chloroform. Concentration of the eluate with addition of ethanol yielded 3.43 g. of long fine needles, m.p. 183–184°. Two recrystallizations from ethanol provided material with a constant melting point of 183.8–184.6° (sintering at 183.2°), $[\alpha]^{21}\mathrm{D}$ +11.0° (*c* 1.02, chloroform).

Anal. Calcd. for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65; 4 OCH_3, 28.98. Found: C, 64.50; H, 5.79; OCH_3, 28.92.

β-Peltatin-B Methyl Ether (I, R = R′ = CH_3).—Crude material, m.p. 180–182°, was obtained in 98% yield from β-peltatin by the method just described, except that it was not necessary to employ a nitrogen atmosphere. Two recrystallizations from ethanol furnished a product melting at 183.8–184.6° (sintering at 183.6°), $[\alpha]^{21}\mathrm{D}$ +10.9° (*c* 1.07, chloroform), λ^{EtOH}_{max} 280 mμ (log ε 3.39), λ^{EtOH}_{min} 260.5 mμ (log ε 3.09). A mixture of 0.20 g. each of pure α-peltatin-B dimethyl ether and β-peltatin-B methyl ether gave, when recrystallized from ethanol, 0.35 g. of homogeneous material, m.p. 183.8–184.6° (sintering at 183.2°).

α-Peltatic Acid.—A solution of 1.0 g. of α-peltatin in 80 cc. of *N* sodium hydroxide was boiled for 15 minutes, then cooled in ice and, after addition of 60 cc. of chloroform, acidified by adding slowly 50 cc. of 2 *N* acetic acid with vigorous shaking. The suspension was kept in the ice-box for a short time, and the solid collected and washed with ice-cold water and chloroform; yield 0.82 g. (54%). It was recrystallized twice by dissolving it in ethanol, and diluting with chloroform, then with water. The acid formed tiny colorless needles, which melted, like α-peltatin-B,[2] at 275–276° (darkening) when immersed below 220°, but melted with foaming, resolidified, and melted again at 275–276° when immersed above 220°. When dried at room temperature, it was found to contain one mole of water of crystallization, which was not completely removed by drying in a vacuum at 80°; if the temperature was raised to 100°, partial lactonization took place. The solvated product had $[\alpha]^{20}\mathrm{D}$ −95° (*c* 1, 10% sodium bicarbonate).

Anal. Calcd. for $C_{21}H_{22}O_9 \cdot H_2O$: C, 57.79; H, 5.54; OCH_3, 14.22. Found: C, 57.47, 57.21; H, 5.76, 5.75; OCH_3, 14.64.

β-Peltatic Acid.—This compound was prepared in 94% yield from β-peltatin by the method used for the preparation of α-peltatic acid and purified analogously. The acid crystallized in small colorless needles, which did not contain any solvent after drying in a vacuum at room temperature; m.p. 202° (foaming), $[\alpha]^{19}\mathrm{D}$ −123.5° (*c* 1, 10% sodium bicarbonate).

Anal. Calcd. for $C_{22}H_{24}O_9$: C, 61.10; H, 5.59. Found: C, 61.07; H, 5.66.

When this acid was heated at 210°, and the melt recrystallized from dilute ethanol, β-peltatin-B was obtained as colorless long needles; m.p. 210–212°, $[\alpha]^{21}\mathrm{D}$ +37° (*c* 0.45, acetone) [lit.[2] m.p. 212.3–213.3°, $[\alpha]^{21}\mathrm{D}$ +40° (*c* 1, acetone)].

