(cor.), could be isolated in pure form by repeated crystallization from methanol.

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 58.99; H, 6.10.

Summary

It has been found that dimethyl and diethyl maleate react in the presence of large quantities of benzoyl peroxide to give the corresponding esters of phenylsuccinic acid and of tetracarboxylic acids which are probably stereoisomeric forms of tetralintetracarboxylic acid. Some higher molecular weight products of unidentified nature are also produced.

When the reaction is carried out in dioxane, dioxyanylsuccinic ester is formed in addition to these products, and in carbon tetrachloride solution, α,α'-bis-trichloromethylsuccinic ester is formed.

URBANA, ILLINOIS RECEIVED AUGUST 29, 1946

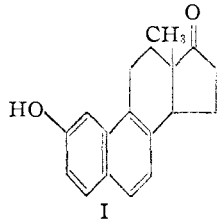
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Synthesis of 2-Hydroxy-17-equilenone

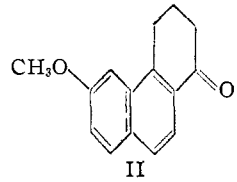
BY W. E. BACHMANN AND W. J. HORTON[1]

2-Hydroxy-17-equilenone[2] (I), the isomer of equilenin in which the OH group is in the 2-position, has been synthesized by the methods employed in the preparation of equilenin[3] and related compounds.[4]

6-Methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (II), an intermediate in the synthesis, was prepared by cyclization of γ-7-methoxy-1-naphthylbutyric acid. This acid was prepared in



I



II

three ways: (a) from 1-amino-7-naphthol through the intermediate 7-methoxy-1-iodonaphthalene and β-7-methoxy-1-naphthylethyl alcohol; (b) from 7-methoxy-1-tetralone through the Reformatsky reaction, Bouveault reduction of the dehydrated ester, a malonic ester synthesis on the bromide of the resulting alcohol and dehydrogenation of the product; (c) by Clemmensen reduction of β-7-methoxy-1-naphthoylpropionic acid. The keto acid was obtained from the reaction between 2-methoxynaphthalene and succinic anhydride in the presence of aluminum chloride in carbon disulfide. Substitution in the 8-position of 2-methoxynaphthalene was unexpected, for it had been reported that succinoylation of 2-methoxynaphthalene in carbon disulfide takes place exclusively in the 1-position.[5]

Plimmer, Short and Hill[6] obtained a glass on cyclization of γ-7-methoxy-1-naphthylbutyric acid by phosphorus pentoxide in benzene. We found that cyclization of the acid chloride by stannic chloride gave a mixture of two crystalline compounds, one (m. p. 100–102°) in 70–80% yield and the other (m. p. 81–82.5°) in about 10–15% yield. The higher melting compound was definitely shown to be 6-methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (II). The lower melting compound is probably the cyclic ketone with a seven-membered ring formed by cyclization to the 8-position,[7] but this has not been established. The particular compound or mixture of compounds which were formed depended on the cyclizing agent and apparently also on certain uncontrollable conditions when phosphorus pentoxide was used, since reproducible results were not always obtained. The most satisfactory methods of preparing II were the method mentioned above and the action of a mixture of phosphorus pentoxide and phosphoric acid on the acid. After this work had been completed, Campbell and Todd[8] reported the formation of crystalline II (m. p. 99–102°) from the reaction between the acid and hydrogen fluoride.

Only one of the two possible forms (*cis* and *trans*) of the final hormone isomer was obtained in the synthesis.

Experimental

γ-7-Methoxy-1-naphthylbutyric Acid. (a) From 1-Amino-7-naphthol.—7-Hydroxy-1-naphthylamine (m. p. 160–166°), which was obtained by alkaline fusion of 1-naphthylamine-7-sulfonic acid, was acetylated by ice cold acetic anhydride; the product was methylated by means of dimethyl sulfate in alkaline solution to **1-acetylamino-7-methoxynaphthalene** in quantitative yield. A sample after recrystallization from water melted at 160–161° (reported,[9] 145°).

