66. *The Unsaturated Centre of the Triterpene Alcohol Lupeol.*

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The monohydric triterpene alcohol lupeol, $C_{30}H_{50}O$, has been isolated in comparatively good yield from Mariposa gutta (*Palaquium leiocarpum*) and the presence of one ethylenic linkage and consequently its pentacyclic nature have been confirmed. Hydrogenation of lupenone gives the ketone lupanone, which is also obtained by the oxidation of lupanol. The presence of a methylene group adjacent to the carbonyl group in this saturated ketone has been demonstrated. The recognition of formaldehyde among the products from the ozonisation of lupenyl acetate shows that the ethenoid linkage is present as an exocyclic methylene group. From the behaviour of lupenyl acetate on oxidation with chromic anhydride, ozone, and hydrogen peroxide it is inferred that lupenol (lupeol) contains a bridge ring in the neighbourhood of the ethenoid linkage and thus differs from the triterpenes (hydropicene derivatives) previously examined in detail. This difference is reflected in the behaviour of lupenol on dehydrogenation, whereby 1 : 2 : 5-trimethylnaphthalene and possibly 1 : 2 : 5 : 6-tetramethylnaphthalene are obtained and not 1 : 2 : 7-trimethylnaphthalene or 1 : 8-dimethylpicene, two characteristic dehydrogenation products of the hydropicene group of triterpenes.

Lupeol has been isolated from a variety of plant species; from *Sapotaceæ* (Tschirch and Schereschensky, *Arch. Pharm.*, 1905, **243**, 358; Cohen, *ibid.*, 1908, **246**, 520; Jungfleisch and Laroux, *Compt. rend.*, 1906, **142**, 1218; 1907, **144**, 1435; Romberg, *Ber.*, 1904, **37**, 3440; *Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 137; Heilbron, Moffet, and Spring, J., 1934, 1583), from *Rutaceæ* (Dieterle, *Arch. Pharm.*, 1919, **257**, 260; Oestling, *Ber. deut. Pharm. Ges.*, 1914, **24**, 308; Ultée, *Berlin Jardin. Bot. Buitenzorg*, 1922, [3], **4**, 315; Goodson, *Biochem. J.*, 1921, **15**, 123; Jones and White, *Amsterdam Sci. Abs.*, 1929, **42**, 49), and from *Leguminosæ* (Likienik, *Ber.*, 1891, **24**, 183, 2709; Schulze, *Z. physiol. Chem.*, 1904, **41**, 474).

We have now isolated it in relatively good yield from Mariposa gutta obtained from *Palaquium leiocarpum* (*Sapotaceæ*) " a large tree found only in Borneo, where it occurs on low-lying ground " (Gutta Percha, Malayan Series, No. XVIII, published by the Government of Malaya for the British Empire Exhibition).* Benzoylation of the non-saponifiable

* Private communication from the Director of the Imperial Institute, South Kensington, London.

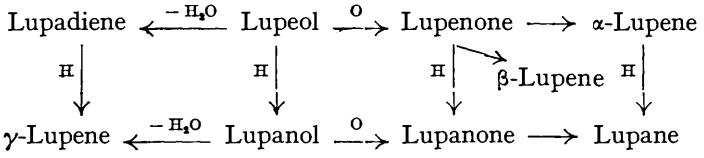
matter of the gutta gives a mixture, from which lupeol benzoate, m. p. 265°, is obtained as the least soluble component. The lupeol occurs in the gutta mainly as its cinnamate, since the latter is isolated from the alcoholic extract of the gutta in comparatively high yield.

Lupeol is a monohydric alcohol, $C_{30}H_{50}O$ (Nojd, *Arch. Pharm.*, 1927, **265**, 381); it contains one ethylenic linkage, since on hydrogenation it easily gives a saturated dihydro-derivative (Ruzicka, Huyser, Pfeiffer, and Seidel, *Annalen*, 1929, **471**, 21). This conclusion we have confirmed by a quantitative micro-catalytic hydrogenation and by a quantitative perbenzoic acid titration of lupeol acetate. Lupeol (lupenol) is therefore pentacyclic and in this respect differs from the sterols and resembles the majority of the triterpenes.

