In Fig. 20 is shown the spectrum of allopregnane-3β-21-diol-20-one acetate in which most of the major bands are assignable to one or other of the functional systems. This constitutes the most complex structure to which this type of band analysis has yet been applied.

Concluding Remarks.—From the point of view of the organic chemist, the value of these curve analyses is restricted at present by the exclusion of compounds substituted in rings B and C. The logical approach to this problem involves a preliminary study of the spectra of monoalcohols, monoacetates and monoketones substituted only in the B or C rings, and studies directed to this end are in progress.

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The Preparation of 17β-Methyl-Δ⁵-androsten-3β-ol

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17β-Methyl-Δ⁵-androsten-3β-ol (IIa) has been unequivocally prepared from 17-methyl-Δ⁵,¹⁶-androstadien-3β-ol 3-acetate (I). The physical constants of IIa do not coincide with those reported for Serposterol.

The report by Ghosh and Basu[1] of a new steroid (Serposterol) isolated from the oleoresin fraction of *Rauwolfia serpentina* roots, which was postulated to have the structure 17β-methyl-Δ⁵-androsten 3β-ol (IIa), prompted us to synthesize the latter compound for comparison purposes.

An appropriate starting material was the already known 17-methyl-Δ⁵,¹⁶-androstadien-3β-ol 3-acetate (I).[2] Preferential reduction of the Δ¹⁶-double bond with 5% palladium-on-carbon in absolute alcohol was achieved readily[3] to give the 17β-methyl-3-acetate IIb. It was assumed that the hydrogenation had taken place from the rear as postulated previously.[2,4]

Saponification of IIb with 5% potassium hydroxide in methanol yielded 17β-methyl-Δ⁵-androsten-3β-ol (IIa). The 3-benzoate IIc was prepared in the usual manner. The structure of IIa was further verified by reducing the Δ⁵-double bond of the acetate IIb in acetic acid with Adams catalyst to afford 17β-methyl-androstan-3β-ol 3-acetate (IV) which compared well with a sample prepared from the Δ⁵,¹⁶-diene I in the authentic fashion.[2] Retention of the Δ⁵-3β-ol grouping in IIa was confirmed by its transformation into 17β-methyl-Δ⁴-androsten-3-one (III) (λ_{max} 241 mμ) through an Oppenauer oxidation.

It is important to notice the disparity of physical constants given by Ghosh and Basu[1] for their compound and derivatives and our compounds as shown in Table I.

TABLE I

	Ghosh and Basu[1] M.p., °C.	(CHCl₃) [α]D	This paper M.p., °C.	(CHCl₃) [α]D
17β-Methyl-Δ⁵-androsten-3β-ol (IIa)	152–154	−47°	164–165	−63°
17β-Methyl-Δ⁵-androsten-3β-ol 3-acetate (IIb)	136–138	...	123.5–124.5	−68
17β-Methyl-Δ⁵-androsten-3β-ol 3-benzoate (IIc)	142–144	...	193–194	−26

It is apparent from these figures that the compound isolated by Ghosh and Basu[1] is otherwise than as indicated by the structure IIa. It may finally be pointed out that the infrared absorption spectrum of IIa contains *one* medium strong band at 10.5 μ in contradistinction to the doublet at 10.3 and 10.4 μ reported for Serposterol.[1]

Androgen Assay.[5]—Subcutaneously as measured by the weight of the ventral prostate in the castrated male rat (single dose in sesame oil, 72 hours) both 17β-methyl-Δ⁵-androsten-3β-ol (IIa) and 17β-methyl-Δ⁴-androsten-3-one (III) were inactive.

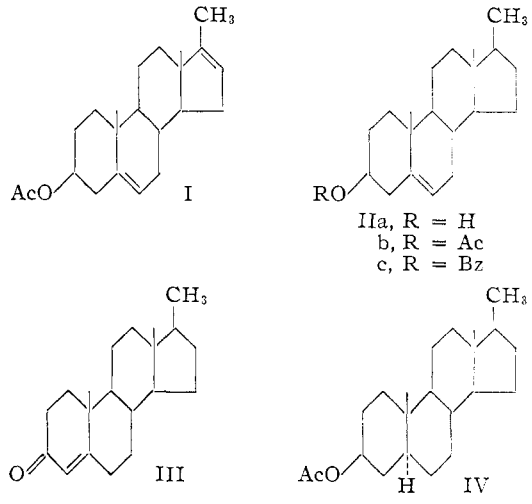
(1) B. P. Ghosh and R. K. Basu, *Naturwiss.*, **42**, 130 (1955).

(2) S. A. Julia and H. Heusser, *Helv. Chim. Acta*, **35**, 2080 (1952).

(3) E. B. Hershberg, E. P. Oliveto, C. Gerold and L. Johnson, THIS JOURNAL, **73**, 5073 (1951), show many examples of preferential reductions of this type.

(4) L. Ruzicka, P. Meister and V. Prelog, *Helv. Chim. Acta*, **30**, 867 (1947).

(5) We are indebted to Dr. F. I. Dessau and his associates for these results.



In the baby chick comb assay (inunction method, propylene glycol) both IIa and III were again inactive.

Addendum.—While this article was in press, R. T. Rapala and E. Farkas, THIS JOURNAL, **77**, 6685 (1955), reported similar findings regarding the non-identity of Serposterol and 17β-methyl-Δ⁵-androsten-3β-ol.

Experimental

Melting Points.—All melting points are uncorrected and were determined with uncalibrated Anschütz thermometers.

