 respectively) is characteristic of a *transoid* heteroannular diene of type (VI).^{2,3} Each of the conjugated dienes (V) and (VI) may be converted into a mixture of both on treatment



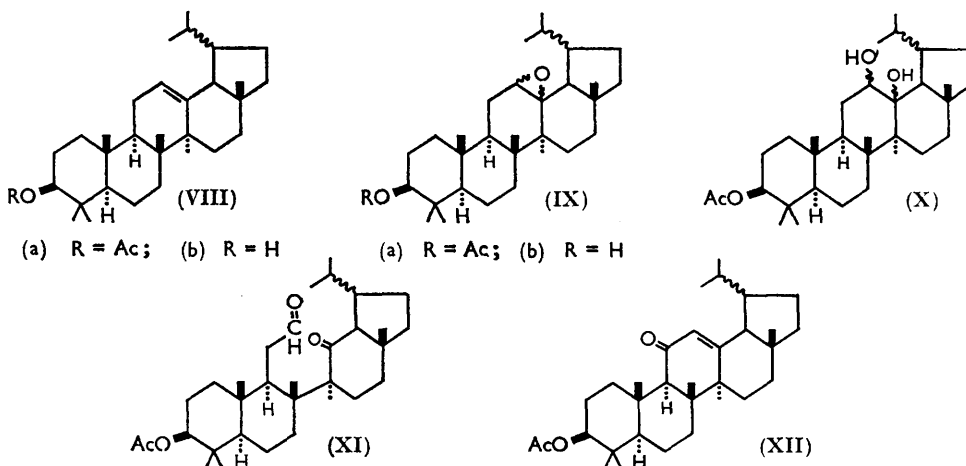
with mineral acid in acetic acid, and hydrogenation of each of the conjugated dienyl acetates (Va) and (VIa) in presence of platinum leads to the fully substituted mono-unsaturated acetate (VIIa), the molecular rotation difference (-1324°) involved in hydrogenation of the *cisoid* dienyl acetate (Va) being in agreement with the increments

² Barton and Brooks, *J.*, 1951, 257.

³ Easton, Manson, and Spring, *J.*, 1953, 943; Beaton, Spring, Stevenson, and Strachan, *J.*, 1955, 2610.

recorded when methyl isodehydro-oleanolate acetate² and 3 β ,28-diacetoxylupa-12,18-diene¹ are hydrogenated (-1410° and -1371° respectively). Also the molecular rotation difference involved in the hydrogenation of the *transoid* dienyl acetate (VIa) ($+254^\circ$) agrees with the increment recorded ($+266^\circ$) when urs-11,13(18)-dienyl acetate is hydrogenated to urs-13(18)-enyl acetate.³

The evidence cited above is in keeping with formulæ (IIa—e) for the dehydro-compounds, and additional evidence came from reactions of the dihydro-derivatives (VIII—X) of the dehydrogenation products (II). Hydrogenation of the dehydro-acetate (IIb) in presence of platinum gave 3 β -acetoxylup-12-ene (VIIIa), whose ultraviolet absorption (λ_{\max} 206 m μ ; ϵ 4000) suggested the presence of a trisubstituted double bond. The olefin (VIIIa) did not absorb in the vinylidene region in the infrared spectrum, thereby showing that only the vinylidene grouping had been reduced. Moreover, the olefin (VIIIa) is readily converted into the saturated epoxylupanyl acetate (IXa) on treatment with either perbenzoic acid or perphthalic acid, and hydroxylation with osmium tetroxide



and subsequent acetylation converts it into 3 β -acetoxylupane-12,13-diol (X). Lead tetra-acetate cleaves the diol to the keto-aldehyde (XI) whose infrared spectrum (in chloroform) indicates the presence of a keto-aldehyde.

Finally chromic acid oxidised isolupenyl acetate (VIIIa) to the $\alpha\beta$ -unsaturated ketone (XII) which on hydrogenation over platinum regenerated isolupenyl acetate. These reactions are characteristic of α - and β -amyrin derivatives⁴ in which the double bond is known to be in the 12,13-position.