Hydrogenation of lupenyl acetate in presence of Adams's platinum oxide in glacial acetic acid yields *lupanyl acetate*, m. p. 245—246°, hydrolysis of which gives lupanol, m. p. 201—202° (*benzoate*, m. p. 259—260°), identical with that previously described by Ruzicka, Huyser, Pfeiffer, and Seidel (*loc. cit.*). Oxidation of lupanol with chromic anhydride gives mainly *lupanone*, m. p. 204—205°, together with a small amount of *lupanedicarboxylic acid*, m. p. 272°. Lupanone is also obtained in excellent yield by the catalytic hydrogenation of lupenone (Cohen, *Rec. trav. chim.*, 1909, **28**, 368) with Adams's platinum oxide as catalyst; it is characterised by the formation of a *hydrazone*, m. p. 341—342°, and a m-*nitrobenzylidene* derivative, m. p. 127°, the formation of the latter indicating the presence of the system $-CO-CH_2-$ in lupanone and consequently of the system $-CH(OH)-CH_2-$ in lupeol. Reduction of lupanone by either the Clemmensen or the Kishner–Wolff method gives *lupane*, m. p. 184°. Reduction of lupenone by the Kishner–Wolff process gives α-*lupene*, m. p. 163°, which is catalytically reduced to lupane, identical with that prepared from lupanone. When, however, lupenone is reduced by the Clemmensen method, an isomeric β-*lupene*, m. p. 191°, is formed which is resistant to catalytic hydrogenation.

Lupenone does not exhibit the typical selective absorption of an αβ-unsaturated ketone. A further proof that the ethenoid linkage is not in the αβ-position to the hydroxyl group is forthcoming in the observation that lupadiene, prepared by the dehydration of lupeol with phosphorus pentachloride (Nojd, *loc. cit.*), does not show selective absorption in the ultra-violet and hence cannot contain a conjugated system of ethylenic linkages. On catalytic reduction, lupadiene absorbs only one mole of hydrogen to give γ-*lupene*, m. p. 197—199°, which is also obtained by the dehydration of lupanol with phosphorus pentachloride and cannot be further hydrogenated.

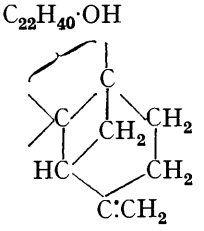
Ozonolysis of lupenyl acetate gives formaldehyde in 18% yield, characterised as its dimedon derivative, from which it follows that the ethenoid linkage of lupeol is present as an exocyclic methylene group. Ozonolysis of either β- or γ-lupene fails to give formaldehyde, whereas similar treatment of α-lupene gives this aldehyde, indicating that it is the parent hydrocarbon of lupeol.



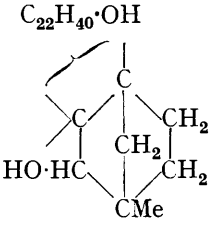
With the object of examining the nature and location of the unsaturated centre of lupeol, the oxidation of lupenyl acetate has been investigated. Using chromic anhydride, Cohen (*loc. cit.*) isolated an acidic product which was not characterised; we obtained a similar product which is still being investigated. From the neutral fraction obtained by oxidation of lupenyl acetate with either chromic anhydride or ozone, we have isolated a monoacetate, $C_{32}H_{52}O_3$, m. p. 260—262°, which is unaltered by treatment with acetic anhydride and from which on hydrolysis an *alcohol*, $C_{30}H_{50}O_2$, m. p. 232°, is obtained. The acetate, which does not contain an active hydrogen atom (Zerewitinoff), is saturated (tetranitromethane in chloroform) and is extremely stable, being unaffected after prolonged treatment with chromic anhydride in boiling acetic acid. Although the acetate does not react with the usual carbonyl reagents, its ketonic character is revealed by spectroscopic examination. The presence of a carbonyl group has moreover been confirmed by reduction with sodium

and alcohol, a *dihydric alcohol*, $C_{30}H_{52}O_2$, m. p. 258°, being obtained which has been characterised by the formation of its *diacetate*, m. p. 238—239°.

An insight into the mechanism of formation of the saturated *keto-acetate*, m. p. 260—262°, has been obtained from a study of the action of hydrogen peroxide on lupenyl acetate. Hydrolysis of the crude reaction product gives a saturated dihydric alcohol identical with that obtained by reduction of the keto-acetate. Hydrogen peroxide, therefore, has effected the addition of a molecule of water, a reaction similar in all respects to the hydration of β-pinene to fenchyl alcohol (Henderson and Chisholm, J., 1924, **125**, 107). The behaviour of lupenyl acetate on oxidation thus allows us to give to lupeol the hypothetical partial structure (I), which adequately interprets the reactions involving the ethenoid linkage, the diol, m. p. 258°, being (II) and the keto-acetate (III). Lupeol thus differs from the triterpenes hitherto examined in detail (the oleanolic acid group) in that *it is not a derivative of hydropicene*.



