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MODIFIED STEROID HORMONES—XXXIV[1]

21-ACETYL-16α,17α-ISOPROPYLIDENEDIOXY-20-KETOPREGNENES AND SOME OF THEIR TRANSFORMATIONS

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Abstract—A route to 21-acetyl-16α,17α-isopropylidenedioxy-20-ketopregnenes has been developed. Some reactions of these compounds are described.

EXPLORATORY studies into the preparation and reactions of some 21-acetyl-16α,17α-isopropylidenedioxy-20-ketopregnenes are herein reported. Treatment of 3β-acetoxy-16α,17α-isopropylidenedioxypregn-5-en-20-one[2] (I; R = H)* in acetic anhydride with boron trifluoride etherate[3] for five minutes at room temperature afforded in good yield, a crystalline compound to which the constitution 3β-acetoxy-21-acetyl-16α,17α-isopropylidenedioxypregn-5-en-20-one (II; R = H, R^1 = Ac) has been assigned on the basis of the following observations. The UV absorption spectrum, λ_{max}^{EtOH} 279 mμ (ε, 13,000) was shifted by alkali to λ_{max}^{EtOH} 300 mμ (ε, 24,000), a behaviour characteristic of a β-diketone.[4] The NMR spectrum revealed a 6-proton peak at 7·98τ consistent with 3β-acetoxy and 21-acetyl groupings. A one-proton band at 4·15τ, attributable to an olefinic proton at C-21, and, in the IR spectrum, a broad intense band between 1630 and 1570 cm^{-1}, together with the absence of observable OH stretching bands, indicate that the compound exists in solution in the enolic chelate form.

Treatment of the diketone (II; R = H, R^1 = Ac) with diazomethane gave a methyl enol ether (III; R = OMe, R^1 = Ac), the NMR spectrum of which showed

* A detailed analysis of the NMR spectrum of a 16α,17α-isopropylidenedioxy-20-ketopregnene has not been reported hitherto. Observations obtained with compound (I; R = H) are now presented. Four 3-proton singlet bands at 9·4, 8·98, 7·98 and 7·78τ arise from the C-13 and C-10 methyl and the 3β-acetoxy and 17β-acetyl groups respectively. Two additional 3-proton singlet peaks at 8·83 and 8·53τ are ascribed to the methyl group components of the 16α,17α-isopropylidenedioxy residue. Both methyl groups are subject to deshielding by the acetonide oxygen atoms, and to some extent by the 20-ketone. One methyl group, however, is nearer to and beneath the plane of the 20-oxo function (assuming that the isopropylidenedioxy residue has no effect upon the conformation of the 17β-acetyl group[5]), and may therefore be expected to be subject to slight *shielding*.[6] This interpretation explains the observed difference in chemical shift of 0·3 ppm. A broad hump at *circa* 5·5τ and a multiplet at 4·65τ are assigned to the C-3α and C-6 protons respectively. The analysis is completed by the assignment of a broad doublet ($J \simeq 4$ c/s) at 4·96τ to the C-16β proton coupled to the protons at C_{15}.

[1] Part XXXIII, *Tetrahedron* **20**, 597 (1964).
[2] G. Cooley, B. Ellis, F. Hartley and V. Petrow, *J. Chem. Soc.* 4373 (1955).
[3] See D. P. N. Satchell, *Quart. Revs. Chem. Soc.* **XVII**, No. 2, 160 (1963).
[4] See e.g. G. S. Hammond, W. G. Borduin and G. A. Guter, *J. Amer. Chem. Soc.* **81**, 4682 (1959).
[5] N. L. Allinger and M. A. DaRooge, *J. Amer. Chem. Soc.* **83**, 4256 (1961).
[6] L. M. Jackman, *Applications of NMR Spectroscopy in Organic Chemistry* Chap. 7. Pergamon Press, London (1959).

reduction of the 7·98τ peak to 3-proton intensity, and a new methyl resonance of like intensity at 7·70τ. The latter band arises from the protons of an acetyl grouping (at C-21) in conjugation with an olefinic centre.[7]

Condensation of the diketone (II; R = H, R^1 = Ac) with pyrrolidine was surprisingly accompanied by saponification of the 3β-acetoxy grouping to give an enamine formulated as (III; R =  , R^1 = H), the C-21 acetyl and C-21 olefinic proton resonances appearing in the NMR spectrum at 7·49τ and 4·70τ respectively. The mono-2,4-dinitrophenylhydrazone derivative of the same diketone is regarded as (IV), as NMR revealed the absence of the C-21 olefinic proton, the presence of a C-21 methylene group (2-proton AB quartet, 5·93 and 6·49τ, J_{HH} = 18·0 c/s), and the shifting of the C-21 acetyl peak to 7·88τ, consistent with the ending of conjugation.[7]