EXPERIMENTAL

Rotations were determined for CHCl_3 solutions at room temperature, ultraviolet absorption spectra for EtOH solutions (Unicam S.P. 500 spectrophotometer), and infrared spectra for Nujol mulls (unless otherwise stated). Light petroleum refers to the fraction of b. p. $60-80^\circ$. Microanalysis were by Dr. A. C. Syme and Mr. W. McCorkindale.

3 β -Acetoxylupa-12,20(30)-diene (IIb).—Lupenyl acetate (10 g.) in chloroform (200 ml.) was treated with mercuric acetate (120 g.) in solution in acetic acid (2 l.) at room temperature for 14 days or at 100° for 5 hr. The mercurous acetate was filtered off, and the filtrate diluted with water and extracted with chloroform. Evaporation of the washed extracts gave an orange solid which was dissolved in pyridine, treated with hydrogen sulphide, and filtered through kieselguhr. Removal of the solvent *in vacuo* gave a solid (8.5 g.) which was dissolved in

⁴ Spring and Vickerstaff, *J.*, 1937, 249; Ruzicka, Leuenberger, and Schellenberg, *Helv. Chim. Acta*, 1937, 20, 1271; Ruzicka, Müller, and Schellenberg, *ibid.*, 1939, 22, 758; Beynon, Sharples, and Spring, *J.*, 1938, 1233.

benzene–light petroleum (1 : 4) and filtered through alumina (300 g.), to give $\beta\beta$ -acetoxy $\text{lupa-12,20(30)-diene}$ (1.7 g.), crystallising from chloroform–methanol as needles, m. p. 229–231°, $[\alpha]_D + 47^\circ$ (c 1.3), λ_{max} 207 m μ (ϵ 7000), ν_{max} 1736, 1248, 1626, and 891 cm.⁻¹ (OAc and vinylidene groups). The compound gave a deep yellow colour with tetranitromethane (Found: C, 82.4; H, 10.9. $\text{C}_{32}\text{H}_{50}\text{O}_2$ requires C, 82.3; H, 10.8%). Treatment of the acetate with lithium aluminium hydride gave $\text{lupa-12,20(30)-dien-}\beta\beta\text{-ol}$ (IIa) which crystallised from chloroform–methanol as needles, m. p. 218–222°, $[\alpha]_D + 31^\circ$ (c 1.15), λ_{max} 207 m μ (ϵ 6500), ν_{max} 3509 (OH), 1631 and 891 cm.⁻¹ (vinylidene) (Found: C, 84.8; H, 11.4. $\text{C}_{30}\text{H}_{48}\text{O}$ requires C, 84.8; H, 11.4%).

The alcohol (IIa) was also obtained by direct dehydrogenation of lupeol with mercuric acetate as described above, the crude product in benzene–ether (9 : 1) being filtered through alumina before crystallisation.

$\beta\beta$ -Benzoyloxy $\text{lupa-12,20(30)-diene}$ (IIc).—Lupenyl benzoate (17 g.) was treated with mercuric acetate as described above and a solution of the product in benzene–light petroleum (1 : 4) was filtered through alumina (500 g.). Removal of the solvent and crystallisation of the residue from benzene–ethanol gave $\beta\beta$ -benzoyloxy $\text{lupa-12,20(30)-diene}$ as rods (3.9 g.), m. p. 280–281°, $[\alpha]_D + 67.6^\circ$ (c 1.11), λ_{max} 204 and 229 m μ (ϵ 7400 and 4450, respectively), ν_{max} 1733 and 1279 cm.⁻¹ (benzoate), and 890 cm.⁻¹ (vinylidene) (Found: C, 84.0; H, 10.2. $\text{C}_{37}\text{H}_{52}\text{O}_2$ requires C, 84.0; H, 9.9%). Hydrogenolysis of the benzoate with lithium aluminium hydride gave the alcohol (IIa), identical with the product described above.