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Observations on the Degradation of 12-Ketosapogenins to Pregnane Derivatives

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It has been demonstrated by Fukushima and Gallagher[1] that treatment of a Δ^{16}-20-ketosteroid with alcoholic potassium hydroxide results in the conversion of the α,β-unsaturated ketone system to an equilibrium mixture of the unsaturated and 16-alkoxy ketones. These authors have pointed out that the products reported by Marker[2] from the alcoholic hydroxide treatment of oxidized 12-ketopseudosapogenins are quite probably the 16-alkoxy compounds rather than 17-hydroxy derivatives. These findings seem to eliminate any uncertainties concerning the conversion of 12-ketosapogenins to pregnane derivatives.[2,3]

We have had occasion to reinvestigate the degradation of kammogenin to compounds of the pregnane series and wish to record the properties of the products obtained. Aqueous alcoholic potassium bicarbonate hydrolysis of the oxidation product of pseudokammogenin triacetate furnished the expected **5,16-pregnadien-2,3β-diol-12,20-dione diacetate.** Methanolic and ethanolic potassium hydroxide hydrolyses, followed by acetylation, yielded products with properties and analyses which indicate them to be **16α-methoxy-5-pregnen-2,3β-diol-12,20-dione diacetate** and **16α-ethoxy-5-pregnen-2,3β-diol-12,20-dione diacetate,** respectively.[4] We were unable to obtain a product corresponding to the compound reported by Marker.[2]

The ultraviolet absorption maximum of the 12-keto-Δ^{16}-20-ketone obtained in this work occurs at 225 mm.; a similar hypsochromic shift was observed in the spectrum of 16-allopregnen-3β-ol-12,20-dione acetate ($\lambda_{max.}$ 228 mm.).[5] This displacement thus appears to be characteristic of Δ^{16}-12,20-diones.

Experimental

All melting points are corrected.

Oxidation of Pseudokammogenin Triacetate.—Pseudokammogenin triacetate[6] prepared from 6.0 g. of kammogenin (m.p. 238–242°) was dissolved in 125 cc. of glacial acetic acid and treated at 20–23° for 95 minutes with 4.5 g. of chromium trioxide. The solution was diluted with water and extracted with ether. The ether solution was washed with potassium carbonate solution and water and evaporated to a pale yellow glass.

Potassium Bicarbonate Hydrolysis.—One-half of the material from the oxidation was dissolved in 25 cc. of methanol. To the hot solution was added a solution of 2.5 g. of potassium bicarbonate in 10 cc. of water. The resulting cloudy amber solution was warmed for 4 min. and then diluted with water (100 cc.) until the steroid began to precipitate. After cooling, the solution was extracted with ether and the ethereal solution was washed with water, dried with magnesium sulfate and evaporated. The poorly crystalline residue was reacetylated with acetic anhydride and pyridine and the product was then crystallized from ether as small white crystals. The material had the following properties: m.p. 242–244°, $\alpha^{25}\mathrm{D}$ −1.2° (chloroform), $\lambda^{alc.}_{max.}$ 225 mμ (log ε 3.9).

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53. Found: C, 69.93; H, 7.51.

Methanolic Potassium Hydroxide Hydrolysis.—One-fourth of the oxidation product was dissolved in 30 cc. of methanol and the solution was refluxed gently with 1.0 g. of potassium hydroxide in 5 cc. of water for 15 min. The dark brown solution was treated with 0.7 cc. of acetic acid to neutralize the base and was then concentrated to a volume of 15 cc. After diluting with water, the solution was extracted with ether. The ether solution was washed with potassium bicarbonate solution, then with water. After drying with magnesium sulfate the solution was evaporated to an oily residue which could not be in-

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(1) D. K. Fukushima and T. F. Gallagher, This Journal, 73, 196 (1951).

(2) R. E. Marker, *ibid.*, 71, 4149 (1949).

(3) R. B. Wagner, J. A. Moore and R. F. Forker, *ibid.*, 71, 3865, 4159 (1949).

(4) The configurations of the 16-alkoxy groups have been assigned by D. K. Fukushima and T. F. Gallagher.

(5) R. B. Wagner, J. A. Moore and R. F. Forker, This Journal, 72, 1856 (1950).

