off in a vacuum as completely as possible without heating the bath to over 150°. The residue remaining in the distilling flask was dissolved in 10 cc. of warm 95% alcohol. This solution was allowed to stand at room temperature until crystallization of the new compound reached completion. Cooling to 0° would precipitate sirupy reducing compounds which had not been removed by the distillation. The crystallization at room temperature was very satisfactory although low yields of the non-reducing compound necessitated the use of seed crystals. The solid product was then filtered and purified by recrystallization from a small amount of absolute alcohol. One recrystallization served to free the product from reducing materials and further recrystallizations caused no more change in its physical constants. The crystals were diamond-shaped plates and melted at 184.5–185.5°; $[\alpha]^{23}\text{D}$ +69.2° (0.1705 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.30° to the right). Recrystallized from benzene the compound formed needles which melted at 167–169°; $[\alpha]^{23}\text{D}$ +69.5° (0.1774 g. in 9.98 cc. of chloroform in a 1.1-dm. tube rotated 1.36° to the right). Neither crystalline form lost any weight on drying over phosphorus pentoxide at 78° in a vacuum.

The new compound was secured in yields of from 0.1 to 1 g. for each 90 g. of acetobromoarabinose reduced. The yields of diacetylarabinal and triacetylarabinose were 34 g. and 8 g., respectively.

The compound was easily soluble in chloroform, warm alcohol, ethyl acetate and acetic acid, slowly soluble in benzene, insoluble in cold alcohol and ether and very insoluble in water.

The non-reducing material gave a molecular weight of 390 (0.5706 g. in 80.5 g. benzene gave a freezing point lowering of 0.094°). A tetraacetyl desoxypentose disaccharide would have a molecular weight of 418.

Anal. Calcd. for $C_{18}H_{26}O_{11}$ (418): C, 51.65; H, 6.26; CH_3CO, 41.1. Found: C, 51.44; H, 6.25; CH_3CO, 40.7.

Desoxypentose Disaccharide.—Three-tenths gram of tetraacetyl desoxypentose disaccharide was deacetylated by dissolving in 25 cc. of water containing 1 g. of barium hydroxide. The solution was freed of excess barium hydroxide by carbon dioxide. The barium carbonate was removed by filtration and the water evaporated off under reduced pressure. The residue, which still contained inorganic salts, was extracted several times with warm absolute alcohol and the alcohol was removed by a vacuum distillation. The residue remaining in the distilling flask was extracted with a small amount of water to free the preparation from any compound which had not been deacetylated. The water solution was evaporated slowly in a vacuum desiccator over phosphorus pentoxide. After the water had been removed the compound solidified. The yield was 0.16 g. or 90%. After recrystallization from isopropyl alcohol and ether the desoxypentose disaccharide melted at 177–180°. The melting point was not sharp and there was a great deal of decomposition.

Anal. Calcd. for $C_{10}H_{18}O_7$ (250): C, 48.00; H, 7.25. Found: C, 47.80; H. 6.81.

Acknowledgment—The author wishes to express his appreciation to Dr. R. M. Hixon and Dr. W. Freudenberg for their advice and suggestions and to Dr. I. B. Johns for the micro-analyses.

Summary

The reduction of acetobromoarabinose was found to yield a non-reducing compound which had not been previously reported. The analysis of the new compound showed it to be a tetraacetyl desoxypentose disaccharide. The free disaccharide was also prepared in crystalline form.

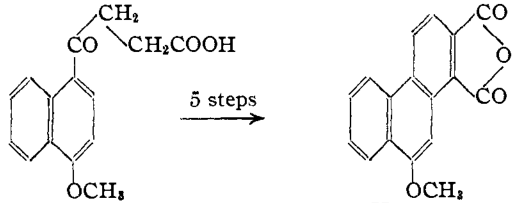
AMES, IOWA RECEIVED SEPTEMBER 29, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. IV. Hydroxylated Compounds

BY L. F. FIESER AND E. B. HERSHBERG

This work was undertaken with the idea that the introduction of hydroxyl or methoxyl groups into the phenanthrene dicarboxylic anhydrides[1] and the hexa- or octahydrophenanthrene dicarboxylic anhydrides[2] previously described might afford substances of oestrogenic activity, the presence of hydroxyl and carbonyl groups in different parts of the molecule establishing at least a superficial resemblance to oestrone. One such compound was prepared from the condensation product of succinic anhydride and α-methoxynaphthalene, I, by reduction, esterification, condensation with ethyl oxalate, cyclization and dehydrogenation, giving 9-methoxyphenanthrene-1,2-dicarboxylic anhydride, II.