$\text{Lupa-12,20(30)-dien-3-one}$ (IId).—(a) *Dehydrogenation of lupenone*. Lupenone (4 g.) was treated with mercuric acetate as above, and the product (1.2 g.) eluted from alumina (120 g.) with light petroleum. Removal of solvent and crystallisation from chloroform–methanol gave $\text{lupa-12,20(30)-dien-3-one}$ as rods (0.8 g.), m. p. 156–158°, $[\alpha]_D + 66.3^\circ$ (c 0.93), λ_{max} 207 m μ (ϵ 7750), ν_{max} 1701 (C=O), 1623 and 890 cm.⁻¹ (vinylidene). The compound gives a dark yellow colour with tetranitromethane (Found: C, 85.3; H, 11.1. $\text{C}_{30}\text{H}_{46}\text{O}$ requires C, 85.2; H, 11.0%).

(b) *Oxidation of lupa-12,20(30)-dien-}\beta\beta\text{-ol} (IIa). A solution of the alcohol (IIa) (0.2 g.) in acetone (15 ml.) was treated dropwise with a 17% solution (1 ml.) of sodium dichromate in 5*N*-sulphuric acid and set aside for 5 min. Gradual dilution with water then precipitated $\text{lupa-12,20(30)-dien-3-one}$, identical with the product described above.*

$\text{Lupa-12,20(30)-diene}$ (IIe).—(a) *Dehydrogenation of α -lupene*. α -Lupene (4 g.) was treated with mercuric acetate as in previous cases. The product, eluted from alumina (120 g.) with light petroleum, recrystallised from chloroform–methanol to give $\text{lupa-12,20(30)-diene}$ (0.9 g.), m. p. 160–162°, $[\alpha]_D + 29.3^\circ$ (c 2.00), λ_{max} 207 m μ (ϵ 6400), ν_{max} 3075, 1626, and 890 cm.⁻¹ (vinylidene) (Found: C, 88.4; H, 11.9. $\text{C}_{30}\text{H}_{48}$ requires C, 88.2; H, 11.8%). The compound depressed the m. p. of α -lupene.

(b) *Reduction of lupa-12,20(30)-dien-3-one*. The ketone (0.13 g.) in ethanol (5 ml.) was heated in an autoclave with sodium (0.15 g.), ethanol (7 ml.), and 100% hydrazine hydrate (0.5 ml.) at 195° for 6 hr. Isolation of the product in the usual way followed by chromatography on alumina and crystallisation from chloroform–methanol gave $\text{lupa-12,20(30)-diene}$ (0.07 g.), m. p. and mixed m. p. 160–162°, $[\alpha]_D + 30^\circ$ (c 1.42).

$\beta\beta$ -Acetoxy-12,13:20,30-diepoxy lupane (III).—A solution of $\beta\beta$ -acetoxy $\text{lupa-12,20(30)-diene}$ (IIb) (1 g.) in benzene (50 ml.) was treated with 1.9*N*-perbenzoic acid (10 ml.) at room temperature for 48 hr. The product was isolated by means of benzene and crystallised several times from chloroform–methanol, to give $\beta\beta$ -acetoxy-12,13:20,30-diepoxy lupane as needles (0.44 g.), m. p. 275–277° (*in vacuo*), $[\alpha]_D + 49^\circ$ (c 0.95), ν_{max} 1739 and 1250 cm.⁻¹ (OAc). The compound showed no selective absorption in the ultraviolet region and did not give a colour with tetranitromethane (Found: C, 77.0; H, 10.2. $\text{C}_{32}\text{H}_{50}\text{O}_4$ requires C, 77.1; H, 10.1%).