(I.)



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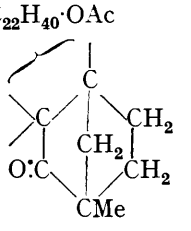
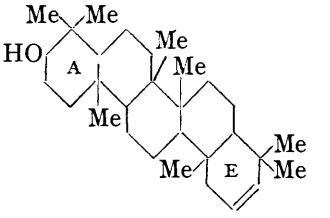


(III.)



(IV.)

Note : The investigations described in this communication have been in progress during the last three years. Since the section described above was completed a paper by Ruzicka, Furter, Pieth, and Schellenberg (*Helv. Chim. Acta*, 1937, **20**, 1564) has appeared in which the isolation of 1 : 2 : 5-trimethylnaphthalene and 6-hydroxy-1 : 2 : 5-trimethylnaphthalene from the dehydrogenation product of lupeol is described. We have made an incomplete study of the dehydrogenation of lupeol and have also isolated 1 : 2 : 5-trimethylnaphthalene together with a solid hydrocarbon which may be 1 : 2 : 5 : 6-tetramethylnaphthalene, but the amount available has not allowed a complete characterisation. A hypothetical formula (IV) for lupeol is advanced by Ruzicka in which this pentacyclic alcohol is represented as a derivative of the symmetrical, fully cyclised squalene, the ethenoid linkage being located in ring E. This formula will not give an interpretation of the results of oxidation of lupenyl acetate described above.

Experimental.

Isolation of Lupeol from Mariposa Gutta.—The powdered gutta (1 kg.) was heated under reflux for 2 hours with successive portions of alcohol (3, 2, and 2 l.). The combined extract was cooled; the white solid (A) which then separated (270 g.; m. p. 135—145°) was hydrolysed by heating under reflux with alcoholic potassium hydroxide (2750 c.c.; 10%) for 3 hours. The solution was diluted with water (5 l.) and after 5 hours the coagulated white precipitate of non-saponifiable material was collected (200 g.; m. p. 145—150°). The non-saponifiable matter (150 g.) in benzene (150 c.c.) was treated with benzoyl chloride (95 g.) and pyridine (60 c.c.), and the mixture heated on the steam-bath for 10 hours. After removal of the solvents under reduced pressure the residue was triturated with methyl alcohol and then heated under reflux with acetone (1 l.) for ½ hour. After cooling and filtration, the solid was crystallised repeatedly from benzene–alcohol (1 : 3), from which lupenyl benzoate (31 g.) was obtained in large plates, $[\alpha]_D^{20°}$ + 60·1° * (l = 1, c = 3·02), m. p. 265°, which showed no depression on admixture with an authentic specimen (Found: C, 83·6; H, 10·1. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·3%). Hydrolysis of the benzoate gave lupeol, which separated from dilute alcohol in long needles, $[\alpha]_D^{20°}$ + 26·4° (l = 1, c = 3·51), m. p. 211—212°, showing no depression in admixture with an authentic specimen (Found: C, 84·3; H, 11·7. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%) and giving lupenyl acetate, m. p. 214—215°, $[\alpha]_D^{20°}$ + 47·3° (l = 1, c = 2·33), on acetylation.

Microhydrogenation. A solution of the lupenyl acetate (11·02 mg.) in glacial acetic acid in

* All rotations were measured in chloroform solution.

the presence of platinum-black absorbed 0·595 c.c. of hydrogen at 20·7° and 749 mm., corresponding to 1·04 double bonds. *Perbenzoic acid titration:* After 24 and 48 hours the acetate (0·1560 g.) in chloroform solution had absorbed the equivalent of 4·8 mg. and 4·85 mg. respectively of oxygen, corresponding to 0·90 and 0·91 ethylenic linkage.