Anal. Calcd. for $C_{13}H_{13}O_2N$: N, 6.5. Found: N, 6.7.

A mixture of 22.7 g. of powdered 1-acetylamino-7-methoxynaphthalene, 11.3 cc. of water and 27.4 cc. of concentrated hydrochloric acid was refluxed for one hour. On cooling, the clear solution deposited the hydrochloride of 7-methoxy-1-naphthylamine; yield, 17.4 g. (78%). This was used directly for diazotization. A sample of the free **7-methoxy-1-naphthylamine** after evaporative distilla-

(1) From the Ph.D. dissertation of W. J. Horton, 1942.

(2) For the nomenclature employed for these compounds see Bachmann and Wilds, THIS JOURNAL, **62**, 2084 (1940).

(3) Bachmann, Cole and Wilds, *ibid.*, **62**, 824 (1940).

(4) Preceding paper, Bachmann and Morin, *ibid.*, **66**, 553 (1944).

(5) Short, Stromberg and Wiles, *J. Chem. Soc.*, 319 (1936).

(6) Plimmer, Short and Hill, *ibid.*, 694 (1938).

(7) Compare the cyclization of γ-5-methoxy-1-naphthylbutyric acid to the 8-position [Kon and Soper, *ibid.*, 790 (1939)].

(8) Campbell and Todd, THIS JOURNAL, **64**, 928 (1942).

(9) Davis, *Chem. News*, **74**, 302 (1896).

tion at 200–250° (0.6 mm.) crystallized from aqueous methanol in flat diamond-shaped crystals; m. p. 79–80°.

Anal. Calcd. for $C_{11}H_{11}ON$: N, 8.1. Found: N, 8.3.

A solution of 42 g. of the amine hydrochloride in 125 cc. of water, 125 cc. of acetic acid and 50 cc. of concentrated hydrochloric acid was diazotized at −10 to 0° by addition of a solution of 16 g. of sodium nitrite in 70 cc. of water. Thirty minutes after the nitrite had been added, a solution of 3 g. of urea in a small amount of water was added, and after another thirty minutes 30 cc. of concentrated hydrochloric acid and a solution of 40 g. of potassium iodide were introduced. The mixture was covered with a layer of benzene and allowed to stand in a refrigerator for twelve hours, after which it was warmed to 80°. The product, isolated in the usual manner, solidified after distillation; b. p. 134–135° (0.3 mm.); m. p. 69–74°; yield, 25.1–29.4 g. (44–52%). After four recrystallizations from methanol a sample of the **1-iodo-7-methoxynaphthalene** formed large colorless rhombs, m. p. 74.5–75°.

Anal. Calcd. for $C_{11}H_9OI$: I, 44.7. Found: I, 44.8, 44.5.

A solution of 57 g. of the iodo compound and 14.7 cc. of ethyl bromide in 150 cc. of dry benzene was added in six portions to 9.8 g. of powdered magnesium in 100 cc. of dry ether. The reaction started immediately; after addition was complete, the mixture was refluxed for five hours. The solution was diluted with 200 cc. of dry benzene, cooled to 5° and treated with 32 g. of ethylene oxide. After twelve hours at 5°, the mixture was warmed for one hour in a water-bath (50–80°) and then worked up in the usual manner.[3] The product boiling at 160° (0.4 mm.) solidified; yield, 33.1 g.; m. p. 60–65°. A sample of the **β-7-methoxy-1-naphthylethyl alcohol** after two recrystallizations from benzene–petroleum ether formed clusters of flat, colorless prisms; m. p. 83.5–85.5°.

An ice-cold solution of 14.8 g. of the alcohol in 50 cc. of benzene was treated with 5.25 cc. of phosphorus tribromide in 19 cc. of benzene. The mixture was then warmed gradually to 75° and kept there for three hours and worked up according to the procedure described for a similar compound.[10] The **β-7-methoxy-1-naphthylethyl bromide** was obtained as a nearly colorless liquid; b. p. 169° (0.4 mm.); yield, 11.7 g. About 2.1 g. of good alcohol was recovered.

