Ethyl 3α,12α-Dihydroxy-7-ketocholanate (XXI) (H. B. MacPhillamy), R. D. (Fig. 4): $[\alpha]_{700}$ +4°, $[\alpha]_{589}$ +4°, $[\alpha]_{250}$ −374°, "max." $[\alpha]_{312}$ +176°, "min." $[\alpha]_{270}$ −340°, *c* 0.1, temp. 25–28°.

Methyl 3α-Acetoxy-11-ketocholanate (XXII) (T. F. Gallagher), R. D. (Fig. 5): $[\alpha]_{700}$ +42°, $[\alpha]_{589}$ +71°, $[\alpha]_{250}$ +514°, "max." $[\alpha]_{325}$ +495°, "min." $[\alpha]_{322.5}$ +491°, "max." $[\alpha]_{317.5}$ +499°, "min." $[\alpha]_{285}$ +198°, *c* 0.1, temp. 23–26.

12-Ketocholanic Acid (XXIII) (T. Reichstein), R. D. (Fig. 5): $[\alpha]_{700}$ +61°, $[\alpha]_{589}$ +95°, $[\alpha]_{245}$ +665°, "max." $[\alpha]_{305}$ +825°, "min." $[\alpha]_{272}$ +222°, *c* 0.1, temp. 28–29°.

Methyl 12-Ketocholanate (XXIV) (S. Bergstrom), R. D. (Fig. 5): $[\alpha]_{700}$ +62°, $[\alpha]_{589}$ +101°, $[\alpha]_{260}$ +374°, "max." $[\alpha]_{307}$ +887°, "min." $[\alpha]_{275}$ +264°, *c* 0.1, temp. 32–35°.

Methyl 3α-Hydroxy-12-Ketocholanate (XXV) (H. B. MacPhillamy), R. D. (Fig. 5): $[\alpha]_{700}$ +65°, $[\alpha]_{589}$ +101°, $[\alpha]_{250}$ +693°, "max." $[\alpha]_{306}$ +797°, "min." $[\alpha]_{270}$ +361°, *c* 0.1, temp. 24–27°.

Methyl 3α-Acetoxy-12-ketocholanate (XXVI) (T. Reichstein), R. D. (Fig. 5): $[\alpha]_{700}$ +83°, $[\alpha]_{589}$ +104°, $[\alpha]_{245}$ +958, "max." $[\alpha]_{305}$ +772°, "min." $[\alpha]_{272.5}$ +546°, *c*, 0.1, temp. 24–27°.

Methyl 3α-Acetoxy-12-ketoetianate (XXVII), R. D. (Fig. 5): $[\alpha]_{700}$ +111°, $[\alpha]_{589}$ +157°, $[\alpha]_{255}$ +841°, "max." $[\alpha]_{307.5}$ +1404; "min." $[\alpha]_{270}$ +422°, *c* 0.1, temp. 24–26°.

Ethyl 3,7-Diketo-12α-hydroxycholanete (XXIX) (H. B. MacPhillamy), R. D. (Figs. 6, 8): $[\alpha]_{700}$ +31°, $[\alpha]_{589}$ +37°, $[\alpha]_{250}$ +487°, "max." $[\alpha]_{260}$ +544°, "min." $[\alpha]_{310}$ −29°, *c* 0.1, temp. 25–27°.

Methyl 3,7-Diketo-12α-acetoxycholanate (XXX) (T. F. Gallagher), R. D.: $[\alpha]_{700}$ +28.6°, $[\alpha]_{589}$ +40.2°, $[\alpha]_{250}$ +376°, "max." $[\alpha]_{265}$ +519°, "min." $[\alpha]_{307.5}$ −50°, *c* 0.1, temp. 24–29°.

Methyl 3,12-Diketocholanate (XXXI) (T. Reichstein), R. D. (Figs. 6, 9): $[\alpha]_{700}$ +71°, $[\alpha]_{589}$ +95°, $[\alpha]_{250}$ +1060°, "inflection" $[\alpha]_{310\text{-}320}$ +450°, *c* 0.1, temp. 31–32°.

3,12-Diketocholanic Acid (XXXII) (S. Bergstrom), R. D.: $[\alpha]_{700}$ +63°, $[\alpha]_{589}$ +97°, $[\alpha]_{255}$ +920°, "inflection" $[\alpha]_{310\text{-}320}$ +451°, *c* 0.1, temp. 24–28°.

Methyl 3,11-Diketocholanate (XXXIII) (T. Reichstein), R. D. (Figs. 6, 10): $[\alpha]_{700}$ +46°, $[\alpha]_{589}$ +71°, $[\alpha]_{260}$ +617°, "max." $[\alpha]_{325}$ +538°, "min." $[\alpha]_{290}$ +157°, *c* 0.1, temp. 25–28°.

3α-Hydroxy-7,12-diketocholanic Acid (XXXIV) (S. Bergstrom), R. D. (Figs. 6, 11): $[\alpha]_{700}$ +15°, $[\alpha]_{589}$ +37°, $[\alpha]_{250}$ +53°, "max." $[\alpha]_{307.5}$ +413°, "min." $[\alpha]_{270}$ −99°, *c* 0.1, temp. 24–28°.

Ethyl 7,12-Diketocholanate (XXXV) (T. Reichstein), R. D.: $[\alpha]_{700}$ +18°, $[\alpha]_{589}$ +23°, $[\alpha]_{250}$ −60°, "max." $[\alpha]_{305}$ +323°, "min." $[\alpha]_{267}$ −219°, *c* 0.1, temp. 31–34°.

Methyl 11,12-Diketocholanate (XXXIX) (T. Reichstein), R. D. (Fig. 13): $[\alpha]_{700}$ +50°, $[\alpha]_{589}$ +81°, $[\alpha]_{250}$ +1043°, "max." $[\alpha]_{290}$ +467°, "min." $[\alpha]_{305}$ −1489°, "inflection," $[\alpha]_{340}$ −453°, *c* 0.1, temp. 22–27°.

3α-Succinoxy-11,12-diketocholanic Acid Dimethyl Ester (XL) (O. Wintersteiner), R. D. (Fig. 13): $[\alpha]_{700}$ +75°, $[\alpha]_{589}$ +106°, $[\alpha]_{260}$ +1810°, "max." $[\alpha]_{390}$ +534°, "min." $[\alpha]_{305}$ −1368°, "inflection", $[\alpha]_{340}$ −368°, *c* 0.1, temp. 25–27°.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORY OF THE INDIAN INSTITUTE OF SCIENCE, BANGALORE AND COLLEGE OF ENGINEERING & TECHNOLOGY, BENGAL]

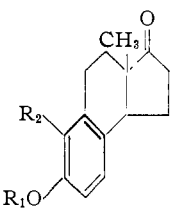
Stereospecific Syntheses of *trans*-1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane, *trans*-1β-Hydroxy-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane and *d,l*-Equilenin Methyl Ether

BY D. K. BANERJEE, S. CHATTERJEE, C. N. PILLAI AND M. V. BHATT

RECEIVED SEPTEMBER 30, 1955

By modification of Johnson, Peterson and Gutsche's synthesis of equilenin[5] it has been possible to realize stereospecific syntheses of *trans*-1β-hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane, *trans*-1β-hydroxy-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane and *d,l*-equilenin methyl ether.