Lupenyl Cinnamate from Mariposa Gutta.—The solid (A) was crystallised four times from acetone; the product, m. p. 195—206°, after repeated crystallisation from benzene–alcohol, attained the constant m. p. 234—235°, not depressed by authentic lupenyl cinnamate (Cohen, *loc. cit.*) (Found: C, 84·1; H, 10·1. Calc. for $C_{39}H_{56}O_2$: C, 84·1; H, 10·1%).

Lupanyl Acetate.—A solution of lupenyl acetate (5·5 g.) in glacial acetic acid (150 c.c.) was shaken with hydrogen and Adams's platinum oxide catalyst (0·3 g.) at 70° for 3 hours. The solution was filtered, and the product precipitated with water and crystallised twice from alcohol; *lupanyl acetate* then separated in triangular plates (5·0 g.), m. p. 245—246°, $[\alpha]_D^{20°}$ — 1·8° ($l = 1$, $c = 7·21$) (Found: C, 81·7; H, 11·5. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). Hydrolysis of the acetate with alcoholic potassium hydroxide gave lupanol, which crystallised from alcohol in needles, m. p. 201—202°, $[\alpha]_D^{20°}$ — 17·8° ($l = 1$, $c = 2·84$) (Found: C, 83·9; H, 12·2. Calc. for $C_{30}H_{52}O$: C, 84·0; H, 12·2%). *Lupanyl benzoate* separated from benzene–alcohol (1 : 3) in hexagonal plates, m. p. 259—260°, $[\alpha]_D^{20°}$ + 27·1° ($l = 1$, $c = 3·37$) (Found: C, 83·1; H, 10·7. $C_{37}H_{56}O_2$ requires C, 83·4; H, 10·6%). Neither lupanol nor its derivatives gave a coloration with tetranitromethane in chloroform solution.

Lupanone.—(a) Lupenone, prepared by Cohen's method (*loc. cit.*), separated from alcohol in large hard needles, m. p. 169·5—170·5°, $[\alpha]_D^{20°}$ + 63·5° ($l = 1$, $c = 1·63$) (Found: C, 84·9; H, 11·4. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). It was characterised by the preparation of the *hydrazone*, which separated from aqueous alcohol either in plates or in needles, m. p. 341—342° (decomp.), the two forms being interconvertible (Found: C, 82·0; H, 11·7; N, 6·2. $C_{30}H_{50}N_2$ requires C, 82·1; H, 11·5; N, 6·4%). Lupenone (5·0 g.) was hydrogenated by the method adopted for the preparation of lupanyl acetate. *Lupanone* separated from alcohol in plates, m. p. 204—205°, $[\alpha]_D^{20°}$ + 16·2° ($l = 1$, $c = 1·76$) (Found: C, 84·2; H, 11·8. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). The *oxime* separated from ethyl acetate in long fine needles, m. p. 270° (Found: C, 81·3; H, 11·5; N, 3·1. $C_{30}H_{51}ON$ requires C, 81·5; H, 11·6; N, 3·2%). *Lupanonehydrazone* separated from alcohol–nitrobenzene (2 : 1) in needles, m. p. 341—342° (decomp.) (Found: C, 81·4; H, 11·7; N, 6·2. $C_{30}H_{52}N_2$ requires C, 81·7; H, 11·9; N, 6·35%). A solution of the ketone (0·7 g.) and *m*-nitrobenzaldehyde (0·62 g.) in glacial acetic acid (20 c.c.) and chloroform (12·5 c.c.) was saturated with dry hydrogen chloride at 0°. After standing at room temperature for 3 days, the mixture was washed successively with water, aqueous sodium hydroxide, and water. Removal of the solvent from the dried solution, followed by crystallisation of the residue from alcohol, gave the m-*nitrobenzylidene* derivative of lupanone in pale yellow needles, m. p. 127° (Found: C, 79·0; H, 9·9; N, 2·8. $C_{37}H_{53}O_3N$ requires C, 79·4; H, 9·5; N, 2·5%).

(b) Lupanol (2·85 g.) in glacial acetic acid (230 c.c.) was treated with a solution of chromic anhydride (3 g.) in water (5 c.c.), and glacial acetic acid (35 c.c.) added slowly with shaking during 15 minutes. The mixture was heated on the steam-bath for 2 hours, diluted with water, and extracted with ether. The ethereal solution was washed with potassium hydroxide solution (10%) (extract A) and then with water. After removal of ether from the dried solution the residue was crystallised thrice from alcohol to give lupanone, m. p. 204—205°, identical with the specimen prepared by method (a). Extract A was acidified with dilute sulphuric acid, and the solution extracted with ether. The acidic fraction, isolated in the usual manner, was crystallised twice from aqueous acetic acid and twice from alcohol; *lupanedicarboxylic acid* was then obtained in microscopic plates, m. p. 272° (decomp.) (Found: C, 75·4; H, 10·6. $C_{30}H_{50}O_4$ requires C, 75·9; H, 10·6%).