Hydroxylation of $\beta\beta$ -Acetoxy $\text{lupa-12,20(30)-diene}$ (IIb).—The dienyl acetate (1 g.) in pyridine (10 ml.) was treated with osmium tetroxide (1.6 g.) in ether (20 ml.) and kept in darkness for 11 days. The mixture was diluted with ether (100 ml.), and the osmic ester decomposed by addition of lithium aluminium hydride (4 g.) in ether (50 ml.) during 0.5 hr. followed by 1 hour's refluxing. Isolation of the product through ether gave the crude pentahydroxy-derivative as a gum (0.9 g.) which showed strong absorption at 3300 cm.⁻¹ (OH) and only slight end absorption in the ultraviolet region.

Cleavage of the Pentahydroxy-derivative with Lead Tetra-acetate.—The pentahydroxy-derivative (0.24 g.) in chloroform (3 ml.) and acetic acid (24 ml.) was treated with lead tetra-acetate

(1 g.) and left for 20 hr. Extraction with water (50 ml.) gave formaldehyde which was isolated as the dimethone (m. p. and mixed m. p. 192°) by addition of a saturated aqueous solution of dimesone to the aqueous extract (Found: C, 69.6; H, 8.0. Calc. for $C_{11}H_{24}O_4$: C, 69.8; H, 8.3%). The reaction mixture was extracted with chloroform after removal of formaldehyde, but material from the chloroform extract did not crystallise.

3 β ,30-Diacetoxylupa-12,13,20-triol (IVb).—The pentahydroxy-compound (0.65 g.) in pyridine (5 ml.) was treated with pyridine-acetic anhydride (1:1; 30 ml.) at room temperature for 22 hr. Isolation of the product by means of ether followed by chromatography on alumina (25 g.) from benzene-light petroleum (1:1; 150 ml.) gave 3 β ,30-diacetoxylupa-12,13,20-triol that crystallised from chloroform-light petroleum as plates (0.3 g.), m. p. 239–240° (*in vacuo*), $[\alpha]_D +4.6^\circ$ (*c* 2.64), ν_{\max} 3484 (OH), 1736, 1712, and 1212 cm^{-1} (OAc) (Found: C, 70.7; H, 9.8. $C_{34}H_{56}O_7$ requires C, 70.8; H, 9.8%).

Isomerisation of the Non-conjugated Diene (IIb) with Acid: 3 β -Acetoxylupa-12,18-diene.—3 β -Acetoxylupa-12,20(30)-diene (IIb) (2 g.) in acetic acid (200 ml.) at 100° was treated with concentrated hydrochloric acid (5 ml.) and kept at 100° for 15 min. Evaporation of the solvent *in vacuo* and chromatography of the residue on alumina (80 g.) from light petroleum (200 ml.) gave 3 β -acetoxylupa-12,18-diene (Va) (0.72 g.) which crystallised from chloroform-methanol as needles, m. p. 179–181°, $[\alpha]_D +260^\circ$ (*c* 1.43), λ_{\max} 234 $\text{m}\mu$ (ϵ 9500), ν_{\max} 1730, 1253, and 1642 cm^{-1} (OAc and diene) (Found: C, 82.2; H, 11.0. $C_{32}H_{50}O_2$ requires C, 82.3; H, 10.8%). Treatment of the conjugated dienyl acetate (Va) with lithium aluminium hydride in ether and crystallisation of the product from chloroform-methanol gave lupa-12,18-dien-3 β -ol (Vb), needles, m. p. 208–211°, $[\alpha]_D +82^\circ$ (*c* 0.82), λ_{\max} 234 $\text{m}\mu$ (ϵ 8800), ν_{\max} 3584 and 1639 cm^{-1} (OH and diene) (Found: C, 84.9; H, 11.7. $C_{30}H_{48}O$ requires C, 84.8; H, 11.4%). Both compounds gave a brown colour with tetranitromethane. After removal of the *cisoid* dienyl acetate (Va) from the column, elution with benzene-light petroleum (1:4; 2 l.) and crystallisation from chloroform-methanol gave 3 β -acetoxylupa-11,13(18)-diene (VIa) (0.3 g.), needles, m. p. 155–156°, $[\alpha]_D -74.5^\circ$ (*c* 1.12), λ_{\max} 244, 252, 260 $\text{m}\mu$ (ϵ 23,000, 27,000, and 19,400), ν_{\max} 1736, 1245, and 1639 cm^{-1} (OAc and diene) (Found: C, 82.3; H, 10.9. $C_{32}H_{50}O_2$ requires C, 82.3; H, 10.8%). Treatment of the *transoid* dienyl acetate (VIa) with lithium aluminium hydride in ether and crystallisation of the product from chloroform-methanol gave lupa-11,13(18)-dien-3 β -ol (VIb), needles, m. p. 205–207°, $[\alpha]_D -80^\circ$ (*c* 0.66), λ_{\max} 242, 250, 260 $\text{m}\mu$ (ϵ 21,000, 24,400, and 16,100), ν_{\max} 3448 and 1639 cm^{-1} (OH and diene) (Found: C, 84.7; H, 11.7. $C_{30}H_{48}O$ requires C, 84.8; H, 11.4%). Both compounds gave a brown colour with tetranitromethane.