The present paper describes stereospecific syntheses of *trans*-1β-hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane (XIVa) and *trans*-1β-hydroxy-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane (XIVb), which, in view of recent developments[1] in the technique of Birch reduction, are considered to be useful intermediates for the synthesis of steroids. Two isomers of each of the corresponding ketones Ia and Ib were previously prepared by Bachmann and Thomas,[2] and Martin and Robinson,[3] respectively, by following the classical procedure of Bachmann, Cole and Wilds[4] for the synthesis of equilenin. The American workers failed to assign definite configuration to the isomers of Ia, whereas the British workers indicated the probable structures of the isomers of Ib on the basis of solubility.



Ia, $R_1 = CH_3$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$

In Johnson's[5] synthesis of equilenin, the Stobbe condensation product (II) obtained from 1-keto-2-methyl-2-cyano-7-methoxy-1,2,3,4-tetrahydrophenanthrene on saponification followed by decarboxylation yielded two isomeric unsaturated ketones (III) and (IV). The latter on catalytic reduction furnished exclusively *d,l*-isoequilenin methyl ether, the hydrindene ring in IV assuming the more

(1) A. L. Wilds and N. A. Nelson, THIS JOURNAL, **75**, 5360 (1953); W. S. Johnson, B. Bannister, B. M. Bloom, A. D. Kemp, R. Pappo, E. R. Rogier and J. Szmuszkovicz, *ibid.*, **75**, 2275 (1953); W. S. Johnson, R. Pappo and A. D. Kemp, *ibid.*, **76**, 3353 (1954); W. S. Johnson, B. Bannister, R. Pappo and J. E. Pike, *ibid.*, **77**, 817 (1955).

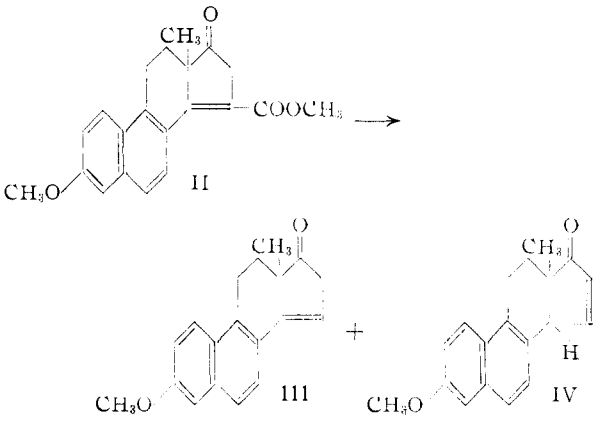
(2) W. E. Bachmann and D. G. Thomas, *ibid.*, **64**, 94 (1942).

(3) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 491 (1943).

(4) W. E. Bachmann, W. Cole and A. L. Wilds, THIS JOURNAL, **62**, 824 (1940).

(5) W. S. Johnson, J. W. Petersen and C. D. Gutsche, *ibid.*, **69**, 2942 (1947).

stable *cis* configuration[6] during migration of the double bond. Thus, with a view to obtaining definite information regarding the steric configuration of the isomers of Ia, the synthesis following the method of Johnson, *et al.*,[5] was carried out.



6-Methoxytetralone (Va) on condensation with ethyl formate in the presence of sodium alkoxides gave 2-hydroxymethylene-6-methoxytetralone (VIa) in almost quantitative yield, which on treatment with hydroxylamine hydrochloride yielded the isoxazole VIIa. In some experiments the β-keto nitrile VIII also was formed. Both VIIa and VIII could be converted into 2-methyl-2-cyano-6-methoxy-α-tetralone (IXa) by treatment with potassium *t*-butoxide and methyl iodide. The over-all yield of IXa from Va was 82%.

The Stobbe condensation of IXa with dimethyl succinate in the presence of potassium *t*-butoxide was best carried out at room temperature for a prolonged period to furnish the tricylic unsaturated keto ester Xa in 49% yield. The ultraviolet and infrared spectral data are in excellent agreement with the structure assigned to the compounds.

In agreement with the observation of Johnson, *et al.*,[5,7] distillation of the crude saponification product of Xa under vacuum failed to decarboxylate the acid, to which the structure XIIa has been assigned on the basis of ultraviolet data.

The crude acid was next smoothly decarboxylated by refluxing with pyridine and hydrochloric acid to give a neutral oil in 75% yield, the ultraviolet data indicating it to be a mixture of unsaturated ketones XVIIa and XVIIIa. This mixture was resolved by chromatography into its crystalline components, which were characterized by their ultraviolet spectra. The α,β-unsaturated ketone XVIIIa was catalytically hydrogenated to furnish an oil, which could not be induced to crystallize and was demethylated to the phenolic ketone XXa, the melting point of which corresponds with the α-isomer of demethylated Ia obtained by Bachmann and Thomas.[2] For reasons already discussed, XVIIIa, XIXa, XXa and evidently the α-isomer of Bachmann should possess the *cis* configuration.

For stereospecific synthesis of the *trans*-hydrindane system, which was our main objective because of *trans*-C/D fusion in natural steroids, the unsaturated keto ester Xa was chosen as the starting material. It is obvious that the shifting of the double bond during saponification and decarboxylation of Xa occurs under the influence of the ketonic group. In order to prevent this migration, which invariably leads to the *cis* configuration of the hydrindane ring, methyl 1-keto-8-methyl-4,5(4′-methoxybenzo)-$\Delta^{3(9)}$-hydrindene-3-carboxylate-(Xa) was first treated with sodium borohydride in alcoholic solution to furnish, by preferential reduction of the keto group, the unsaturated hydroxy ester XIa in 98% yield; the ultraviolet and infrared spectra are in agreement with its structure. Saponification of XIa yielded the corresponding acid XIIb in 95% yield, which could be decarboxylated by heating to give XIIIa in good yield. The unsaturated alcohol XIIIa could also be obtained from the XVIIa by reduction with sodium borohydride. Catalytic hydrogenation of the unsaturated alcohol XIIIa furnished *trans*-1β-hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane (XIVa) in 90% yield. The aforementioned structure, *i.e.* β-configuration[8] of the hydroxyl group and *trans* fusion of the hydrindane ring, has been assigned to the saturated alcohol XIVa on the basis of following consideration. Lithium aluminum hydride reduction of 17-keto steroids gives chiefly the β-oriented alcohol,[9a] and catalytic reduction of 17β-substituted Δ^{14}-steroids leads exclusively to the formation of *trans*-C/D fusion.[9b] The oxidation of XIVa with pyridine–chromic acid complex[10] gave the ketone XVa in 40% yield, and the latter on demethylation furnished the phenolic ketone XVIa. The melting points of XVa and XVIa correspond with those of the β-isomers of Ia and demethylated Ia obtained by Bachmann and Thomas,[1] which on the basis of present investigation may be regarded as *trans* isomers.