Reaction of the diketone (II; R = H, R^1 = Ac) with hydrazine in acetic acid gave the disubstituted pyrazole (V; R = H, R^1 = Ac), the constitution of which followed from (a) the NMR spectrum* which showed, *inter alia*, the presence of the 16α,17α-isopropylidenedioxy residue, and indicated the presence of a —CH= ring proton and aromatic C—CH_3 (singlet absorptions at 4·01τ and 7·71τ respectively) (b) the IR spectrum which showed bands at 1583 and 1566 cm^{-1} (Nujol) attributed to pyrazole ring stretching modes,[8] and (c) the UV spectrum which showed only end absorption.[8] Alkaline saponification of this derivative gave the 3β-alcohol (V; R = R^1 = H), converted by Oppenauer oxidation into the corresponding steroidal-4-en-3-ketone. 16α,17α-Isopropylidenedioxy-6α-methyl-17β-(3′-methylpyrazol-5′-yl)-androst-4-en-3-one was also prepared by application of the same reaction sequence to 3β-acetoxy-21-acetyl-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one (II; R = Me, R^1 = Ac), obtained from 3β-acetoxy-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one[9] (I; R = Me) and acetic anhydride–boron trifluoride etherate.

Acetylation of 16α,17α-isopropylidenedioxyprogesterone[10] and of its 6α-methyl analogue[9] at C-21 with the acetic anhydride–boron trifluoride reagent was accompanied by 3-enol acetylation, giving the derivatives (VI; R = H) and (VI; R = Me) respectively. Crystalline products were not obtained when attempts were made to regenerate the 4-en-3-one system by treatment of the last two compounds with alkali. In contrast, the 3β-acetoxy-21-acetyl derivatives (II; R = H, R^1 = Ac) and (II; R = Me, R^1 = Ac) were readily saponified to the crystalline 3β-alcohols (II; R = R^1 = H) and (II; R = Me, R^1 = H).

Treatment of the diketone (II; R = H, R^1 = Ac) with hot methanolic hydrochloric acid unexpectedly gave a dihydroxy unsaturated diketone, $C_{23}H_{32}O_4$, which formed a diacetate $C_{27}H_{36}O_6$. The NRM spectrum of the latter compound failed to reveal the presence of an 16α,17α-isopropylidenedioxy residue, and a downfield shift of the

* The pyrazole ring leads to increased screening of the C-18 protons and of the vicinal methyl group of the acetonide residue. Upfield resonance shifts were 0·12 p.p.m and 0·16 p.p.m., respectively.

[7] J. N. Shoolery and M. T. Rogers, *J. Amer. Chem. Soc.* **80**, 5121 (1958).

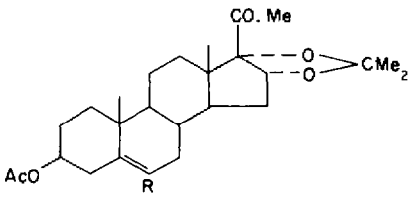
[8] A. R. Katritzky and P. Ambler in *Physical Methods in Heterocyclic Chemistry* Chap. 10. Academic Press (1963), and Refs. cited therein, in particular C. R. Rondestvedt, jnr. and P. K. Chang, *J. Amer. Chem. Soc.* 77, 6532 (1955).

[9] B. Ellis, S. P. Hall, V. Petrow and S. Waddington-Feather, *J. Chem. Soc.* 4111 (1961).

[10] G. Cooley, B. Ellis, F. Hartley and V. Petrow, *J. Chem. Soc.* 4373 (1955).

C-13 methyl resonance from 9·35τ to 8·98τ, to coincide with the C-10 methyl absorption points to a D-homo structure.[11] It is hoped to examine these products in greater detail at a later date.

3β-Acetoxypregn-5-en-20-one and 3β,17α-diacetoxypregn-5-en-20-one were each recovered unchanged after treatment with the acetic anhydride–boron trifluoride etherate reagent for five minutes at room temperature.