Equilibration of the Conjugated Dienyl Acetates with Acid.—(a) 3 β -Acetoxylupa-12,18-diene (Va) (0.04 g.) in acetic acid (50 ml.) and concentrated hydrochloric acid (1 ml.) was heated at 100° for 1 hr. Removal of solvent followed by chromatography on alumina (3 g.) from light petroleum (10 ml.) gave starting material (0.02 g.) which was identified by m. p., mixed m. p., and infrared and ultraviolet absorption comparison. Continued elution with light petroleum gave a fraction (0.02 g.) which crystallised from methanol to give 3 β -acetoxylupa-11,13(18)-diene, needles, m. p. and mixed m. p. 152–154°. The ultraviolet and infrared spectra were identical with those of an authentic sample.

(b) 3 β -Acetoxylupa-11,13(18)-diene (VIa) (0.08 g.) in acetic acid (50 ml.) and concentrated hydrochloric acid (1 ml.) was heated at 100° for 1 hr. Isolation of the products as in (a) gave the *cisoid* dienyl acetate (Va) and the *transoid* dienyl acetate (VIa), which were identified by m. p., mixed m. p., and absorption data.

Hydrogenation of the Conjugated Dienyl Acetates to give 3 β -Acetoxylup-13(18)-ene (VIIa).—(a) Hydrogenation of 3 β -acetoxylupa-12,18-diene (0.12 g.) in acetic acid (100 ml.) containing platinum (from platinum oxide, 100 mg.) for 20 hr. and isolation of the product in the usual manner gave 3 β -acetoxylup-13(18)-ene (0.09 g.), needles (from methanol), m. p. 184–185° (*in vacuo*), $[\alpha]_D -20.7^\circ$ (*c* 1.33), λ_{\max} 207 $\text{m}\mu$ (ϵ 10,100), ν_{\max} 1730 and 1241 cm^{-1} (OAc) (Found: C, 82.2; H, 11.4. $C_{32}H_{52}O_2$ requires C, 82.0; H, 11.2%). The compound gave a yellow colour with tetranitromethane.

(b) Hydrogenation of 3 β -acetoxylupa-11,13(18)-diene (0.15 g.) as in (a) also gave 3 β -acetoxylup-13(18)-ene (0.11 g.), m. p. and mixed m. p. 184–185° (*in vacuo*). The infrared and ultraviolet spectra were identical with those of the product obtained as in (a). Treatment of the isolupenyl acetate (VIIa) with lithium aluminium hydride in ether and crystallisation of the product from methanol gave lup-13(18)-en-3 β -ol (VIIb), m. p. 193–196°, $[\alpha]_D -39.4^\circ$ (*c* 1.22)

λ_{\max} . 207 m μ (ϵ 9300), ν_{\max} . 3367 cm.⁻¹ (OH) (Found: C, 84.1; H, 11.9. C₃₀H₅₀O requires C, 84.4; H, 11.8%). The compound gives a yellow colour with tetranitromethane.