The higher homolog, *trans*-1 β-hydroxy-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane (XIVb), has also been prepared following the aforementioned procedure. 5-Methyl-6-methoxytetralone (Vb) required for this purpose was prepared by the method of Martin and Robinson.[2] However, the reduction of 2-methoxy-1-naphthaldehyde (XXI) did not proceed in the expected manner when carried out under the conditions described by them, the main product being a crystalline substance, which has not been so far investigated; only a small quantity of the desired 5-methyl-6-methoxy-tetralin (XXII) was obtained. The yield of the latter product was considerably improved when the modification recommended by Stork,[11]

(6) W. E. Bachmann and A. S. Dreiding, THIS JOURNAL, **72**, 1323 (1950); W. E. Bachmann and F. Ramirez, *ibid.*, **72**, 2527 (1950); W. Klyne, *Nature*, **161**, 434 (1948); D. H. R. Barton and C. F. Laws, *J. Chem. Soc.*, 53 (1954), have shown that the *trans*-hydrindane system in reduced steroids is more stable; *cf.* A. S. Dreiding, *Chemistry and Industry*, 992 (1954).

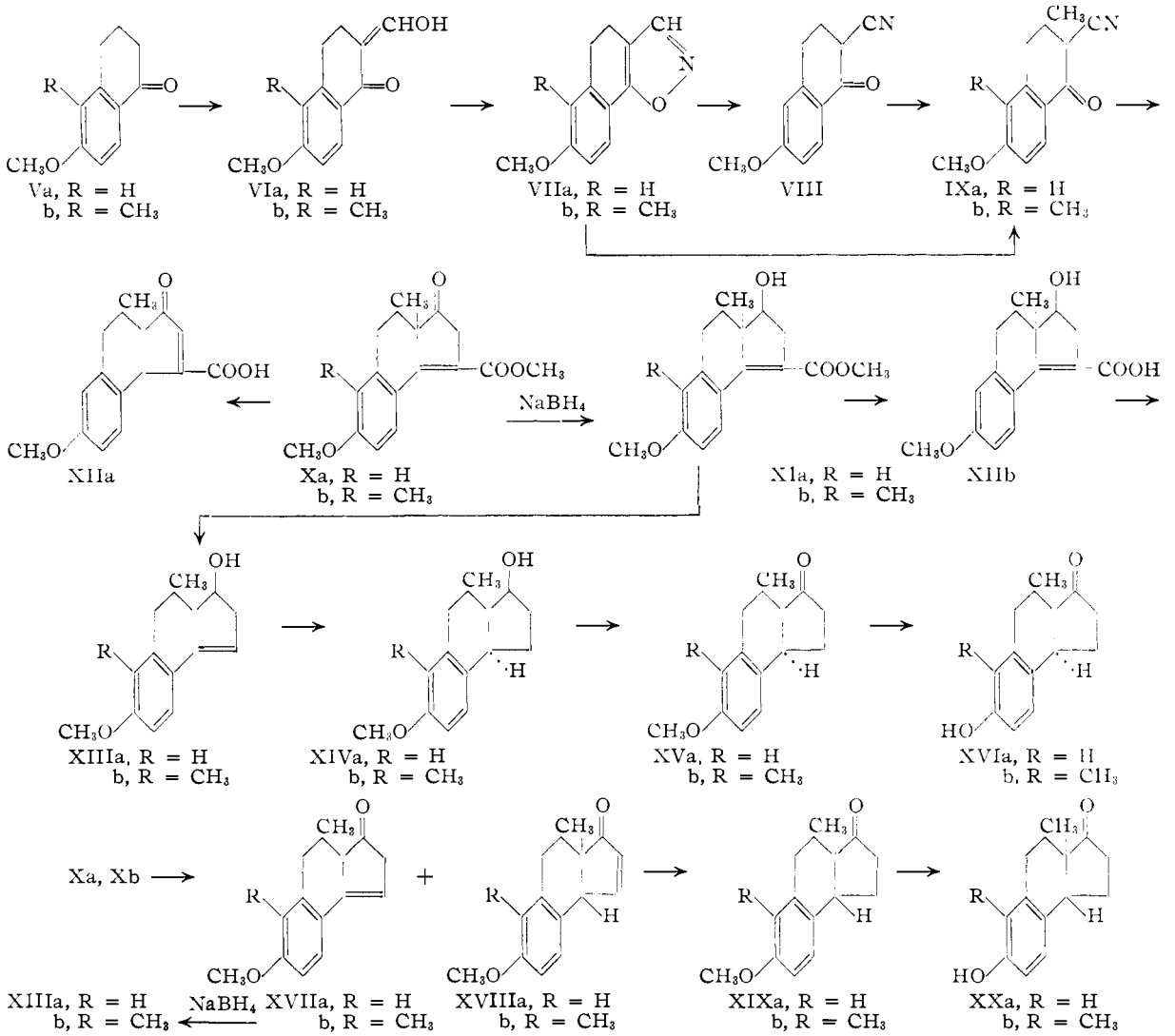
(7) W. S. Johnson and V. L. Stromberg, THIS JOURNAL, **72**, 505 (1950).

(8) Steroid nomenclature.

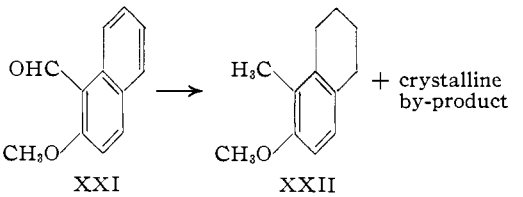
(9) (a) L. F. Fieser, *Experientia*, **6**, 312 (1950); C. W. Shoppee, *Nature*, **166**, 107 (1950); (b) Von P. Speiser and T. Reichstein, *Helv. Chim. Acta*, **30**, 2143 (1947); Pl. A. Plattner, L. Ruzicka, H. Heusser and E. Angliker, *ibid.*, **30**, 395 (1947); Von A. Lardon, *ibid.*, **32**, 1517 (1949).

(10) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 427 (1953).

(11) G. Stork, *ibid.*, **69**, 576 (1947).



the addition of glacial acetic acid, was employed. The occurrence of this by-product was not reported by Martin and Robinson.[12] The tetralone Vb was converted to the keto nitrile IXb in 85% yield *via* the formyl derivative VIb and the isoxazole VIIb. Stobbe condensation of IXb with dimethyl succinate gave the unsaturated keto ester Xb in 53% yield. The unsaturated by-product,



hydroxy ester XIb, obtained in an excellent yield by the reduction of Xb with sodium borohydride, on saponification and careful warming furnished the unsaturated alcohol XIIIb in 99% yield. *trans*-1β-Hydroxy-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane (XIVb) was obtained by the catalytic reduction of XIIIb.