The condensation of the bromide (39 g.) with the sodio derivative of malonic ester (75 g.) was carried out as described for a similar case[3] and the substituted malonic acid (35 g.) was decarboxylated at 180–200° (twenty to thirty minutes); by the addition of 2 cc. of acetic acid to the decarboxylating mixture, material clinging to the walls of the flask was washed down. The clear hot melt was poured into 15 cc. of acetic acid, a few drops of water were added and the solution was allowed to cool; yield, 22.8 g. After recrystallization from water and then from dilute acetic acid a sample formed long thin needles; m. p. 108–109.5° (reported,[6] 105–106°). Colorless crystals of the γ-7-methoxy-1-naphthylbutyric acid can be obtained readily by extraction with petroleum ether (90–100°) in a Soxhlet extractor.

(b) From **7-Methoxy-1-tetralone**.—To a solution of 8.8 g. of γ-4-anisylbutyric acid in 175 cc. of benzene, cooled in an ice-water bath, was added 12.5 g. of phosphorus pentachloride with swirling. After twelve hours at room temperature, the mixture was chilled and treated with 9.3 cc. of anhydrous stannic chloride with swirling. After one hour in the cooling bath, the deep red solution and orange precipitate were poured onto a mixture of ice and hydrochloric acid, and the product was isolated and purified in the usual manner; yield, 6.7 g. (76%); m. p. 56–61°. After distillation at 103° (0.2 mm.) and recrystallization from petroleum ether, the 7-methoxy-1-tetralone formed large hexagonal plates; m. p. 61–62.5°. This compound has been prepared previously by other methods of cyclization.

The steps in the following synthesis vary only slightly from those of Plimmer, Short and Hill.[6] The product of the Reformatsky reaction between 1.23 g. of 7-methoxy-1-tetralone, zinc and methyl bromoacetate, carried out as described for another compound,[3] was dissolved in 50 cc. of benzene and the solution was refluxed with 5 g. of phosphorus pentoxide for forty-five minutes.[6] The product obtained by evaporation of the filtered solution distilled at 167–173° (0.4 mm.); yield, 1.41 g. A boiling solution of the unsaturated ester in 5 cc. of absolute alcohol was treated rapidly with 1 g. of sodium cut into small pieces. When no more sodium remained, some water was added and the solution was refluxed for two hours. The **β-7-methoxy-1,2,3,4-tetrahydro-1-naphthylethyl alcohol** boiled at 179–182° (0.3 mm.); yield, 0.73 g. Its 3,5-dinitrobenzoate melted at 119–119.5° (reported,[6] 119.5–120°). The alcohol was converted to its bromide by reaction with 0.2 cc. of phosphorus tribromide in 2.8 cc. of chloroform (twelve hours at 0° and then warming to 75°); b. p. 164° (0.4 mm.); yield, 0.47 g.

A solution of 1.14 g. of the β-7-methoxy-1,2,3,4-tetrahydro-1-naphthylethyl bromide in 2 cc. of benzene was added to the sodio malonic ester prepared from sodium ethoxide (0.3 cc. of absolute alcohol, 1 cc. of benzene and 0.14 g. of sodium) and 2.12 g. of diethyl malonate. After twelve hours of heating, the mixture was hydrolyzed with alcoholic potassium hydroxide. The substituted malonic acid was decarboxylated at 200°, the product was evaporatively distilled at 0.5 mm., and the distillate was chilled until it solidified; yield, 0.42 g.; m. p. 58–62°. A sample of the **γ-7-methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric acid** after five recrystallizations from petroleum ether formed flat hexagonal plates; m. p. 59.5–62° (reported[6] as an oil).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.6; H, 8.1. Found: C, 72.2; H, 7.8.