(6) R. E. Marker, R. B. Wagner, P. R. Ulshafer, E. L. Wittbecker, D. P. J. Goldsmith and C. H. Ruof, *ibid.*, 69, 2167 (1947).

duced to crystallize. After acetylation with pyridine and acetic anhydride the product was crystallized from ether containing a few drops of methanol. This material had the following properties: m.p. 212–214°, $\alpha^{26}\text{D}$ −10.2° (chloroform), *M*D −47°. The ultraviolet absorption spectrum showed no maximum below 275 mμ. The infrared spectrum showed a peak at 9.54 μ, which is in the range associated with the carbon–oxygen stretching of an aliphatic ether. The peak at 2.6–2.8 μ characteristic of a hydroxyl group was completely absent.

Anal. Calcd. for $C_{26}H_{36}O_7$: C, 67.80; H, 7.88. Found: C, 67.69; H, 8.01.

Ethanolic Potassium Hydroxide Hydrolysis.—The remaining one-fourth portion of the oxidized pseudokammogenin triacetate was dissolved in 40 cc. of absolute ethanol containing 1.0 g. of potassium hydroxide and the solution was allowed to stand at 60–65° for 15 min. After cooling and neutralizing with acetic acid, the solution was evaporated *in vacuo* and the oily steroid was extracted with ether. After processing in the manner described above, the acetylated product was crystallized from methanol–ether; m.p. 202–203°, mixed m.p. with product from methanol hydrolysis 186–187°, $\alpha^{26}\text{D}$ −12.3° (chloroform), *M*D −58°; no ultraviolet absorption below 270 mμ. It is of interest to note that the molecular rotation difference between the ethoxy and methoxy derivatives, (*M*D-OEt − *M*D-OMe), −11°, corresponds quite closely to the same value (Δ*M*D −13°) for the ethoxy and methoxy derivatives reported by Fukushima and Gallagher.

Anal. Calcd. for $C_{27}H_{38}O_7$: C, 68.33; H, 8.07. Found: C, 68.18; H, 8.39.

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Some Thermochromic Spirans

BY C. F. KOELSCH AND W. R. WORKMAN[1]

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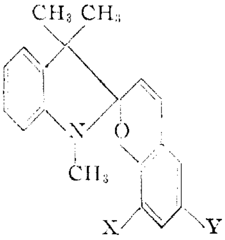
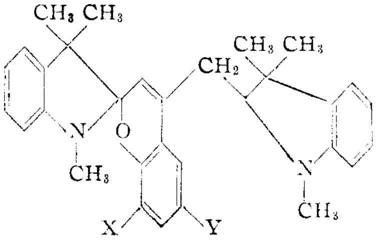
A theory was advanced almost simultaneously by Knott[2] and by one of us[3] to account for the thermochromism of certain spirans. The report of Knott included supporting evidence based on a study of spirans bearing polar substituents, and therefore our projected investigation into this aspect of the problem is no longer necessary. The present paper describes some results we had already obtained, differing in small details from those of previous investigators. These differences in no way affect the conclusions drawn by Knott and concurred in by us.

Condensation of salicylaldehyde with 1,3,3-trimethyl-2-methyleneindoline has been reported[4] to form a compound, m.p. 208°, assigned structure I. It has been found that the reaction actually yields two products: I, m.p. 93–94°, and II, m.p. 206–207°. Analytical figures for carbon and hydrogen, relied on in the older work, are not sufficient to identify I or II, nitrogen content, however, is characteristic. A separate synthesis of II, demethylation of *o*-methoxybenzalbis-(1,3,3-trimethyl-2-methyleneindoline), further supports the structure now suggested.