α-Lupene.—Lupenonehydrazone (2·7 g.) was heated with a solution of sodium ethoxide (from 1·7 g. of sodium) in alcohol (20 c.c.) for 8 hours in a sealed tube at 180°. The mixture was diluted with water, and the precipitated solid collected and crystallised twice from dilute alcohol; *α-lupene* then separated in hard needles (0·7 g.), m. p. 163°, $[\alpha]_D^{20°}$ + 30·2° ($l = 1$, $c = 3·56$), which gave a yellow coloration with tetranitromethane in chloroform solution (Found: C, 87·65; H, 12·2. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%).

Lupane.—(a) α-Lupene (0·25 g.) in ethyl acetate (150 c.c.) was shaken at 40° with hydrogen for 3 hours, Adams's platinum oxide (0·05 g.) being used as catalyst. After two crystallisations from ethyl alcohol the product gave *lupane* in long needles, m. p. 184°, $[\alpha]_D^{20°}$ — 1·1° ($l = 1$, $c = 8·33$), which did not give a coloration with tetranitromethane in chloroform solution (Found: C, 87·2; H, 12·7. $C_{30}H_{52}$ requires C, 87·3; H, 12·7%).

(b) Lupanone (2·0 g.) in glacial acetic acid (200 c.c.) was heated under reflux for 10 hours with amalgamated zinc (20 g.) and concentrated hydrochloric acid (50 c.c.), added in five equal portions at intervals of 2 hours. After decantation, the solution was diluted with water, and the mixture extracted with ether. The product, isolated in the usual manner, was repeatedly crystallised from alcohol to give lupane in long hard needles, m. p. 184°, identical with that prepared by method (a).

(c) Lupanonehydrazone (1·8 g.) was heated for 8 hours at 180° in a sealed tube with a solution of sodium ethoxide (from 1·1 g. of sodium) in alcohol (15 c.c.). The product was diluted with water, and the precipitated solid collected and crystallised thrice from alcohol to give lupane (0·5 g.), m. p. 184°, not depressed by the specimens prepared by methods (a) and (b).

β-*Lupene.*—Lupenone (2 g.) was reduced under the conditions described for the preparation of lupane [method (b)]. After many crystallisations from methyl alcohol–ether, β-*lupene* was obtained in small needles (0·05 g.), m. p. 191°, $[\alpha]_D^{20°}$ + 21·4° (l = 1, c = 0·627), giving a yellow colour with tetranitromethane in chloroform solution (Found: C, 87·6; H, 12·2. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%).

γ-*Lupene.*—(a) Lupadiene prepared by Nojd's method (*loc. cit.*) had m. p. 175°, $[\alpha]_D^{20°}$ + 24·6° (l = 1, c = 1·07) (Found: C, 88·0; H, 12·0. Calc. for $C_{30}H_{48}$: C, 88·1; H, 11·9%). Lupadiene (1·0 g.) in ethyl acetate (150 c.c.) was shaken with hydrogen and Adams's platinum oxide catalyst (0·15 g.) at 40° for 3 hours. Removal of the solvent, followed by crystallisation of the residue from ether–alcohol and then from ethyl acetate, gave γ-*lupene* in large hard needles, m. p. 197—199°, $[\alpha]_D^{20°}$ — 19·7° (l = 1, c = 3·25). The product gave a yellow coloration with tetranitromethane in chloroform solution (Found: C, 87·6; H, 12·3. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%).

(b) Lupanol (1·5 g.) was added in small portions to a suspension of phosphorus pentachloride in light petroleum (b. p. 40—60°; 25 c.c.) during 4 hours. The mixture was heated under reflux for 30 minutes, cooled, and washed repeatedly with water. After removal of the solvent from the dried solution, the residue was crystallised repeatedly from alcohol–ether, from which γ-lupene separated in short hard needles (0·6 g.), m. p. 197—199°, identical with the specimen prepared by method (a).