I II

An anhydride of a second type was obtained

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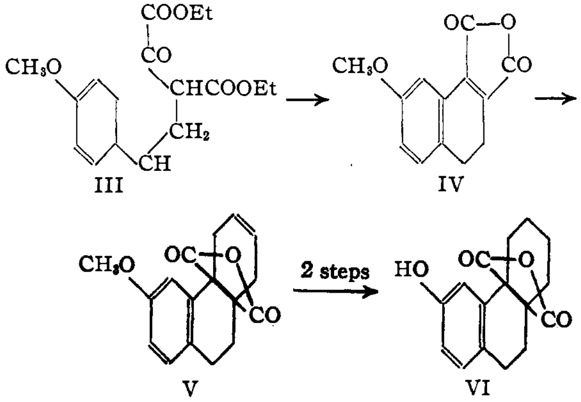
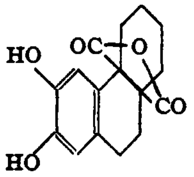
[1] Fieser and Hershberg, THIS JOURNAL, 57, 1851 (1935).

[2] Fieser and Hershberg, *ibid.*, 57, 2192 (1935).

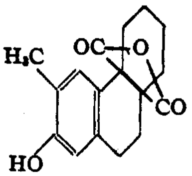
from γ-(4-methoxyphenyl)-butyric acid, readily prepared from anisole and succinic anhydride, through the oxalyl derivative III, the unsaturated anhydride IV, and the butadiene addition product V. After saturation of the active double bond this was demethylated satisfactorily, giving VI.



The 6,7-dihydroxyoctahydrophenanthrene-11,12-dicarboxylic anhydride VII was prepared similarly starting with veratrole, while VIII was obtained from Martin's γ-(3-methyl-4-methoxyphenyl)-butyric acid.[3] The only noteworthy observation to be recorded in connection with the syntheses is that in the Bougault cyclization of oxalyl derivatives such as III, or that from I, with sulfuric acid the unsaturated anhydride is often accompanied by a considerable amount of the corresponding aromatic anhydride. Since this has not been observed in other cases it appears that methoxyl groups render the dihydro derivatives particularly susceptible to the dehydrogenating action of sulfuric acid. By using acid just strong enough to effect the cyclization, the aromatization in some cases can be prevented or at least minimized. It should be noted that by heating the unsaturated compounds or the crude mixtures with sulfur, naphthalene derivatives of use in general synthetic work can be obtained easily in good yield. The 6-methoxy-, 7-methoxy- and 6-methoxy-7-methyl derivatives of 1,2-naphthalic anhydride (naphthalene-1,2-dicarboxylic anhydride) are described in this paper.



VII



VIII

In the first paper of this series[1] we cited a preliminary report from Dr. G. Pincus regarding the physiological activity of phenanthrene-1,2-dicarboxylic anhydride and its 3,4-dihydro derivative. The statements unfortunately were incomplete and misleading, as it was implied that the standard technique of bio-assay had been employed. Actually the anhydrides have given only negative results when injected subcutaneously into either spayed mice or immature rats even in large dosages. The reported cornifications were observed following the intraperitoneal injection into spayed mice of two 0.1-cc. doses of a solution of the material in sesame oil made twelve hours apart, and the appearance of a single cornified smear in any individual in six days was considered positive. In later experiments Pincus and Werthessen[4] abandoned the first technique as unreliable and developed a second special test method, also based on intraperitoneal injections, which seems to have promise as a preliminary guide. They report that in this more rigid test phenanthrene-1,2-dicarboxylic anhydride and its dihydro compound are inactive in relatively large dosages but that the compounds II, VI, VII and VIII described in the present paper give positive results and seem to be comparable with 1-keto-1,2,3,4-tetrahydrophenanthrene in oestrogenic activity, as judged by the special test. According to their ratings the dihydroxy compound VIII is the most active substance of the group and is more potent than ketotetrahydrophenanthrene.

Experimental Part[5]

Condensation of Phenol Ethers with Succinic Anhydride.—The Friedel and Crafts reactions of anisole and veratrole with succinic anhydride have been conducted in carbon bisulfide[6] or benzene[7] solution (no yields given) and, apparently with better results, using nitrobenzene[8,9] or tetrachloroethane.[10] After many trials in this Laboratory with these and other ethers, we found the following procedure very satisfactory and convenient: 0.4 mole of anisole (or veratrole) is dissolved with 0.42 mole of succinic anhydride in 400 cc. of tetrachloroethane and 100 cc. of nitrobenzene. The stirred solution is cooled to 0–5° (thermometer in liquid) and 0.84 mole of aluminum chloride ($AlCl_3$) is added gradually, keeping the temperature at 0–5°. At the end of the addition (one to two hours) a clear solution usually is obtained and it is allowed to stand

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[3] Martin, This Journal, **58**, 1438 (1936).

[4] Pincus and Werthessen, *Science*, **84**, 45 (1936).

[5] All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

[6] Bargellini and Giua, *Gazz. chim. ital.*, **42**, I, 197 (1912).

[7] Krollpfeiffer and Schäfer, *Ber.*, **56**, 630 (1923).

[8] Haworth and Mavin, *J. Chem. Soc.*, 1485 (1932).

[9] Rosenmund and Schapiro, *Arch. Pharm.*, **272**, 313 (1934).

