pentachloride. A violent reaction took place. The resulting mixture was kept at room temperature for one hour. Water was then added (100 cc.), the two layers were separated, and the chloroform layer removed to the steam-bath. During the evaporation of the chloroform the chloride crystallized. It was filtered and dissolved in ether. The ether solution was washed with sodium hydroxide to remove acidic esters. The ether residue after one crystallization gave an almost pure chloride; yield 0.76 g.; m. p. 153°. The mother liquor was evaporated and the residue was distilled in high vacuum and recrystallized from methyl alcohol; yield 0.12 g.; total yield 0.88 g. (83%). Further repeated recrystallizations did not raise the melting point above 154° (uncorr.); $[\alpha]^{22}D$ +14.6° (19.2 mg. in 2 cc. of chloroform solution gave $\alpha^{22}D$ +0.14°, 1-dm. tube).

Summary.—A simple method is described for the preparation of dehydroandrosteryl chloride in good yield. The chloro ketone so prepared melts at 154° and has a specific rotation $[\alpha]^{22}D$ +14.6°.

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The Separation of the C_{17}-Epimers of Oestradiol by Digitonin

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It has been shown by Schwenk and Hildebrandt[1] that two epimeric forms of oestradiol can be obtained by catalytic reduction of the 17-keto group of oestrone (theelin). The lower melting α-isomer (m. p. 178°, $[\alpha]D$ +81°), which occurs in follicular fluid[2] and in the urine of pregnant mares,[3] is the most potent oestrogenic compound known. The higher melting β-isomer (m. p. 223°, $[\alpha]D$ +54°), which is much less active physiologically, has only recently been prepared in pure form. Its properties will be described in more detail in a separate communication.[4] We have found recently that the two isomers can be separated conveniently by digitonin, whereby the laborious separation by fractional crystallization may be avoided. Only the lower-melting α-isomer forms a sparingly soluble digitonide, when treated with a solution of digitonin in 80% alcohol. The molecular compound deposits slowly in form of beautiful needles, which melt at about 265° after partial decomposition at 195°, and from which the diol can be regenerated easily by the usual methods. Also the 3-benzoate of the α-isomer yields a crystalline precipitate with digitonin, though more slowly than the free diol. Neither the high melting β-oestradiol nor its 3-benzoate precipitates with digitonin under identical conditions. These results show clearly that it is the configuration of the 17-carbon atom which determines the capacity to form insoluble digitonides of this type.

The digitonin reaction is also negative with oestriol (theelol), dihydroequilenin (δ-follicular hormone)[5] and 17-*trans*-testosterone.[6] Furthermore, no precipitate was obtained with a crude preparation of androstenediol-3-acetate, which according to the mode of its preparation should have contained some of the 17-*cis*-epimer. The melting point of dihydroequilenin, and that of its benzoate, its low specific rotation ($[\alpha]D$ −4.7°), its low physiological potency, and its failure to precipitate with digitonin would place this compound in the β-series of oestrogenic diols. On the other hand, if the same criteria be applied to 17-*trans*-testosterone, all the data except the negative digitonin reaction speak for its steric relationship to α-oestradiol. Caution is obviously necessary in interpreting the behavior of C_{17}-epimers toward digitonin as an indication of stereochemical relationships.

In the pregnane series, Butenandt and coworkers[7] have employed digitonin for the separation of C_{17}-epimers. *allo*-Pregnanedione, *allo*-pregnanol-3-one-20-3-acetate, and Δ^5-pregnenol-3-one-20, but not their C_{17}-epimers, termed *iso*-compounds by these workers, form insoluble digitonides.

(1) Schwenk and Hildebrandt, *Naturwiss.*, **21**, 177 (1933).
(2) MacCorquodale, Thayer and Doisy, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1182 (1935); *J. Biol. Chem.*, **115**, 435 (1936).
(3) Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1087 (1935).
(4) Whitman, Wintersteiner and Schwenk, forthcoming publication.
(5) Wintersteiner, Schwenk, Hirschmann and Whitman, THIS JOURNAL, **58**, 2652 (1936).
(6) Ruzicka and Kägi, *Helv. Chim. Acta*, **19**, 842 (1936).
(7) Butenandt and Mamoli, *Ber.*, **68**, 1847 (1935); Butenandt and Fleischer, *ibid.*, **70**, 96 (1937).

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Reaction of Lanthanum Oxide with Ammonium Iodide

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By following the general method of Reed, Hopkins and Audrieth[1] for the preparation of the chlo-

(1) Reed with Hopkins and Audrieth, THIS JOURNAL, **57**, 1159 (1935).