The acid (0.21 g.) was esterified with diazomethane and the ester was heated with 20 mg. of palladium–charcoal catalyst[11] at 300–325° in an atmosphere of nitrogen for eight hours. On hydrolysis of the dehydrogenated ester with alcoholic potassium hydroxide, 80 mg. of γ-7-methoxy-1-naphthylbutyric acid was obtained. After one recrystallization from aqueous acetic acid, it formed clusters of colorless needles; m. p. 108–109.5°.

(c) From **2-Methoxynaphthalene**.—Aluminum chloride (73.5 g.) was added to a mechanically stirred mixture of 39.5 g. of 2-methoxynaphthalene, 25 g. of succinic anhydride and 500 cc. of carbon disulfide, and the resulting mixture was refluxed with stirring for two and one-half hours, when the viscosity of the mixture prevented further stirring. After hydrolysis of the mixture with ice and water, the carbon disulfide was removed by distillation and the residual dark red oil was treated repeatedly with aqueous sodium bicarbonate to extract the keto acids. The combined extracts were filtered and acidified. The product which separated from the solution was isolated, dissolved in 10% sodium hydroxide and treated with 12 cc. of dimethyl sulfate. The solution was kept alkaline and warm for some time and after an ether extraction the aqueous solution was acidified. The solid (21.7 g.) was esterified by ethanolic hydrogen chloride and the ester was distilled at 210° (0.7 mm.). The product (10.15 g.), which solidified, crystallized in yellowish needles from alcohol; yield, 4.91 g.; m. p. 71–78°. After two more recrystallizations, a sample of the ethyl ester of β-7-methoxy-1-naphthoylpropionic acid was obtained as nearly colorless rods; m. p. 79.5–81°. Hydrolysis of 0.75 g. of the pure ester by methanolic sodium hydroxide gave 0.61 g. of **β-7-methoxy-1-naphthoylpropionic acid**; m. p. 145–146°. A sample crystallized from methanol in long thin rods; m. p. 148–149°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5. Found: C, 69.6; H, 5.2.

Oxidation of 0.55 g. of the acid by 60 cc. of a solution 0.25 *M* with respect to sodium hypochlorite and 0.5 *M* with respect to sodium hydroxide at 80° for twenty minutes and at the boiling point for the same length of time gave

(10) Cohen, Cook and Hewett, *J. Chem. Soc.*, 52 (1926).

(11) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1935).

0.14 g. of 7-methoxy-1-naphthoic acid, which crystallized from ethyl acetate in colorless needles; m. p. 166–168°. The melting point was not depressed when the acid was mixed with the acid prepared from 1-iodo-7-methoxynaphthalene and carbon dioxide through the Grignard reaction.

A mixture of 6.1 g. of the keto acid, 9.1 g. of amalgamated zinc, 7 cc. of water, 16 cc. of concentrated hydrochloric acid, and 9 cc. of toluene was refluxed for twenty-four hours; during this period four 5-cc. portions of hydrochloric acid were added. The product which was isolated was dissolved in 10% sodium hydroxide and treated with 5 cc. of dimethyl sulfate with shaking. After two hours the solution was decolorized with Norit, filtered and acidified. The acid was purified through its methyl ester, which was evaporatively distilled and then hydrolyzed. By recrystallization from petroleum ether–benzene, 1.5 g. of nearly colorless crystals (m. p. 91–101°) was obtained. After evaporative distillation and recrystallization, the γ-7-methoxy-1-naphthylbutyric acid melted at 102–105° alone and when mixed with the acid obtained in (a) and in (b). The acids obtained by the three methods gave the same products on cyclization.