Hydrogenation of the Non-conjugated Dienyl Acetate (IIb).—3 β -Acetoxylupa-12,20(30)-diene (1.5 g.) was hydrogenated in ethyl acetate-acetic acid (1:1; 600 ml.) over pre-reduced platinum oxide (0.5 g.) for 28 hr. Isolation of the product in the usual manner and crystallisation from chloroform-methanol gave 3 β -acetoxylup-12-ene (VIIa) as blades (1.2 g.), m. p. 249–251° (*in vacuo*), $[\alpha]_D + 9^\circ$ (*c* 1.40), λ_{\max} . 206 m μ (ϵ 3600), ν_{\max} . 1739 and 1240 cm.⁻¹ (OAc) (Found: C, 81.7; H, 11.2. C₃₂H₅₂O₂ requires C, 82.0; H, 11.2%). The compound gave a pale yellow colour with tetranitromethane and on treatment with lithium aluminium hydride in ether, or with 3% alcoholic potassium hydroxide, and crystallisation from methanol gave lup-12-en-3 β -ol (VIIb) as needles, m. p. 225–227° (*in vacuo*), $[\alpha]_D - 12.5^\circ$ (*c* 1.21), λ_{\max} . 206 m μ (ϵ 6000), ν_{\max} . 3448 cm.⁻¹ (OH) (Found: C, 84.2; H, 12.0. C₃₀H₅₀O requires C, 84.4; H, 11.8%).

3 β -Acetoxylup-12-en-11-one (XII).—3 β -Acetoxylup-12-ene (0.5 g.) in stabilised acetic acid (150 ml.) was treated at room temperature with chromium trioxide (0.2 g.) in 90% acetic acid (70 ml.) for 20 hr. The excess of oxidant was destroyed with methanol, and the product isolated through ether. Chromatography on alumina (20 g.) and elution with light petroleum gave an acetate (0.07 g.), m. p. 272–274°, $[\alpha]_D + 24^\circ$ (*c* 1.1), which had no ultraviolet absorption (Found: C, 81.75; H, 11.4%). A second saturated acetate (0.08 g.), m. p. 244–246°, $[\alpha]_D + 36.5^\circ$ (*c* 0.7), was eluted with light petroleum-benzene (1:2) (Found: C, 81.6; H, 11.5%). Elution with benzene and benzene-ether (4:1) gave fractions which crystallised from chloroform-methanol to yield 3 β -acetoxylup-12-en-11-one (XII) as plates (0.26 g.), m. p. 290–292°, $[\alpha]_D - 61^\circ$ (*c* 0.9), λ_{\max} . 244 m μ (ϵ 13,500), ν_{\max} . 1730, 1235, and 1689 cm.⁻¹ (OAc and $\alpha\beta$ -unsaturated ketone) (Found: C, 79.8; H, 10.7. C₃₂H₅₀O₃ requires C, 79.6; H, 10.4%). The compound gave a faint yellow colour with tetranitromethane. Hydrogenation of the $\alpha\beta$ -unsaturated keto-acetate (XII) (0.05 g.) in acetic acid (75 ml.) over pre-reduced platinum oxide (0.04 g.) for 48 hr. and isolation of the product in the usual way gave 3 β -acetoxylup-12-ene (VIIa) (0.04 g.), m. p. and mixed m. p. 248–250° (*in vacuo*), $[\alpha]_D + 9^\circ$ (*c* 1.68). The infrared spectrum was identical with that of an authentic specimen.