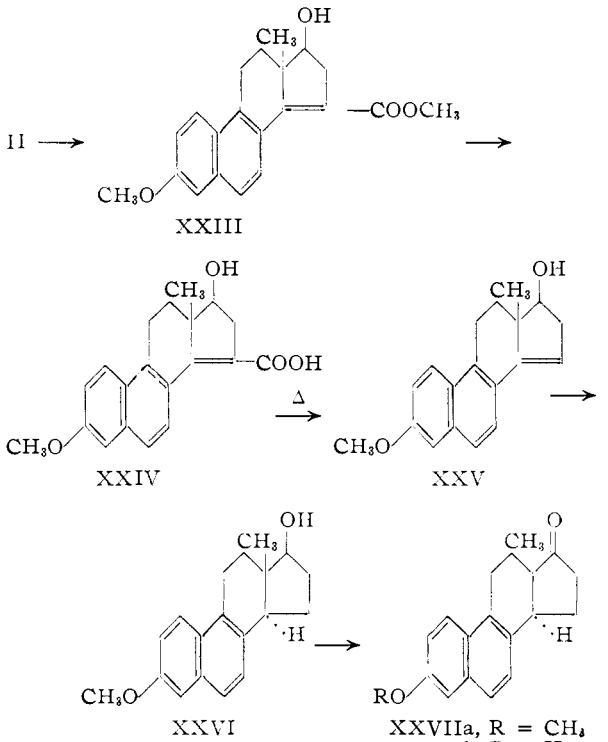
As the yield in the oxidation of XIVa with pyridine–chromic acid complex was not satisfactory, the oxidation of XIVb was carried out in the cold with sodium dichromate in benzene–acetic acid solution and the ketone XVb was obtained in 70% yield. Demethylation of XVb yielded the phenolic ketone XVIb. For considerations already discussed XIVb, XVb and XVIb should possess the *trans* configuration.

The authentic *cis* isomer of Ib was next prepared, as the reported melting point of the *cis* isomer of Martin and Robinson[2] coincided with that of our *trans* isomer. Saponification of Xb followed by decarboxylation yielded a mixture of isomeric unsaturated ketones XVIIb and XVIIIb, which was resolved by chromatography and characterized by ultraviolet spectra. Catalytic reduction of XVIIIb furnished the *cis*-ketone XIXb, and the latter on demethylation yielded the phenolic ketone XXb, the melting point of which was almost the same as that of the *trans* isomer; the mixed melting point, however, was depressed. The isomer of Ib, considered to be *trans* by Martin and

(12) After submission of this paper, J. W. Cornforth, O. Kauder, J. E. Pike and R. Robinson, *J. Chem. Soc.*, 3353 (1955), have reported the formation of the by-product during reinvestigation of this reduction.

Robinson,[2] has been reported to melt at a considerably higher temperature, and the methyl ethers of these isomers have not been described by them. Therefore it has not been possible for us to assign definite configurations to the British worker's products on the basis of present investigation. Reduction of XVIIb with sodium borohydride furnished the unsaturated alcohol XIIIb in good yield.

Several syntheses of equilenin (XXVIIb) have been reported[4,5,7,13] but not one of these is stereospecific. The new procedure has now been employed with success for the stereospecific synthesis of this female sex hormone. 15-Carbomethoxy-14, 15-dehydroequilenin methyl ether (II), prepared by the method of Johnson, *et al.*,[5] was reduced with sodium borohydride to give the hydroxy unsaturated ester XXIII in 92% yield. The decarboxylation of the corresponding acid XXIV was studied and was best accomplished by heating for a short time small quantities of the acid mixed with glass powder to give 17-hydroxy-14,15-dehydroequilenane methyl ether (XXV) in 67–83% yield. Catalytic reduction of XXV furnished the saturated alcohol XXVI and the latter was oxidized with sodium dichromate in benzene–acetic acid solution to give *d,l*-equilenin methyl ether[14] (XXVIIa) in 71% yield, the melting point of which was not depressed on admixture with an authentic specimen.[15]



(13) W. E. Bachmann and R. E. Holmen, THIS JOURNAL, **73**, 3660 (1951).

(14) Prof. A. L. Wilds and co-workers (private communication) have also completed part of the sequence of reactions in this series starting from III, the reduction of the keto group being accomplished with lithium aluminum hydride.

(15) The authentic specimen of *d,l*-equilenin methyl ether was obtained through the courtesy of Prof. A. L. Wilds and Prof. W. S. Johnson of the University of Wisconsin, Madison 6, Wis., U. S. A.

Experimental[16]

trans-1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane[17]

6-Methoxytetraline (Va).—This compound was prepared by oxidation[18] from 6-methoxytetralin. The latter compound was prepared either by the method of Stork[11] or by the method of Thomas and Nathan.[18] In the latter case the reduction of 7-methoxytetralone to the tetralin was carried out by Huang-Minlon's[19] modified procedure for Wolff–Kishner reduction; previous methods[18,20] involved catalytic or Clemmensen reductions. For this reduction a mixture of 30 g. of 7-methoxytetralone, 50 cc. of 50% hydrazine hydrate and a solution of 34 g. of potassium hydroxide in 250 cc. of diethylene glycol was heated for two hours at 130°. The temperature was then raised to 200° and maintained at that point for another two hours. During the raising of the temperature care was taken to collect the methoxytetralin which distilled over with water. The reaction mixture, after dilution with water, was treated at 70–80° with 17 cc. of dimethyl sulfate in small portions and steam distilled after addition of 10 g. of potassium hydroxide. The combined distillates gave 23 g. (85%) of 6-methoxytetralin, b.p. 92–94° (1.5 mm).

2-Hydroxymethylene-6-methoxytetralone (VIa).—A solution of 20 g. of 6-methoxytetralone in 100 cc. of dry benzene was condensed with 28 cc. of ethyl formate in 50 cc. of dry benzene in the presence of dry sodium ethoxide, prepared from 4.9 g. of sodium and 12.4 cc. of ethanol under benzene, to give a light orange sodium salt which upon acidification gave 21.5 g. (93%) of the hydroxymethylene derivative, m.p. 67–68° (s. at 66°). A small portion of the product was purified by distillation, 130–140° (0.3 mm.), followed by crystallization from petroleum ether (40–60°), m.p. 68–69°. The product gives a deep violet coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.59; H, 5.88. Found: C, 70.61, 70.49; H, 5.39, 5.88.

6-Methoxy-3,4-dihydronaphth[2,1*d*]isoxazole (VIIa).—This compound was prepared by the method of Johnson, *et al.*[5] Thus from 21.6 g. of VIa, 12.5 g. of hydroxylamine hydrochloride and 250 cc. of glacial acetic acid, there was obtained 19.9 g. (93%) of brick colored isoxazole, m.p. 57–58°. This product was insoluble in alkali and on purification by distillation, 130–140° (0.1 mm.), was obtained as yellowish-orange crystals without improvement in the melting point.