Cyclization of γ-7-Methoxy-1-naphthylbutyric Acid. (a) **Stannic Chloride on the Acid Chloride.**—Five grams of powdered acid was added to 25 cc. of anhydrous ether, 2.4 cc. of thionyl chloride and 2 drops of pyridine, and the mixture was allowed to stand at room temperature with occasional shaking for three hours. The volatile constituents were then removed under reduced pressure at room temperature; a 2-cc. portion of benzene was added and likewise evaporated and this operation was repeated. The acid chloride, which crystallized near the end of the process, was dissolved in 100 cc. of benzene and the solution was cooled until the benzene began to freeze; then a solution of 2.47 cc. of stannic chloride in 20 cc. of benzene was added, and the solution was swirled for exactly three minutes. The mixture, which contained a yellow precipitate, was poured into a mixture of 30 cc. of concentrated hydrochloric acid and 30 cc. of ether. The clear, slightly yellowish ether layer was washed three times with 10% hydrochloric acid, once with water, twice with 10% sodium hydroxide (which removed the color) and then several times with water. After the ether–benzene had been evaporated in a current of air on a steam-bath, the residue was warmed with a little ether and cooled, whereupon crystallization took place; yield, 4.23 g. From the filtrate an additional 0.30 g. of crystals was isolated after evaporative distillation under reduced pressure; from the alkaline solution about 0.11 g. of acid was recovered. In a number of runs the yields of ketones varied between 84–96%.

Recrystallization of the first crop material from methanol and water gave colorless diamond or boat-shaped crystals; m. p. 100–102°. The filtrate deposited small needles or long rods, which after several recrystallizations from aqueous methanol and one from petroleum ether formed colorless prisms; m. p. 81–82.5°. This compound formed a dinitrophenylhydrazone and a phenylhydrazone. The high melting ketone was isolated in about 70–80% yield, the low melting compound in about 10–15% yield. A mixture of the two compounds melted at 81–95°. All attempts to change the low melting compound into the higher melting compound failed.

(b) **Phosphorus Pentoxide in Phosphoric Acid on the Acid.**—Phosphorus pentoxide (6.2 g.) was dissolved in 4 cc. of 85% phosphoric acid[12] at 80° and to the warm solution was added 0.25 g. of γ-7-methoxy-1-naphthylbutyric acid. The mixture was kept at 80–85° until the acid dissolved (one and one-half to two hours) and then cooled and hydrolyzed. After separation from unchanged acid, the product was evaporatively distilled at 185° (0.5 mm.) and recrystallized from methanol; yield, 0.17 g.; m. p. 102–103.5° (reported,[8] 99–102°). An additional 30 mg. isolated from the filtrate brought the yield to 86%.

(c) **Other Methods.**—The high melting ketone was obtained by treatment of the acid with zinc chloride in acetic acid and acetic anhydride[13] at 85–90° for one and one-half hours followed by hydrolysis of the product, and by the action of stannic chloride on the acid. Cyclization of the acid with phosphorus pentoxide in dry benzene[6] gave material difficult to purify; only the low melting ketone was isolated in crystalline form and this in poor yield. In one run a fair yield of the low melting ketone was obtained by cyclization of the acid with a suspension of phosphorus pentoxide on Filtercel[14] in boiling benzene; in other runs only the high melting ketone was produced.

Proof of Structure of II. (a) **Conversion into 3-Methoxyphenanthrene.**—The carbinol obtained by aluminum isopropoxide reduction of 0.5 g. of the ketone (m. p. 100–102°) crystallized from benzene–petroleum ether in long colorless rods; m. p. 108–111°; yield, 0.37 g. With concentrated sulfuric acid the **1-hydroxy-6-methoxy-1,2,3,4-tetrahydrophenanthrene** gives a yellow color which changes to purple and then fades.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 79.4; H, 6.8.

A mixture of 80 mg. of the carbinol and 10 mg. of palladium–charcoal catalyst was heated at 265° for one hour. The product (30 mg.) after evaporative distillation at 0.1 mm. melted at 49–54.4° alone and when mixed with authentic 3-methoxyphenanthrene (m. p. 56–58°) prepared from 3-phenanthrylamine. The picrate formed scarlet needles in absolute alcohol; m. p. 121.5–123°, unchanged by admixture with the picrate (m. p. 122.5–123.5°) of 3-methoxyphenanthrene.