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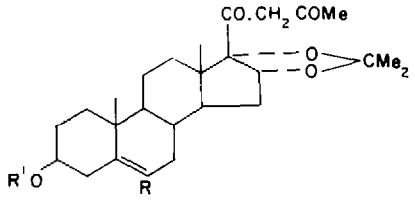

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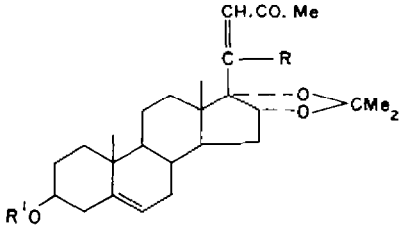

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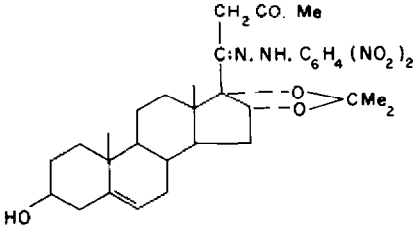

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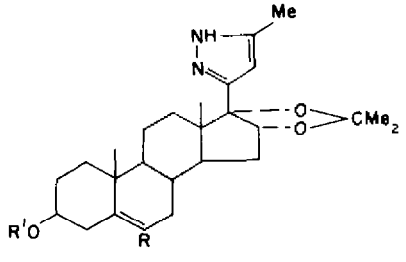
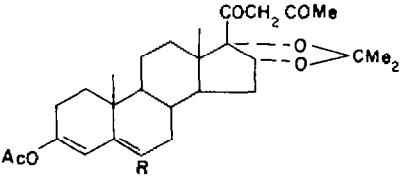


V



VI

EXPERIMENTAL

Optical rotations were determined at concentrations of ca. 1% in A.R. chloroform at laboratory temp, unless otherwise stated. UV spectra, determined with a Perkin–Elmer Model 350 spectrophotometer, refer to solutions in spectro-grade ethanol. IR spectra were determined with a Hilger H800 spectrophotometer fitted with CaF_2 and NaCl prisms for the frequency ranges 4000–1300 and 1350–650 cm^{-1} respectively, the solvents used being as indicated. NMR spectra were determined at

[11] N. R. Trenner, B. H. Arison, D. Taub and N. L. Wendler, *Proc. Chem. Soc.* 214 (1961).

40 Mcs/s with a Perkin–Elmer permanent magnet spectrometer, employing a crystal calibrated decade field shift. Solutions were in deuteriochloroform containing tetramethylsilane as internal reference. Significant NMR data of compounds is given only when changes in resonance greater than 0·05 ppm occur relative to the corresponding bands observed in the spectrum of the model compound (1: R = H).

3β-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxypregn-5-en-20-one (II; R = H, R^1 = Ac). A solution of 3β-acetoxy-16α,17α-isopropylidenedioxypregn-5-en-20-one (2 g) in acetic anhydride (10 ml) and boron trifluoride etherate (2 ml) was left at room temp for 5 min. The mixture was poured into sodium acetate aq, and the washed product purified from methanol–methylene dichloride, yielding II (1·4 g) as needles, m.p. 221°, $[\alpha]_D$ +14·3° (dioxan), λ_{max} 279 mμ (ε 13,140), shifted by 0·1N KOH to 300 mμ (ε 24,000), $\nu_{max}^{CCl_4}$ 1738, 1623, 1596 cm^{-1}. (Found: C, 71·2; H, 8·7. $C_{28}H_{40}O_6$ requires: C, 71·2; H, 8·5%).

3β-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxy-20-methoxypregna-5,20-diene (III; R = OMe, R^1 = Ac). A solution of the foregoing compound (1·0 g) and diazomethane (3 g) in ether (500 ml) was left at 0° for 16 hr, then concentrated under red. press. to ca. 50 ml. The product which separated was recrystallized from methanol–methylene dichloride containing a trace of pyridine, and yielded III (R = OMe, R^1 = Ac; 400 mg) as needles, m.p. 205–207°, $[\alpha]_D$ +32°, λ_{max} 272–273 mμ (ε 15,960), $\nu_{max}^{CH_2Cl_2}$ 1727, 1672, 1592 cm^{-1}, τ6·32 (OMe). (Found: C, 71·9; H, 8·8. $C_{29}H_{42}O_6$ requires: C, 71·6; H, 8·7%).