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 6.81.

2-Cyano-6-methoxytetralone (VIII).—From 1.76 g. of isoxazole VIIa and sodium ethoxide,[5] prepared from 1.5 g. of sodium and 10 cc. of ethanol, there was obtained 1.58 g. (90%) of VIII as a white solid, m.p. 98–99°, not improved by crystallization from ether–petroleum ether (40–60°). This product is soluble in alkali and was occasionally formed during the preparation of the isoxazole VIIa.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47. Found: C, 71.88; H, 5.57.

2-Methyl-2-cyano-6-methoxytetralone (IXa).—Simultaneous isomerization and alkylation[5] of 21.19 g. of the isoxazole VIIa with 15.8 g. of potassium in 400 cc. of dry *t*-butyl alcohol and 80 cc. of methyl iodide yielded 21.1 g. (93%) of a light yellow viscous oil, which solidified on standing; crystallized from petroleum ether (40–60°), m.p. 70°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.05. Found: C, 72.92; H, 5.99.

The β-keto nitrile VIII was also converted into IXa by similar treatment.

Methyl 1-Keto-8-methyl-4,5-(4′-methoxybenzo)-$\Delta^{3(9)}$-hydrindene-3-carboxylate (Xa).—The Stobbe condensation

(16) All melting points are uncorrected and ranges of temperature less than one degree have not been recorded

(17) Experiments described in this Section were presented at the Symposium on Steroid Synthesis held under the auspices of the Forty-Second Session of the Indian Science Congress Association, Baroda (January, 1955).

(18) D. G. Thomas and A. H. Nathan, THIS JOURNAL, **70**, 331 (1948).

(19) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(20) P. C. Mitter and S. De, *J. Indian Chem. Soc.*, **12**, 747 (1935).

was carried out by slight but necessary modifications of the method of Johnson, *et al.*[6] A mixture of 42 cc. of dimethyl succinate and a solution of potassium *t*-butoxide, from 13.2 g. of potassium and 360 cc. of *t*-butyl alcohol, was slowly added with stirring to 11.1 g. of IXa at 23–25° under nitrogen. The stirring was continued for 40 hours. The turbid yellow reaction mixture was acidified in the cold with 120 cc. of dilute hydrochloric acid (1:1) and the *t*-butyl alcohol was removed under diminished pressure with minimum application of heat. Upon removal of part of the solvent (after the extractions) under diminished pressure without heating, a white (sometimes pink) crystalline material, m.p. 111–114°, separated out. Addition to the mother liquor of petroleum ether (40–60°) gave further crystalline material, m.p. 110–112°; total yield 7–7.2 g. (47–49%), recrystallized from petroleum ether, m.p. 114–115°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 303 mμ, log ε 4.1; infrared spectrum: $\lambda_{max}^{CS_2}$ 5.67, 5.8, 6.2, 7.48, 8.02, 9.6μ.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.32; H, 6.30. Found: C, 71.09; H, 6.33.

Methyl 1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-Δ$^{3(9)}$-hydrindene-3-carboxylate (XIa).—To a suspension of 15.73 g. of the unsaturated keto ester Xa in 300 cc. of 95% ethanol was added 2 g. of sodium borohydride in small portions. The reaction mixture was allowed to stand overnight when a clear solution resulted. The excess of sodium borohydride was destroyed by careful addition of acetic acid. Most of the alcohol was removed under diminished pressure and the residual solution was diluted with a large quantity of cold water, when the hydroxy compound XIa crystallized out in tufts of silky-white needles, m.p. 125–126°, yield 15.5 g. (98%); on recrystallization from dilute alcohol m.p. 126.5–127°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 302 mμ, log ε 4.1; infrared spectrum: $\lambda_{max}^{CS_2}$ 2.81, 5.82, 6.1, 7.42, 7.89, 9.6μ.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.83; H, 6.94. Found: C, 70.84; H, 6.78.

1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-Δ$^{3(9)}$-hydrindene-3-carboxylic Acid (XIIb).—A mixture of a solution of 0.8 g. of XIa in 19 cc. of 95% ethanol, 1 g. of barium hydroxide octahydrate and 9.5 cc. of water was refluxed for two hours. A part of the alcohol was removed under diminished pressure. After addition of water the reaction mixture was acidified with cold dilute hydrochloric acid. The solid acid was collected, m.p. 210–211° dec., yield 0.72 g. (95%); after recrystallization from 95% ethanol, m.p. 215° dec.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.07; H, 6.57. Found: C, 69.94; H, 6.85.

1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-Δ$^{3(9)}$-hydrindene (XIIIa).—A thorough mixture of 0.2 g. of the unsaturated hydroxy acid XIIb and 0.5 g. of soft glass powder was taken in an evaporative distillation tube, the tube was evacuated (1 mm.), and placed in a preheated bath at 220–230°. The decarboxylated product distilled over smoothly; yield 0.15 g. (90%), m.p. 136–142°; after recrystallization from ether–petroleum ether (40–60°), m.p. 149–150°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 266 mμ, log ε 4.2.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83; CH_3O–, 13.48. Found: C, 77.71; H, 7.76; CH_3O–, 13.66.

While working with comparatively larger quantities of the unsaturated hydroxy ester XIa, the crude saponification product was decarboxylated without loss in yield. Thus 3.04 g. of the crude acid XIIb, m.p. 210–211° dec., obtained by the saponification of 3.2 g. of XIa, furnished 2.2 g. (90% on two steps) of the unsaturated alcohol XIIIa, m.p. 142–145°.

In another experiment, after saponification of the ester XIa the acidified solution was heated for 15–20 minutes on a steam-bath. The resulting dark colored product was extracted with ether–benzene mixture and the residue after removal of the solvent was purified by distillation, 150–180° (0.2 mm.). The oily distillate on crystallization from *n*-hexane furnished XIIIa, m.p. 149–150°, in low yield.

***trans*-1β-Hydroxy-8-methyl-4,5-(4′-methoxybenzo)-hydrindane (XIVa).**—An ethanolic solution of 0.5 g. of the unsaturated alcohol XIIIa was stirred with 0.15 g. of 10% palladium–charcoal in an atmosphere of hydrogen, one molar equivalent of hydrogen being absorbed in one hour. After removal of the catalyst and the solvent the oily residue was dissolved in *n*-hexane and kept in the cold for a few hours when a solid, m.p. 60–65°, was obtained, which after recrystallization from *n*-hexane melted at 75°; yield 0.45 g. (89%); ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 280 mμ, log ε 3.5.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.43; H, 8.62.