3 β -Acetoxy-12,13-epoxylupane (IXa).—The acetoxylupene (VIIa) (0.15 g.) in benzene (5 ml.) was treated with *N*-perbenzoic acid in benzene (1.5 ml.) at room temperature for 20 hr. The product, isolated in the usual way, was chromatographed in light petroleum (25 ml.) on alumina (15 g.). Light petroleum (200 ml.) eluted a fraction (0.02 g.) which crystallised from methanol as plates, m. p. 226–228°, $[\alpha]_D - 20.4^\circ$ (*c* 0.82), ν_{\max} . 1739 and 1242 cm.⁻¹ (OAc). The compound did not show selective ultraviolet absorption or give a colour with tetranitromethane (Found: C, 81.5; H, 11.4. C₃₂H₅₂O₂ requires C, 82.0; H, 11.2%). Elution with benzene-light petroleum (1:3; 1 l.) gave fractions (0.09 g.) which crystallised from methanol, yielding 3 β -acetoxy-12,13-epoxylupane (IXa), blades, m. p. 236–238°, $[\alpha]_D + 32^\circ$ (*c* 0.69), ν_{\max} . 1736 and 1242 cm.⁻¹ (OAc). The compound did not absorb in the ultraviolet region and did not give a colour with tetranitromethane (Found: C, 79.2; H, 10.7. C₃₂H₅₂O₃ requires C, 79.3; H, 10.8%). Treatment of the alcohol (VIIb) (0.5 g.) with an excess of monoperphthalic acid in ether for 5 days at room temperature and isolation of the product in the usual way gave 12,13-epoxylupane-3 β -ol (IXb) (0.48 g.), needles (from methanol), m. p. 234–236° (*in vacuo*), $[\alpha]_D + 28.2^\circ$ (*c* 0.92), ν_{\max} . 3509 cm.⁻¹ (OH). The compound did not absorb in the ultraviolet region (Found: C, 81.3; H, 11.6. C₃₀H₅₀O₂ requires C, 81.4; H, 11.4%).

3 β -Acetoxylupane-12,13-diol (X).—Osmium tetroxide (0.7 g.) in dry ether (10 ml.) was added to 3 β -acetoxylup-12-ene (0.7 g.) in pyridine (5 ml.) and dry ether (10 ml.). The mixture was kept in darkness for 14 days, and the product isolated in the usual manner as a yellow solid (0.62 g.), which was acetylated with pyridine-acetic anhydride at room temperature for 20 hr. Chromatography on alumina (30 g.) from benzene followed by elution with benzene (500 ml.) and benzene-ether (4:1; 1500 ml.) gave a product (0.23 g.) which crystallised from chloroform-methanol affording 3 β -acetoxylupane-12,13-diol (X), plates, m. p. 215–245° (decomp.), $[\alpha]_D + 9^\circ$ (*c* 0.8), ν_{\max} . 3534 cm.⁻¹ (OH), 1712, 1269, and 1255 cm.⁻¹ (OAc). The compound did not absorb in the ultraviolet region (Found: C, 76.6; H, 10.8. C₃₂H₅₄O₄ requires C, 76.4; H, 10.8%).

3 β -Acetoxy-12,13-dioxo-12,13-secolupane (XI).—The triol monoacetate (X) (0.07 g.) in chloroform (10 ml.) and dry benzene (40 ml.) was treated with lead tetra-acetate (0.18 g.) at room temperature for 24 hr., an orange solid separating. The suspension was treated with ethylene glycol (2 drops) and filtered through kieselguhr. Evaporation of the filtrate and

crystallisation of the residue from methanol gave 3 β -*acetoxy*-12,13-*dioxo*-12,13-*secolupane* (XI), plates (0.04 g.), m. p. 186—188°, $[\alpha]_D +39.5^\circ$ (*c* 1.05), $\lambda_{\text{max.}}$ 280 m μ (ϵ 150), $\nu_{\text{max.}}$ (in CCl₄ with a CaF₂ prism) 2882, 1717 cm.⁻¹ (CHO), 1739, 1240 cm.⁻¹ (OAc), 1706 cm.⁻¹ (C=O in a six-membered ring) (Found: C, 76.5; H, 10.4. C₃₂H₅₂O₄ requires C, 76.75; H, 10.5%).

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