I, X = Y = H
III, X = OCH_3, Y = H
V, X = H, Y = Br
VII, X = H, Y = NO_2
VIII, X = Y = NO_2



II, X = Y = H
IV, X = OCH_3, Y = H
VI, X = H, Y = Br

o-Vanillin and 1,3,3-trimethyl-2-methyleneindoline yield not only III, m.p. 123–124° as previously reported,[4] but also IV, m.p. 223–224°. 5-Bromosalicylaldehyde yields two analogous products, V, m.p. 86–87°, and VI, m.p. 199–200°. But 5-nitrosalicylaldehyde gives only one product, VIII, m.p. 179.5–180°.[5] Similarly, 3,5-dinitrosalicylaldehyde gives only one product, VIII, m.p. 270° dec.

Experimental

Condensation of 1,3,3-Trimethyl-2-methyleneindoline with Salicylaldehyde.—A solution of 6.5 g. of the freshly distilled indoline and 4.1 g. of salicylaldehyde in 20 ml. of alcohol was boiled for two hours. The hot mixture was then filtered, and the solid was washed with hot alcohol. Recrystallization from acetone gave 2.5 g. of 1,3,3-trimethyl-4′-(1,3,3-trimethyl-2-indolinylmethyl)-indoline-2-spiro-2′-benzopyran (II), colorless crystals that melted at 209–210° to a pink liquid. The compound gave a violet solution in hot diphenyl ether.

Anal. Calcd. for $C_{31}H_{34}N_2O$: C, 82.6; H, 7.6; N, 6.4. Found[6]: C, 82.55; H, 7.6; N, 6.2.

The reaction mother liquors and the alcohol wash were distilled to a small volume, and the resulting solid was recrystallized from dilute alcohol, giving 5.4 g. of 1,3,3-trimethylindoline-2-spiro-2′-benzopyran (I), colorless crystals that melted to a colorless liquid at 92–94°. The compound gave a colorless solution in boiling xylene, a violet one in boiling diphenyl ether.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.3; H, 6.9; N, 5.0. Found: C, 82.7; H, 6.9; N, 5.1.

***o*-Methoxybenzalbis-(1,3,3-trimethyl-2-methyleneindoline).**—A solution of 5.9 g. of 1,3,3-trimethyl-2-methyleneindoline and 2.4 g. of *o*-methoxybenzaldehyde in 20 ml. of alcohol was boiled for four hours.[7] The product was removed by filtration and crystallized from acetone, giving 5 g. of colorless needles, m.p. 159–161°.

Anal. Calcd. for $C_{32}H_{36}N_2O$: N, 6.04. Found: N, 6.06.

A mixture of 1.0 g. of the methoxy compound, 8.7 g. of aluminum chloride and 20 ml. of benzene was boiled for 2.5 hours. The benzene was then decanted, and the residual thick oil was treated with aqueous potassium hydroxide. The pink solid remaining was crystallized from acetone, giving colorless crystals, m.p. 209–210°, alone or mixed with the compound obtained directly from salicylaldehyde.

Condensation with *o*-Vanillin.—A solution of 1.7 g. of 1,3,3-trimethyl-2-methyleneindoline and 1.5 g. of *o*-vanillin in 40 ml. of alcohol was boiled for 2.5 hours. The solid which separated directly was washed with alcohol and

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(1) From the Ph.D. Thesis of W. R. Workman.

(2) E. B. Knott, *J. Chem. Soc.*, 3038 (1951).

(3) C. F. Koelsch, *J. Org. Chem.*, **16**, 1352 (1951).

(4) R. Wizinger and H. Wenning, *Helv. Chim. Acta*, **23**, 247 (1940).

(5) This is the m.p. reported by Knott for the isomer obtained from 3-nitrosalicylaldehyde, whereas the condensation product from 5-nitrosalicylaldehyde was stated to melt at 147°. In the present work only 5-nitrosalicylaldehyde m.p. 125–126° was used.

(6) The figures for C and H are taken from ref. 4.

(7) *Cf.* A. Ferratine, *Gazz. chim. ital.*, **24II**, 194 (1894); G. Plancher, *ibid.*, **28II**, 37 (1898); *Ber.*, **31**, 1494 (1898).