Oxidation of XIVa.—To a mixture of pyridine–chromic acid complex,[11] prepared from 0.2 g. of chromic acid and 2 cc. of pyridine, was added a solution of 0.2 g. of XIVa in 2 cc. of dry pyridine. A deep yellow complex separated out of the reaction mixture, which was allowed to stand overnight. It was then diluted with cold water, filtered to remove some slimy product, and extracted six times with ether–benzene mixture. The extract was washed with water, 10% hydrochloric acid, and again with water. The solvent was removed and the residue distilled, 140–145° (0.2 mm.). The yellow colored oily distillate on trituration with few drops of *n*-hexane crystallized out as a light pink solid, m.p. 108–110°. On recrystallization from *n*-hexane *trans*-1-keto-8-methyl-4,5-(4′-methoxybenzo)-hydrindane melted at 112–113° (reported[2] m.p. 112–113.5°), yield 0.078 g. (40%).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.27; H, 8.02.

Demethylation of the above ketone was carried out by refluxing for 1.5 hours a mixture of 0.1 g. of XVa, 2 cc. of 48% hydrobromic acid and 2 cc. of acetic acid in an atmosphere of nitrogen. After dilution with water the reaction mixture was extracted with ether–benzene mixture. The extract was first washed with water and then several times with cold 10% sodium hydroxide solution. The alkaline wash after acidification was extracted with ether. After removal of the solvent the residue was distilled, 180–210° (0.2 mm.). The solid phenolic ketone XVIa, m.p. 198–199°, was crystallized from dilute ethanol, m.p. 208–210° (reported[2] m.p. 209–213°).

***cis*-1-Keto-8-methyl-4,5-(4′-hydroxybenzo)-hydrindane[17]**

1-Keto-8-methyl-4,5-(4′-methoxybenzo)-Δ^2-hydrindene-3-carboxylic Acid (XIIa).—The saponification of 2 g. of the unsaturated keto ester Xa was carried out as before (preparation of XIIb) with 2 g. of barium hydroxide octahydrate, 33 cc. of ethanol and 23 cc. of water; on working up in the usual manner 1.9 g. (99%) of an oily product was obtained. A part of the oil was distilled, 150–170° (0.2 mm.). The oily distillate on trituration with few drops of *n*-hexane solidified and was recrystallized from the same solvent, m.p. 109°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 245 mμ, log ε 4.01.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.59; H, 5.88. Found: C, 70.19; H, 6.10.

1-Keto-8-methyl-4,5-(4′-methoxybenzo)-Δ$^{3(9)}$-hydrindene (XVIIa) and 1-Keto-8-methyl-4,5-(4′-methoxybenzo)-Δ^2-hydrindene (XVIIIa).—From 1.7 g. of the crude acid XIIa, there was obtained by Johnson's method of decarboxylation 1.2 g. (84%) of an oily product, after purification by distillation, 130–148° (0.2 mm.); ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 225 mμ, log ε 4.0; 279 mμ, log ε 3.7; 253–254 mμ, log ε 3.6.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.02. Found: C, 79.34; H, 7.22.

A longer period of heating lowers the yield.

The ultraviolet and analytical data indicated that the aforementioned oily product was a mixture of the isomers XVIIa and XVIIIa. A 0.7 g. sample of this oil was chromatographed on 30 g. of an acid-washed alumina[21] column; 0.12 g. of XVIIa, m.p. 129–130° (ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 264.5 mμ, log ε 4.2) was obtained by elution with benzene–*n*-hexane (75:25) mixture.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.02. Found: C, 78.73; H, 6.99.

On further elution with benzene 0.2 g. of another fraction XVIIIa was collected as an oil, which crystallized on standing in the cold with few drops of *n*-hexane, m.p. 60–62°; recrystallized from *n*-hexane, m.p. 62°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 227 mμ, log ε 4.2; 279 mμ, log ε 3.5.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.94; H, 7.02. Found: C, 78.96; H, 6.98.

(21) We are indebted to Merck & Co., Inc., Rahway, N. J., U. S. A., for the gift of acid-washed alumina 9 R 8094.

cis-1-Keto-8-methyl-4,5-(4'-hydroxybenzo)-hydrindane (XXa).—An ethanolic solution of 0.3 g. of XVIIIa was hydrogenated in the presence of 0.15 g. of palladium–charcoal, the calculated amount of hydrogen being absorbed in two hours. After removal of the catalyst and the solvent, the residue was distilled, 110–135° (0.2 mm.), to yield 0.29 g. of an oil (ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 279 mμ, log ε 3.5) which could not be induced to crystallize.

The aforementioned hydrogenated product (0.17 g.), was demethylated with 2 cc. of 48% hydrobromic acid and 2 cc. of acetic acid as described before to yield the phenolic ketone XXa as solid, m.p. 146–150°, after purification by distillation, 140–160° (0.2 mm.), recrystallized from dilute ethanol, m.p. 155–156° (reported[2] m.p. 155–156°), yield 0.075 g.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.78; H, 7.41. Found: C, 77.67; H, 7.61.

Reduction of XVIIa.—A solution of 0.02 g. of 1-keto-8-methyl-4,5-(4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene in 10 cc. of ethanol was treated with 0.02 g. of sodium borohydride and kept overnight at room temperature. After decomposition of the excess of borohydride with dilute acetic acid, most of the solvent was removed under diminished pressure and the residue diluted with water. The precipitated solid was taken up in ether. The ethereal solution was concentrated to a small volume and diluted with *n*-hexane and kept in the cold. After a few hours 0.015 g. of the product crystallized out, m.p. 149–150°, and was found to be identical with 1β-hydroxy-8-methyl-4,5-(4'-methoxybenzo)-hydrindane (XIIIa). Catalytic reduction of XVIIa yielded an uncrystallizable oil.

trans-1β-Hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-hydrindane

The 5-Methyl-6-methoxytetralin (XXII).—A mixture of 25 g. of 2-methoxy-1-naphthaldehyde (XXI),[3] 3 g. of the Raney nickel catalyst, 75 cc. of ethanol and 1 cc. of glacial acetic acid was hydrogenated under an initial pressure of 100 atm. at 100°. The reduction was complete in six hours. After removal of the catalyst and the solvent, the residue was fractionated; (i) a small fraction below 80° (4 mm.) was discarded; (ii) 10 g. (42%) of 5-methyl-6-methoxytetralin, m.p. 50–51° (reported[3] m.p. 51.5–52°), b.p. 105–110° (4 mm.) (ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 278 mμ, log ε 3.2); (iii) 12 g. of a crystalline product, m.p. 64°, b.p. 145–150° (4 mm.).

When a similar reduction without the addition of acetic acid was carried out, the yield of 5-methyl-6-methoxytetralin fell to 25%.

5-Methyl-6-methoxytetralone (Vb).—The oxidation of 5-methyl-6-methoxytetralin (XXII) was carried out by the method of Thomas and Nathan[18] to give a 66% yield of 5-methyl-6-methoxytetralone, m.p. 110–111° (reported[3] m.p. 112–113°); 2,4-dinitrophenylhydrazone, m.p. 249–250° (reported[3] m.p. 249–250°).