21-Acetyl-3β-hydroxy-16α,17α-isopropylidenedioxy-20-N′-pyrrolidylpregna-5,20-diene (III; R =  , R^1 = H). A boiling solution of II(R = H, R^1 = Ac; 700 mg) in methanol (10 ml) and methylene dichloride (5 ml) was treated with pyrrolidine (1 ml). The methylene dichloride was evaporated off, and the mixture cooled to room temp. The product was isolated with ether and crystallized from acetone–hexane to give III (R =  , R′ = H; 300 mg) as needles, m.p. 270–272°, $[\alpha]_D$ +3°, λ_{max} 313 mμ (ε 31,980), $\nu_{max}^{CCl_4}$ 3608 cm^{-1}, $\nu_{max}^{CH_2Cl_2}$ 1623, 1533 cm^{-1} τ 6·62 (multiplet) (pyrrolidyl α,α′CH_2). (Found: C, 74·7; H, 9·7; N, 3·1. $C_{30}H_{45}O_4N$ requires: C, 74·5; H, 9·4; N, 2·9%).

21-Acetyl-20-(2′,4′-dinitrophenylhydrazone)pregn-5-en-3β-ol (IV). A solution of the 21-acetyl steroid (II; R = H, R^1 = Ac; 1·0 g) in ethanol (20 ml) and chloroform (10 ml) was added to a boiling solution of 2,4-dinitrophenylhydrazone (400 mg) in ethanol (25 ml) and conc. HCl (0·5 ml). The mixture was concentrated to 10 ml, cooled, and the crystalline product purified from methanol–methylene dichloride. Compound IV (800 mg) formed needles, m.p. 234–235°, $[\alpha]_D$ +60°, λ_{max} 354 mμ (ε 21,900) and 225 mμ (ε 15,650), $\nu_{max}^{CH_2Cl_2}$ 3609, 3340, 1712, 1620, 1597 and 1517 cm^{-1}. (Found: C, 62·9; H, 7·1; N, 9·0. $C_{32}H_{42}N_4O_8$ requires: C, 62·9; H, 6·9; N, 9·2%).

3β-Acetoxy-17β-(3′-methylpyrazol-5′-yl)-16α,17α-isopropylidenedioxyandrost-5-ene (V; R = H, R^1 = Ac). A solution of the 21-acetyl steroid (II; R = H, R^1 = Ac; 1 g) in acetic acid (10 ml) and hydrazine hydrate (0·5 ml) was left at room temp for 20 hr. The mixture was poured into water, and the product crystallized from methanol aq to give V(R = H, R^1 = Ac; 650 mg) as needles, m.p. 248°, $[\alpha]_D$ +44°, $\nu_{max}^{CH_2Cl_2}$ 3470, 1730, 1569 cm^{-1}, ν_{max}^{Nujol} 1744, 1583, 1566 cm^{-1}, τ9·52 (C-13 methyl). (Found: C, 71·4; H, 8·6; N, 6·1. $C_{28}H_{40}O_4N_2$ requires: C, 71·8; H, 8·6; N, 6·0%).

3β-Hydroxy-17β-(3′-methylpyrazol-5′-yl)-16α,17α-isopropylidenedioxyandrost-5-ene (V; R = R^1 = H). A solution of the foregoing ester (V; R = H, R^1 = Ac; 4·5 g) and KOH (1 g) in methanol (200 ml) and water (10 ml) was refluxed for 1 hr. The mixture was poured into water, and the product recrystallized from methanol aq as needles of V(R = R^1 = H; 4 g), m.p. 249°, $[\alpha]_D$ −37·5°, $\nu_{max}^{CH_2Cl_2}$ 3600, 3450, 1569, 1558 cm^{-1}, τ 9·52 (C-13 methyl). (Found: C, 73·3; H, 9·0; N, 6·1. $C_{26}H_{38}O_3N_2$ requires: C, 73·2; H, 9·0; N, 6·6%).

17β-(3′-Methylpyrazol-5′-yl)-16α,17α-isopropylidenedioxyandrost-4-en-3-one. A solution of the foregoing compound (2 g) and aluminium isopropoxide (4 g) in dry toluene (100 ml) and cyclohexanone (30 ml) was refluxed for 1½ hr. An aqueous solution of potassium sodium tartarate (6%, 100 ml) was added and the solvents were removed by steam distillation. The product was isolated with ether, and crystallized from methanol aq to yield *17β-(3′-methylpyrazol-5′-yl)-16α,17α-isopropylidenedioxy androst-4-en-3-one* (1·3 g) as needles, m.p. 310–312°, $[\alpha]_D$ +95°, λ_{max} 240 mμ (ε 16,520), $\nu_{max}^{CH_2Cl_2}$

3460, 1671, 1611, 1570, 1561 cm^{-1}. (Found: C, 73·6; H, 8·6; N, 6·2. $C_{26}H_{36}O_3N_2$ requires: C, 73·2; H, 9·0; N, 6·6%).