Keto-acetate, $C_{32}H_{52}O_3$ (III).—(a) Lupenyl acetate (10 g.) in acetic acid (300 c.c.) was treated with a solution of chromic anhydride (10 g.) in acetic acid (80 c.c.) and water (7 c.c.), added with stirring during 1 hour at 90°. The mixture was heated under reflux for a further 2 hours, and the solvent then removed under reduced pressure and, after the addition of water, repeatedly extracted with ether. The ethereal solution was washed with dilute sulphuric acid and then with aqueous potassium hydroxide (5%). The insoluble potassium salt separating was removed and washed with ether, the washings being added to the ethereal solution. This was dried (sodium sulphate), and the solvent evaporated; the residue (2·5 g.), m. p. 228—232°, gave, after repeated crystallisation from ethyl alcohol, the *keto-acetate* (0·7 g.) in hard needles, m. p. 260—262°, $[\alpha]_D^{20°}$ + 7·4° (l = 1, c = 1·1) (Found: C, 79·2; H, 11·1. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). *Light absorption in alcohol:* Maximum, approx. 2800 A., ε = 60.

(b) Lupenyl acetate (10 g.) in chloroform (80 c.c.) was treated with a slow stream of ozonised oxygen (6%) at room temperature for 6 hours. The solvent was removed under reduced pressure, and the hard white ozonide decomposed by heating under reflux with water for 1 hour. The mixture was then distilled in steam, and the steam-volatile constituents collected in water. This aqueous distillate was treated with an alcoholic solution of dimedon; the formaldehyde dimedon derivative obtained (1·12 g.) had m. p. 183—185°, not depressed by an authentic specimen.

An ethereal solution of the non-volatile residue was washed successively with aqueous potassium hydroxide (10%) and water. Removal of the solvent from the dried solution gave a white solid (2·5 g.), which after many crystallisations from ethyl alcohol was obtained in hard needles, m. p. 260—262°, showing no depression on admixture with a specimen prepared by method (a).

Keto-alcohol, $C_{30}H_{50}O_2$, *m. p.* 232°.—The keto-acetate (III) (0·35 g.) was heated under reflux with an excess of alcoholic potassium hydroxide (10 c.c.; 5%) for 4 hours. The solid separating on cooling was crystallised from alcohol, from which the *keto-alcohol* separated in needles, m. p. 232°, $[\alpha]_D^{20°}$ — 13·2° (l = 1, c = 2·3) (Found: C, 81·6; H, 11·1. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). *Light absorption in alcohol:* Maximum, 2750 A., ε = 53.

Dihydric Alcohol, $C_{30}H_{52}O_2$ (II).—(a) Lupenyl acetate (10 g.) in acetic acid (250 c.c.) was treated with hydrogen peroxide (Merck's perhydrol; 25 c.c.). The mixture was heated on the steam-bath for 2 hours and largely diluted with water, and the solid collected and hydrolysed

by heating under reflux for 2 hours with an excess of alcoholic potassium hydroxide (5%). The product was isolated by water precipitation and crystallised from alcohol and then repeatedly from ethyl acetate, from which the *diol* separated in long needles, m. p. 258° (Found: C, 81·2; H, 11·5. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). *Active hydrogen determination (Zerewitinoff):* 6·353 Mg. gave 0·75 c.c. of methane, measured at 0° and 760 mm., corresponding to 2·2 atoms of active hydrogen. The *diacetate* was prepared by treatment with acetic anhydride and pyridine and separated from methyl alcohol in plates, m. p. 238—239° (Found: C, 77·5; H, 10·4. $C_{34}H_{56}O_4$ requires C, 77·2; H, 10·7%). Neither the diacetate nor the diol gave a coloration with tetranitromethane in chloroform solution.

(b) A boiling solution of the keto-acetate (III) (1 g.) in alcohol (50 c.c.) was treated with sodium (4 g.), added as rapidly as the reaction would permit. After dilution with alcohol (20 c.c.) a further addition of sodium (2 g.) was made, and the mixture was then heated under reflux for 1 hour and diluted with water. The solid obtained was washed with water and crystallised from alcohol and then from ethyl acetate, from which the diol separated in needles, m. p. 258° either alone or in admixture with the specimen described under (a). Acetylation gave the diacetate, m. p. 238—239°, showing no depression on admixture with that prepared by method (a).

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