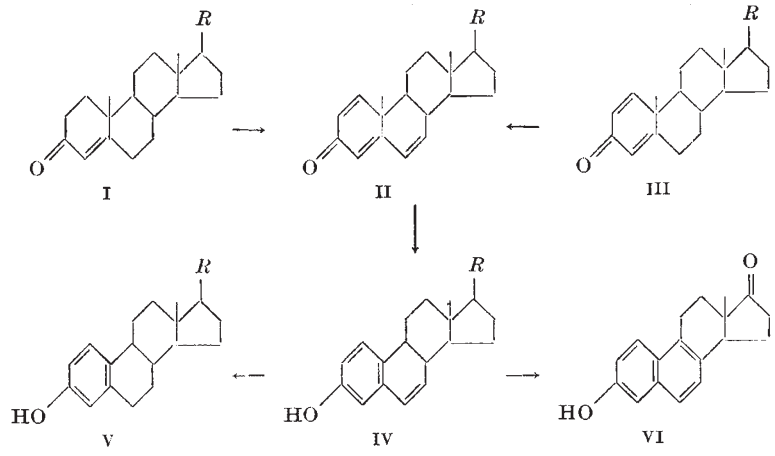
ima at 222, 256 and 298 mμ). The structure of the trienone was proved unequivocally by an independent synthesis from the dienone III via the 6-bromo derivative (prepared with N-bromosuccinimide) and thence collidine treatment. Identical procedures in the case of Δ^4-androstene-3,17-dione (I, $R = O$) led to $\Delta^{1,4,6}$-androstatriene-3,17-dione (V, $R=O$) (m.p. 165–166°, $[\alpha]_D^{20} + 72{\cdot}5°$ (dioxane), ultra-violet absorption maxima at 222, 256 and 298 mμ), and with Δ^4-cholesten-3-one (I, $R=C_8H_{17}$) to $\Delta^{1,4,6}$-cholestatrien-3-one (II, $R=C_8H_{17}$, m.p. 82–83°, $[\alpha]_D^{20}$ 0° (chloroform), ultra-violet absorption maxima at 224, 258 and 300 mμ). This reaction, apparently a general one for Δ^4-3-ketosteroids, can be rationalized only if one assumes the formation of a 2,6-dibromo-Δ^4-3-ketosteroid or an *in situ* rearrangement to such a structure, and thus necessitates revision of a considerable number of structures postulated earlier[1].

Aromatization of mineral oil solutions of the trienones II (R=OAc or O) in the vapour phase at 600° by the general procedure of Inhoffen[2] gave in *c.* 40 per cent yield Δ^6-dehydro-œstradiol 17-monoacetate (IV, R=OAc, m.p. 251–253°, $[\alpha]_D^{20}$ −203° (chloroform) and Δ^6-dehydroœstrone (IV, R=O, m.p. 261–263°, $[\alpha]_D^{20}$ −127° (dioxane), acetate, m.p. 140·5°, benzoate, m.p. 202°), which were smoothly hydrogenated to œstradiol (V, R=OH) and œstrone (V, R=O) respectively. Finally, Δ^6-dehydroœstrone acetate on fifteen minutes treatment with selenium dioxide in acetic acid solution readily afforded equilenin acetate (m.p. 156–158°, $[\alpha]_D^{20} + 72°$ (chloroform)) and, on saponification, equilenin (VI, m.p. 256–258°, $[\alpha]_D^{20} + 86°$ (dioxane)) identical (including spectrum) with the natural hormone. This represents the first partial synthesis of equilenin from a non-aromatic steroid, while the preparation of œstrone and œstradiol from Δ^4-3-ketosteroids constitutes a novel, and in several respects preferable, alternate partial synthesis of the other œstrogens.



A Δ^6-dehydroœstrone described in the literature[3] agrees in all its properties (including biological activity and ultra-violet spectrum) with our substance, with the exception of the rotation, for which a value of $[\alpha]_D + 150°$ (dioxane) was reported. Dr. O. Wintersteiner, with whom we communicated, has indicated that the positive rotation published earlier[3] was most likely in error, as pointed out in the accompanying note[4]. The strongly negative rotation of all our Δ^6-dehydroœstrogens (V, R=OH, OAc, O) gave an average $[\Delta]M_D$ contribution of −754 for the 6,7-double bond, qualitatively quite similar to that observed recently[5] for Δ^6-stenols of the cholestane series. The above transformations, which do not involve hydroxylation at C−8 [3], further confirm the postulate[6] that œstrone and equilenin possess the same configuration at carbon atoms 13 and 14.

A detailed account of these and related investigations will be published elsewhere in the near future.

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Rotation of Δ^6-*iso*Equilin (6-Dehydroœstrone): a Correction

In 1940 we described the conversion of equilin, through 7-ketoœstrone, 7-hydroxyœstrone and 7-chloroœstrone, to its Δ^6 double bond isomer[1]. The specific rotation $[\alpha]_D^{24}$ of this compound was then reported by us as +150° (in dioxane). Dr. St. Kaufmann, of Syntex, S.A., has kindly directed our attention to the widely divergent value (−127°) given by an otherwise apparently identical preparation obtained in that Laboratory from Δ^4-androstenedione (cf. preceding communication by Rosenkranz *et al.*). A check determination now carried out on a small reference sample of Δ^6-*iso*-equilin still in our possession gave −120°, in fair agreement with the value of Rosenkranz *et al.* This preparation (m.p. 258–261°, corr.) did not depress the melting point of a specimen of 6-dehydroœstrone obtained from Dr. Kaufmann which in our hands melted at 257–260°; likewise, the melting point of a mixture of the respective 3-benzoates (m.p. 201°, 200°) was not depressed. It is clear, therefore, that the positive rotation figure originally recorded by us was in error, and that the two compounds in question are identical in every respect.

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