3β-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one (II; R = Me, R^1 = Ac). A suspension of 3β-acetoxy-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one (1·2 g) in acetic anhydride (5 ml) was treated with boron trifluoride etherate (1·2 ml) and the mixture left at room temp for 5 min. The mixture was poured into sodium acetate aq and the washed product purified from methanol–methylene dichloride. *3β-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one* (800 mg) separated in needles, m.p. 204°, $[\alpha]_D$ −5°, λ_{max} 279 mμ (ε 13,100), shifted by 0·1N KOH to λ_{max} 300 mμ (ε 24,100), $\nu_{max}^{CCl_4}$ 1733, 1620, 1597 cm^{-1}. (Found: C, 71·5; H, 8·4. $C_{29}H_{42}O_6$ requires: C, 71·6; H, 8·7%).

3β-Acetoxy-16α,17α-isopropylidenedioxy-6-methyl-17β-(3'-methylpyrazol-5'-yl)-androst-5-ene (V; R = Me, R^1 = Ac). A suspension of the 21-acetyl steroid (II; R = Me, R^1 = Ac; 1 g) in acetic acid (20 ml) and hydrazine hydrate (2 ml) was stirred at room temp for 2½ hr. The product was filtered off, washed, and recrystallized from methanol aq to give V(R = Me, R^1 = Ac; 500 mg), as plates, m.p. 283–285°, $[\alpha]_D$ −50°, $\nu_{max}^{CH_2Cl_2}$ 3460, 1729, 1573 cm^{-1}, τ 9·53 (C-13 methyl). (Found: C, 71·9; H, 8·9. $C_{29}H_{42}O_4N_2$ requires: C, 72·2; H, 8·8%).

3β-Hydroxy-16α,17α-isopropylidenedioxy-6-methyl-17β-(3'-methylpyrazol-5'-yl)-androst-5-ene (V; R = Me, R^1 = H). A solution of the foregoing compound (V; R = Me, R^1 = Ac; 2·2 g) and NaOH (0·5 g) in methanol (60 ml) was refluxed for 1 hr. The mixture was concentrated to ca. 30 ml, and water added until crystallization commenced. The product was purified from methanol aq to give V (R = Me, R^1 = H; 1·6 g) as prisms, m.p. 236–238°, $[\alpha]_D$ −45°. (Found: C, 73·9; H, 9·5. $C_{27}H_{40}O_3N_2$ requires: C, 73·6; H, 9·15%).

16α,17α-Isopropylidenedioxy-6α-methyl-17β-(3'-methylpyrazol-5'-yl)-androst-4-en-3-one. A solution of the foregoing compound (2·2 g) and aluminium isopropoxide (1 g) in dry toluene (110 ml) and cyclohexanone (38 ml) was refluxed for 1 hr. An aqueous solution of potassium sodium tartarate (10%, 100 ml) was added and the solvents removed by steam distillation. The product was isolated with ether and chromatographed on alumina (50 g) in benzene. Elution with benzene–ether(4:1) gave crystalline material which was purified from acetone aq. *16α,17α-Isopropylidenedioxy-6α-methyl-17β-(3'-methylpyrazol-5'-yl)-androst-4-en-3-one* (400 mg) separated in needles, m.p. 255–257°, $[\alpha]_D$ +69°, λ_{max} 240 mμ (ε 15,600), $\nu_{max}^{CH_2Cl_2}$ 3450, 1663, 1604, 1568 cm^{-1}, τ 9·48 (C-13 methyl). (Found: C, 73·3; H, 8·7. $C_{26}H_{35}O_3N_2$ requires: C, 73·2; H, 9·0%).