2-Hydroxymethylene-5-methyl-6-methoxytetralone (VIb).—This was prepared[5] from Vb as before (VIa) except that the insoluble sodio salt of the hydroxymethylene derivative was filtered off and acidified along with the alkaline extract of the benzene layer. The product VIb was obtained as a light red solid, m.p. 66–68°, yield 23 g. (95%). A small portion was purified by distillation, 130–140° (0.5 mm.), followed by crystallization from petroleum ether (40–60°)-benzene, m.p. 67–68°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.63; H, 6.44.

5-Methyl-6-methoxy-3,4-dihydronaphtho[2,1*d*]isoxazole (VIIb).—From crude VIb there was obtained a 95% yield of the isoxazole as brown plates, m.p. 130°. A portion was purified by distillation, 130–140° (1 mm.), and crystallization from methanol, m.p. 131°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.05; N, 6.51. Found: C, 72.36; H, 6.02; N, 6.56.

2,5-Dimethyl-2-cyano-6-methoxytetralone (IXb).—This was prepared by the method of Johnson, *et al.*,[5] to obtain a yellow solid, m.p. 65–71°, in 94% yield. Two crystallizations from petroleum ether (40–60°) gave pure IXb, m.p. 84°.

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.36; H, 6.55. Found: C, 73.41; H, 6.39.

Methyl 1-Keto-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene-3-carboxylate (Xb).—The Stobbe condensation of the keto nitrile IXb was carried out as before for Xa except that the mixture of dimethyl succinate and potassium *t*-butoxide solution was added at 30–35°, and the mixture was stirred for 15 hours at the room temperature. The viscous yellow mass was acidified in the cold with concentrated hydrochloric acid, the solvent removed under diminished pressure at 70° and the residue, after dilution with water, worked up in the usual manner. Sufficient petroleum ether (40–60°) was added to the product containing a little benzene to form a turbidity and the mixture was kept in the cold for 18 hours. Methyl 1-keto-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene-3-carboxylate separated out as thick orange plates, m.p. 139–141°, yield 53%; recrystallized from petroleum ether (40–60°), m.p. 144–145°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 239 mμ, log ε 4.2; 309 mμ, log ε 4.2.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.00; H, 6.67. Found: C, 71.85; H, 6.88.

Methyl 1β-Hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene-3-carboxylate (XIb).—This substance was prepared by the procedure described before for XIa, except that the excess of sodium borohydride was destroyed by the addition of ice-cold hydrochloric acid. From 0.24 g. of the unsaturated keto ester Xa, m.p. 139–141°, in 40 cc. of methanol and 0.04 g. of sodium borohydride, there was obtained 0.23 g. (96%) of light yellow unsaturated hydroxy ester, m.p. 161–162°; recrystallized from aqueous methanol, m.p. 164–165°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.52; H, 7.28. Found: C, 71.61; H, 7.04.

1β-Hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene (XIIIb).—The saponification of 0.1 g. of the unsaturated hydroxy ester XIb, m.p. 161–162°, was carried out as before with 0.11 g. of barium hydroxide octahydrate, 1.5 cc. of alcohol and 1.2 cc. of water. After acidification with 15 cc. of dilute (1:2) hydrochloric acid, the reaction mixture was warmed on a heated water-bath for one hour. After cooling, the product was extracted with ether–benzene mixture and the extract washed with water, dilute alkali, and finally with water. On removal of the solvent 0.08 g. (99%) of the crude unsaturated alcohol XIIIb, m.p. 125°, was obtained. Recrystallization from aqueous methanol yielded the pure product, m.p. 130°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 274 mμ, log ε 4.0.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.31; H, 8.40.

trans-1β-Hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-hydrindane (XIVb).—A solution of 0.41 g. of 1β-hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-$\Delta^{3(9)}$-hydrindene in 50 cc. of 95% ethanol was hydrogenated with 0.2 g. of palladium–charcoal, one molar equivalent of hydrogen being absorbed in four hours. The product was worked up in the usual manner to yield 0.41 g. (99%) of the saturated alcohol XIVb, m.p. 126°; recrystallized from ethanol, m.p. 129° (melting point on admixture with XIIIb 113–116°) ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 278 mμ, log ε 3.2.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 77.58; H, 9.00.

Oxidation of XIVb.—To a stirred solution of 0.041 g. of sodium dichromate dihydrate in 0.5 cc. of glacial acetic acid cooled in an ice-bath was added dropwise a solution of 0.1 g. of *trans*-1β-hydroxy-8-methyl-4,5-(3'-methyl-4'-methoxybenzo)-hydrindane (XIVb) in 1.1 cc. of glacial acetic acid and 1.1 cc. of dry benzene in an atmosphere of nitrogen.[22] The reaction mixture was stirred for 48 hours at room temperature. After dilution with water the product was extracted with ether and the extract washed successively with water, sodium bicarbonate solution and water. On removal of the solvent 0.07 g. (70%) of the crude yellow ketone XVb, m.p. 95°, was obtained. Repeated recrystallizations from aqueous methanol gave white crystalline product, m.p. 98.5°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 277.5 mμ, log ε 3.1.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.22; H, 8.20.

(22) We are indebted to Prof. A. L. Wilds of the University of Wisconsin, U. S. A., for the information that yields of such oxidations are improved when carried out with the exclusion of oxygen.

The demethylation of 0.1 g. of the *trans*-ketone was carried out in the usual manner with 1 cc. of 48% hydrobromic acid and 2 cc. of acetic acid (five hours refluxing) to give the phenolic ketone XVIb in poor yield as a white crystalline solid, m.p. 189–190° (in evacuated sealed tube, reported[3] m.p. 230–231°), ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 281.5 mμ, log ε 3.3, after purification by distillation, 130–135° (0.05 mm.), followed by crystallization from benzene.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 77.61; H, 7.86.

cis-1-Keto-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane

The 1-Keto-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-Δ³⁽⁹⁾-hydrindene (XVIIb) and 1-Keto-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-Δ²-hydrindene (XVIIIb).—The saponification of 1 g. of the unsaturated keto ester Xb was carried out in the usual manner with use of 1.1 g. of barium hydroxide octahydrate, 7.5 cc. of ethanol and 6.2 cc. of water to yield 0.85 g. of the acid as a brown solid, m.p. 102–107°. This crude product was decarboxylated by Johnson's procedure[5] with 10 cc. of pyridine and 20 cc. of concentrated hydrochloric acid to give 0.64 g. (79% on two steps) of a pasty solid, after purification by distillation, 130–140° (2 mm.). This was dissolved in *n*-hexane and passed through a column of 20 g. of acid-washed alumina and eluted with the same solvent, when 0.27 g. of the β,γ-unsaturated ketone XVIIb, m.p. 121–125° (ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 268 mμ, log ε 4.3) was obtained as the first fraction.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44. Found: C, 79.48; H, 7.81.