By refluxing a mixture of 1 g. of the ketone, 1.2 g. of semicarbazide hydrochloride, 30 cc. of absolute alcohol and 1.5 cc. of pyridine for eight hours the **semicarbazone of 1-keto-6-methoxy-1,2,3,4-tetrahydrophenanthrene** was obtained in quantitative yield. It crystallized from acetic acid–toluene in fluffy colorless crystals; m. p. 267–269° dec. to 272–279° depending on the rate of heating.

Anal. Calcd. for $C_{16}H_{17}O_2N_3$: N, 14.8. Found: N, 14.5.

The semicarbazone (0.5 g.) was heated with a solution of sodium ethoxide (from 1.05 g. of sodium and 30 cc. of absolute alcohol) at 180° for twenty-four hours, and the product was converted into its picrate (orange-red needles; m. p. 124.5–126°). The regenerated **6-methoxy-1,2,3,4-tetrahydrophenanthrene** (m. p. 46–49.5°) crystallized on evaporation of a benzene solution of the compound. The same compound was obtained by Clemmensen reduction of the ketone; in this reaction 2.26 g. of the ketone, 3.9 g. of amalgamated zinc, 6.8 cc. of concentrated hydrochloric acid, 2.9 cc. of water and 4 cc. of toluene were refluxed for twenty-four hours with additions of 1.94 cc. of hydrochloric acid at six-hour intervals. The crude isolated product was placed in aqueous potassium hydroxide and treated with two 0.5-cc. portions of dimethyl sulfate, and the mixture was warmed briefly. The product after being washed and distilled crystallized from acetone–methanol (when seeded with the product of the Wolff–Kishner reaction) in colorless prisms; m. p. 48–51°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 84.6; H, 7.2.

The 6-methoxy-1,2,3,4-tetrahydrophenanthrene prepared by the two methods was dehydrogenated with palladium-on-charcoal (three hours at 310°) to 3-methoxyphenanthrene.

(b) **Formation of 1-Methyl-6-methoxyphenanthrene.**—By interaction of the ketone (m. p. 100–102°) with methylmagnesium iodide, followed by treatment of the methyl carbinol (m. p. 117–120°) with palladium–charcoal at 310°, 1-methyl-6-methoxyphenanthrene was obtained; m. p. 90–91.5° after four recrystallizations from methanol (reported,[6] 87–87.5°). The deep orange picrate crystallized in long rectangular rods; m. p. 143–144.5° (reported,[6] 140°).

6-Methoxy-2-methylcarbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene.—From 2.26 g. of 6-methoxy-1-keto-

(12) Koebner and Robinson, *J. Chem. Soc.*, 1994 (1938).

(13) Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

(14) Schoepfle and Kosolapoff, unpublished results.

1,2,3,4-tetrahydrophenanthrene 2.52–3.02 g. (80–96%) of **methyl 6-methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene-2-glyoxalate** was obtained by the method described for its isomer[3]; m. p. 142–146°. It crystallized from acetone in long, fine, orange-yellow prisms; m. p. 144.5–147°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.1. Found: C, 69.8; H, 4.9.

By heating 1.7 g. of recrystallized glyoxalate with 0.85 g. of powdered soft glass at 180° for thirty minutes as described,[3] extracting the product with boiling petroleum ether (90–100°), and evaporating and recrystallizing the residue from methanol, 1.29 g. (83%) of colorless needles of **6-methoxy-2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene** was obtained; m. p. 90–100° with solidification and remelting at 125.5–127°. The keto ester gives a blue-green color with an alcoholic ferric chloride solution.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.6. Found: C, 71.7; H, 5.6.

By the procedure described[3] 1.17 g. of the keto ester was methylated to give **6-methoxy-2-methyl-2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene**, which crystallized from acetone–methanol in short colorless prisms; m. p. 145–148°; yield, 0.84 g. (76%). The compound gives no color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.9; H, 5.9.