3β-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxypregna-3,5-dien-20-one (VI; R = H). A solution of 16α,17α-isopropylidenedioxypregn-4-ene-3,20-dione (2 g) in acetic anhydride (10 ml) and boron trifluoride etherate (2 ml) was left at room temp for 5 min. The mixture was poured into sodium acetate aq and the washed product crystallized from methanol–methylene dichloride to give VI (R = H; 1·2 g) as needles, m.p. 207·5°–208°, $[\alpha]_D$ −41°, λ_{max} 235 mμ (ε 19,200) and 279 mμ (ε 12,890), $\nu_{max}^{CH_2Cl_2}$ 1762, 1620 cm^{-1}, τ 7·94 (21-acetyl), 4·14 (21-olefinic proton). (Found: C, 71·25; H, 8·2. $C_{28}H_{38}O_6$ requires: C, 71·5; H, 8·1%).

3-Acetoxy-21-acetyl-16α,17α-isopropylidenedioxy-6-methylpregn-3,5-dien-20-one (VI; R = Me). A solution of 16α,17α-isopropylidenedioxy-6α-methylpregn-4-ene-3,20-dione (1 g) in acetic anhydride (3 ml) and boron trifluoride etherate (1 ml) was left at room temp for 5 min. The mixture was poured into sodium acetate aq, and the product crystallized from methanol to give VI (R = Me; 300 mg) as plates, m.p. 153–155°, $[\alpha]_D$ −44°, λ_{max} 245 mμ (ε 16,870) and 277·5 mμ (ε 13,520), $\nu_{max}^{CH_2Cl_2}$ 1760, 1623, 1602 cm^{-1}, τ 8·36 (6-methyl), 7·87 (21-acetyl), 4·16 (21-olefinic proton). (Found: C, 71·6; H, 8·2. $C_{29}H_{40}O_6$ requires: C, 71·9; H, 8·3%).

21-Acetyl-3β-hydroxy-16α,17α-isopropylidenedioxypregn-5-en-20-one (II; R = R^1 = H). A solution of the 3β-acetoxy steroid (II; R = H, R^1 = Ac; 1 g) and NaOH (0·5 g) in methanol (30 ml) was refluxed for 1 hr, poured in water and the product isolated with ether. Recrystallization from acetone aq gave II (R = R^1 = H; 300 mg) as needles, m.p. 201°, $[\alpha]_D$ +12°, λ_{max} 280 mμ (ε 13,050) shifted by 0·1N KOH to 300 mμ (ε 23,850), $\nu_{max}^{CH_2Cl_2}$ 3605, 1617, 1598 cm^{-1}, τ 7·95 (21-acetyl), 4·18 (21-olefinic proton). (Found: C, 72·3; H, 8·8. $C_{26}H_{36}O_5$ requires: C, 72·5; H, 8·9%).

21-Acetyl-3β-hydroxy-16α,17α-isopropylidenedioxy-6-methylpregn-5-en-20-one (II; R = Me, R^1 = H). A suspension of the 3β-acetoxy steroid (II; R = Me, R^1 = Ac; 3 g) in methanol (90 ml) was treated with NaOH aq (5%, 20 ml), and the mixture was refluxed for 1 hr. Water was added until crystallization commenced. The product was purified from methanol–methylene dichloride to give II (R = Me, R^1 = H; 2·6 g) as needles, m.p. 240–240·5°, $[\alpha]_D$ +3°, λ_{max} 279 mμ (ε 12,760), $\nu_{max}^{CH_2Cl_2}$

3610, 1618, 1595 cm^{-1}, τ 8·39 (6-methyl), 7·96 (21-acetyl), 4·19 (21-olefinic proton). (Found: C, 72·4; H, 8·8. $C_{27}H_{40}O_6$ requires: C, 72·9; H, 9·1%).

Acid hydrolysis of the diketone (II; R = H, R^1 = Ac). A suspension of the diketone (3 g) in methanol (150 ml) and conc. HCl (10 ml) was heated under reflux for 1½ hr. Water was added to the clear solution until crystallization began. The mixture was cooled, and the product purified from methanol aq to give a *compound* (2·1 g), as needles, m.p. 260°, λ_{max} 265 mμ (ε 8,650), ν_{max}^{Nujol} 3450, 3320, 1667 and 1576 cm^{-1}. (Found: C, 73·9; H, 8·8. $C_{23}H_{32}O_4$ requires: C, 74·2; H, 8·7%). The *diacetate* crystallized from acetone aq, as needles, m.p. 195·5°, $[\alpha]_D$ +3°, λ_{max} 263 mμ (ε 9,550). $\nu_{max}^{CHCl_3}$ 1730, 1694 and 1609 cm^{-1}. (Found: C, 70·5; H, 7·8. $C_{27}H_{36}O_6$ requires: C, 71·0; H, 7·95%),