Optical Rotation.—The solvent was chloroform.

Absorption Spectra.—The ultraviolet absorption spectra were determined in absolute alcohol with a Beckman spectrophotometer (model DU) or a Cary recording spectrophotometer (model 11S). The infrared absorption spectra (pressed potassium bromide) were determined with a Perkin–Elmer spectrophotometer (model 21).

All evaporations were carried out under reduced pressure.

17β-Methyl-Δ⁵-androsten-3β-ol 3-Acetate (IIb).—A mixture of 163 mg. of 17-methyl-Δ⁵,¹⁶-androstadien-3β-ol 3-acetate (I, m.p. 133–135°),[6] 50 ml. of absolute ethanol and 20 mg. of 5% palladium-on-carbon was hydrogenated until no further hydrogen was taken up (only 1 mole equivalent was absorbed). After filtration and removal of the solvent, the resultant solid was crystallized three times from methanol–water to give 106 mg. of IIb, m.p. 123.5–124.5°; ν_{max} 1730, 1675 (weak) and 1235 cm.$^{-1}$; $[\alpha]^{25}D$ −68° (*c* 0.89).

Anal. Calcd. for $C_{22}H_{34}O_2$ (330.49): C, 79.95; H, 10.37. Found: C, 79.93; H, 10.29.

17β-Methyl-Δ⁵-androsten-3β-ol (IIa).—A solution of the 3-acetate IIb (338 mg.) in 5% potassium hydroxide in methanol was refluxed for 1 hour, poured into cold water and filtered. Recrystallization of the resultant solid from methanol furnished 258 mg. of IIa, m.p. 164–165°; ν_{max} 3480 and 1672 (weak) cm.$^{-1}$; $[\alpha]^{25}D$ −63° (*c* 1.055).

(6) Reference 2 gives m.p. 134–135°.

Anal. Calcd. for $C_{20}H_{32}O$ (288.46): C, 83.27; H, 11.18. Found: C, 83.07; H, 11.20.

17β-Methyl-Δ⁵-androsten-3β-ol 3-Benzoate (IIc).—To a solution of 340 mg. of the 3β-ol IIa in 10 ml. of pyridine was added 1 ml. of benzoyl chloride and the resultant mixture heated on a steam-bath 1 hr. The solution was poured into dilute sodium bicarbonate and the precipitated solid filtered. After being treated with Norite in an ether–benzene solution, the solid was crystallized from benzene–methanol and finally methanol to give 186 mg. of IIIc, m.p. 193–194°. This was dissolved in a 3-to-1 mixture of petroleum ether (Skellysolve B) and benzene and washed through a column of neutral alumina (activity II on the Brockman scale). Recrystallization from methanol afforded the analytical sample of m.p. 193–194°; λ_{max} 229 mμ (ε 14,200), 273 mμ (ε 950) and 280 mμ (ε 750); ν_{max} 1712, 1602, 1588, 1270 and 710 cm.$^{-1}$; $[\alpha]^{26}D$ (*c* 1.11).

Anal. Calcd. for $C_{27}H_{36}O_2$ (392.56): C, 82.60; H, 9.24. Found: C, 82.82; H, 9.56.

17β-Methyl-Δ⁴-androsten-3-one (III).—A solution of the 3β-ol (IIa, 500 mg.) in dry toluene (60 ml.) and cyclohexanone (6 ml.) was treated with a solution of aluminum isopropoxide in toluene (0.2 g./ml.) (3 ml.) while hot and the mixture was refluxed for one-half hour. A saturated solution of potassium sodium tartrate (*ca.* 20 ml.) was added, and the resultant mixture was steam distilled until all traces of cyclohexanone were removed. The mixture was extracted with ether and benzene, dried and treated with Norite. After removal of the solvent, the resultant oil was crystallized from methanol–water to give 234 mg., m.p. 103–105°. Several crystallizations from the same solvent pair yielded III, m.p. 109.5–110.5°, λ_{max} 241 mμ (ε 14,400); ν_{max} 1678 and 1612 cm.$^{-1}$; $[\alpha]^{25}D$ +123° (*c* 0.79).

Anal. Calcd. for $C_{20}H_{30}O$ (286.44): C, 83.86; H, 10.56. Found: C, 83.94; H, 10.63.

17β-Methyl-androstan-3β-ol 3-Acetate (IV). A.—To a solution of 279 mg. of the Δ⁵-3-acetate IIb in 30 ml. of acetic acid was added 30 mg. of platinum oxide and the mixture was shaken under hydrogen at atmospheric pressure until there was no further uptake of hydrogen. Filtration and removal of the solvent gave a solid which was recrystallized in methanol to yield 143 mg. of IV,[7] m.p. 98.5–99°; ν_{max} 1740 and 1260 cm.$^{-1}$; $[\alpha]^{26}D$ −2° (*c* 2.984).

Anal. Calcd. for $C_{22}H_{36}O_2$ (332.51): C, 79.46; H, 10.92. Found: C, 79.26; H, 10.62.

B.—To a solution of 195 mg. of the Δ⁵,¹⁶-3-acetate I in 15 ml. of glacial acetic acid was added 30 mg. of platinum oxide and the mixture was hydrogenated as in the above example. Three recrystallizations from methanol gave 44 mg. of IV, m.p. 98–99°. Admixture melting point determination with the sample prepared above showed identity, m.p. 98–99°. The infrared absorption spectra of preparations A and B were identical in all respects.

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(7) Reference 2 gives m.p. 94–95° and $[\alpha]^{24}D$ −6.5° (chloroform).