Dimethyl Ester of 6-Methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic Acid.—Treatment of 1.5 g. of the aforementioned methylated keto ester with zinc and methyl bromoacetate in the manner described[3] yielded the dimethyl **ester of 6-methoxy-2-methyl-2-carboxy-1-hydroxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid**; m. p. 103–118°; yield, 1.57 g. A sample crystallized from methanol in fine colorless prisms; m. p. 130–130.5°. It gives a brown color with concentrated sulfuric acid.

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.7; H, 6.5. Found: C, 67.8; H, 6.3.

The Reformatsky ester (2.25 g.) was dehydrated and the product was hydrolyzed by aqueous-alcoholic potassium hydroxide as described.[3] After removal of the alcohol the aqueous solution was shaken with 50 g. of 2% sodium amalgam for thirty minutes. The reduced acid (1.82 g.) was dissolved in a boiling mixture of 5.7 cc. of acetic acid and 8.6 cc. of xylene; on cooling 1.51 g. of acid (m. p. 210–217°) crystallized. After a second recrystallization the **6-methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid** melted at 225–227.5° and was suitable for the next step. A purer sample prepared by hydrolysis of its dimethyl ester crystallized in long thin rods; m. p. 228–229.5°. It was not possible to isolate an isomeric acid.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.5; H, 6.1. Found: C, 70.0; H, 6.1.

The **dimethyl ester**, prepared in practically quantitative yield by means of diazomethane, crystallized from methanol in fine colorless needles; m. p. 114–117.5°. A sample after four recrystallizations melted at 118–120.5° (cor.).

Anal. Calcd. for $C_{21}H_{24}O_5$: C, 70.8; H, 6.7. Found: C, 71.2; H, 6.7.

2-Hydroxy-17-equilenone (I).—The aforementioned dimethyl ester was half hydrolyzed to **6-methoxy-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid** in quantitative yield.[3] From ethyl acetate it crystallized in colorless needles; m. p. 175.5–177.5° with previous softening at 170°.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.2; H, 6.4. Found: C, 70.5; H, 6.2.

The acid ester (1.24 g.) was converted through an Arndt-Eistert synthesis in the manner described[3] to the **dimethyl ester of 6-methoxy-2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrene-1-β-propionic acid**; yield, 1.03 g. (76%); m. p. 108–110°. A sample crystallized from methanol in colorless needles; m. p. 110–112.5° with previous softening.

Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.3; H, 7.1. Found: C, 71.2; H, 6.7.

The dimethyl ester was cyclized by the Dieckmann method as described[3] (three hours refluxing) to **2-methoxy-16-carbomethoxy-17-equilenone** in 80% yield; m. p. 130–134°. It crystallized from methanol in colorless prisms; m. p. 135.5–137° (vac.). The compound gives a muddy green color with an alcoholic ferric chloride solution.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.5; H, 6.5. Found: C, 74.7; H, 6.3.

A mixture of 0.2 g. of the cyclic keto ester, 9.6 g. of acetic acid, 4.75 cc. of concentrated hydrochloric acid and 9 cc. of water was refluxed under nitrogen for ten hours. The crystals (0.12 g.) which were filtered from the cooled solution were dissolved in 20 cc. of 2.5% aqueous potassium hydroxide, the solution was decolorized with Norit, and then acidified. From alcohol containing a small amount of acetone the **2-hydroxy-17-equilenone** crystallized in square colorless plates; yield, 50 mg.; m. p. 203–204° (vac.).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.1; H, 6.3.

Summary

A new reaction product, β-7-methoxy-1-naphthoylpropionic acid, was isolated from the reaction between 2-methoxynaphthalene and succinic anhydride in carbon disulfide.

Cyclization of the acid chloride of γ-7-methoxy-1-naphthylbutyric acid with stannic chloride takes place chiefly to the 2-position and to some extent apparently to the 8-position.

The synthesis of 2-hydroxy-17-equilenone, an isomer of equilenin, is described.

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