On continuing to elute with *n*-hexane a middle fraction of 0.08 g., m.p. 60–75°, was collected. Finally 0.20 g. of the α,β-unsaturated ketone XVIIIb, m.p. 80–85°, was obtained; recrystallized from aqueous methanol, m.p. 85–87°; ultraviolet spectrum $\lambda_{max}^{alcohol}$ 221 mμ, log ε 4.2; 278 mμ, log ε 3.4.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44. Found: C, 79.49; H, 7.35.

***cis*-1-Keto-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-hydrindane (XIXb).**—A solution of 0.2 g. of 1-keto-8-methyl-4,5-(3′-methyl-4′-methoxybenzo)-Δ²-hydrindene (XVIIIb) in 50 cc. of 95% ethanol was hydrogenated in the presence of 0.1 g. of palladium–charcoal catalyst; the absorption was complete in one hour. The product was worked up in the usual manner to yield 0.2 g. of the saturated ketone XIXb, m.p. 100–102°; purified by distillation, m.p. 108°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 277 mμ, log ε 3.1.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.69; H, 8.20. Found: C, 78.16; H, 8.23.

The demethylation of 0.18 g. of the *cis*-ketone XIXb was carried out as before for XVb with 2 cc. of 48% hydrobromic acid and 4 cc. of acetic acid to yield 0.08 g. of the phenolic ketone XXb, m.p. 189–190° (in evacuated sealed tube; reported[3] m.p. 189–191°) recrystallized from benzene, m.p. 189–191° (melting point on admixture with XVIb, 160–165°).

Reduction of XVIIb.—A solution of 0.1 g. of the β,γ-unsaturated ketone XVIIb in 50 cc. of methanol was treated with 0.04 g. of sodium borohydride and worked up as described before for XVIIa to yield 0.09 g. of a product, m.p. 130° (recrystallized from aqueous methanol, m.p. 131°), which was found to be identical with the unsaturated alcohol XIIIb.

d,l-Equilenin Methyl Ether[17]

Methyl 3-Methoxy-17β-hydroxy-14,15-dehydroequilenane-15-carboxylate (XXIII).—The required amount of 15-carbomethoxy-14,15-dehydroequilenin methyl ether (II) required for this purpose was prepared from 1-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene[23] by the method of Johnson, *et al.*[5] The reduction of 1.3 g. of the unsaturated keto ester II in 110 cc. of methanol with 1.2 g. of sodium borohydride was carried out as described before to yield the crystalline hydroxy unsaturated ester XXIII, m.p. 176–177°; recrystallized from methanol, m.p. 179°; yield 1.3 g. (99%); ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 230 mμ, log ε 4.45; 265 mμ, log ε 4.3; 320 mμ, log ε 4.2.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.56; H, 6.51. Found: C, 74.80; H, 6.76.

The acetyl derivative was prepared by allowing a mixture of XXIII, pyridine and acetic anhydride to stand for 24 hours at room temperature, followed by refluxing for 15 minutes and pouring into cold water. The precipitated solid was filtered, washed with cold 2% hydrochloric acid, water and crystallized from 95% ethanol, m.p. 182–183°.

Anal. Calcd. for $C_{23}H_{24}O_5$: C, 72.63; H, 6.32. Found: C, 72.70; H, 6.43.

3-Methoxy-17β-hydroxy-14,15-dehydroequilenane-15-carboxylic Acid (XXIV).—The saponification of 1.2 g. of the unsaturated hydroxy ester XXIII was carried out as described before with 1.6 g. of barium hydroxide octahydrate in 20 cc. of 95% ethanol to yield 1 g. (87%) of the crude acid as a white solid; recrystallized from glacial acetic acid, m.p. 260° dec.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.07; H, 6.17. Found: C, 74.08; H, 6.31.

The acetyl derivative of the acid XXIV was prepared as described before and crystallized from 95% ethanol, m.p. 208°.

Anal. Calcd. for $C_{22}H_{22}O_5$: C, 72.13; H, 6.01. Found: C, 72.13; H, 6.23.

3-Methoxy-17β-hydroxy-14,15-dehydroequilenane (XXV).—A thorough mixture of 0.1 g. of the acid XXIV and finely powdered soft glass under nitrogen atmosphere was introduced into a preheated bath at 300–310°. After the evolution of carbon dioxide ceased (10–12 minutes), the product was cooled under nitrogen and then distilled, 180–220° (0.1 mm.), to give a yellow solid, which was taken up in ether–benzene mixture and washed with cold 5% sodium hydroxide solution and water. After removal of the solvent the residue was crystallized from benzene–petroleum ether (40–60°), m.p. 187–190°; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 235 mμ, log ε 4.45; 255 mμ, log ε 4.4; 263 mμ, log ε 4.4; 291 mμ, log ε 4.00; 303 mμ, log ε 4.0; 332 mμ, log ε 3.2; 347 mμ, log ε 3.0; yield 0.36 g. (83%) from five such experiments.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.43; H, 7.14; CH_3O–, 11.07. Found: C, 80.97; H, 7.71; CH_3O–, 10.86.

The yield was considerably reduced when the acid was heated for a longer period for decarboxylation or when the quantity exceeded 0.15 g. at a time.

3-Methoxy-17β-hydroxyequilenane (XXVI).—A solution of 0.52 g. of the unsaturated alcohol XXV in 95% ethanol was hydrogenated in the presence of 0.2 g. of palladium–charcoal catalyst and worked up in the usual manner to yield 0.47 g. of 3-methoxy-17β-hydroxyequilenane, m.p. 179–180°, after recrystallization from 95% ethanol; ultraviolet spectrum: $\lambda_{max}^{alcohol}$ 228 mμ, log ε 4.7; 278 mμ, log ε 3.7; 324 mμ, log ε 3.3; 339 mμ, log ε 3.4.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.85; H, 7.80. Found: C, 80.26; H, 8.00.

***d,l*-Equilenin Methyl Ether (XXVIIa).**—A solution of 0.1 g. of 3-methoxy-17β-hydroxyequilenane in 1 cc. of benzene and 1 cc. of glacial acetic acid was treated with a solution of 0.036 g. of sodium dichromate dihydrate in 0.37 cc. of glacial acetic acid as described before for the oxidation of XIVb, except that the reaction mixture remained in contact with atmospheric air,[24] to yield 0.07 g. (70%) of the crude *d,l*-equilenin methyl ether; recrystallized from methanol–acetone, m.p. 184–185°; no depression in mixed melting point with an authentic sample.[15] It seems that the presence of oxygen, under the aforementioned condition of oxidation, has hardly any detrimental effect on the yield.

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(23) We are grateful to Prof. W. S. Johnson of the University of Wisconsin, Madison, Wis., for the gift of entire quantity of this material required for experiments described in the present paper.

(24) This experiment was carried out before receiving the communication from A. L. Wilds.[22]