[10] Mitter and De, *J. Indian Chem. Soc.*, **12**, 747 (1935).

at 0–5° (packed in ice in the cold room) for three days, during which time a complex sometimes separates. After adding ice and hydrochloric acid and removing the solvent with steam, the product is either allowed to crystallize directly or it is dissolved in soda solution, the solution is clarified with Norite and acidified. The keto acid is obtained in a colorless or nearly colorless condition quite satisfactory for further use. In this way β-(4-methoxybenzoyl)-propionic acid was obtained as colorless needles, m. p. 146–147°, in 85% yield. The results were duplicated by W. P. Campbell and by H. L. Holmes, the latter using as much as 173 g. of anisole in one experiment. By the same procedure β-(3,4-dimethoxybenzoyl)-propionic acid, m. p. 157–159°, was obtained in 67% yield, and H. L. Holmes obtained the same yield using 341 g. of veratrole. In other experiments with veratrole it was found that when using the tetrachloroethane–nitrobenzene mixture the yield dropped to 40% or less when the amount of aluminum chloride was changed from two equivalents to either one or three equivalents, and that the yield was also decreased by conducting the reaction at room temperature (43%, m. p. 152–154°). Following the procedure of Haworth and Mavin,[8] using nitrobenzene alone and operating at room temperature, we obtained material somewhat inferior (brown, m. p. 150–155°) to that above in slightly better yield (73%). Using carbon bisulfide[6] the yield was low (46%) and product of poor quality.

β-(4-Methoxy-1-naphthoyl)-propionic[11] acid was prepared by the above procedure but using tetrachloroethane alone as the solvent, the yield of material melting at 170–172° being 98%; the recrystallized acid melted at 171–172°.

Clemmensen Reduction.—A report has already been made[3] of the yields obtained by Martin's modified method of reduction in the preparation of γ-(4-methoxyphenyl)-butyric acid (ethyl ester, b. p. 177–178°, 15.5 mm.), γ-(3,4-dimethoxyphenyl)-butyric acid (ethyl ester, b. p. 186–189°, 8.5 mm.) and **γ-(4-methoxy-1-naphthyl)-butyric acid** (ethyl ester, b. p. 239–242°, 16 mm.). Crystallized from alcohol and from benzene–ligroin, γ-(4-methoxy-1-naphthyl)-butyric acid formed small colorless plates, m. p. 129–130°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.74; H, 6.59. Found: C, 73.92; H, 6.18.

γ-(3-Methoxy-4-methylphenyl)-butyric acid (ethyl ester, b. p. 171–173°, 11 mm.) was prepared from β-(*p*-toluyl)-propionic acid (230 g.) according to Martin,[3] the yields throughout being essentially as reported.

Conversion of the γ-Arylbutyric Esters into Cyclic Unsaturated Anhydrides.—The condensations of the esters with ethyl oxalate were carried out with the use of potassium ethylate, although in subsequent experiments in this Laboratory it was found that sodium ethylate is satisfactory with at least some of the methoxy compounds (H. L. Holmes). In the standard procedure 0.104 mole of potassium, cleaned by boiling with purified dioxane, was powdered under toluene in a nitrogen atmosphere and treated in ether suspension under reflux with 0.104 mole of absolute ethyl alcohol. At the end of the reaction 0.15 mole of ethyl oxalate was added and the resulting clear solution was treated with 0.1 mole of the γ-arylbutyric ester in absolute ether. In all 300–350 cc. of ether was used. The solution usually was refluxed for eight to ten hours to complete the reaction, and the potassium derivative of the product often separated during this time in a solid condition or as an oil. In this case the salt was separated by filtration or decantation, washed with dry ether, and decomposed with ice-cold 60% sulfuric acid in the presence of ether, the oxalyl derivative being recovered by extracting with ether and flashing off the solvent at the water pump. Any material remaining in the mother liquor was similarly recovered and worked separately. Some experimentation was necessary in each case to determine the strength of sulfuric acid most suitable for effecting the cyclization of the oxalyl derivative, and the specific data are noted below. Unlike the unsubstituted unsaturated anhydrides, the methoxylated compounds have a tendency to undergo partial dehydrogenation under the influence of the sulfuric acid and the aromatic anhydrides are often present in the crude reaction products.

7 - Methoxy - 3,4 - dihydronaphthalene - 1,2 - dicarboxylic Anhydride.—The potassium salt of the oxalyl derivative separated nearly completely as a solid, and 24.5 g. of the salt was added in small portions to 75 cc. of 60% sulfuric acid, stirred mechanically and cooled in an ice-salt bath. The resulting oily suspension was heated for fifteen minutes on the steam-bath, cooled, treated with 150 cc. of 80% sulfuric acid and heated fifteen minutes longer, when the oil had changed to a yellow solid. On pouring the mixture into water, collecting and washing the product, 13.6 g. (77% yield from the butyric ester) of good anhydride was obtained. The material from the ether mother liquor yielded 0.8 g. of less pure anhydride. After repeated crystallization from benzene–ligroin (readily soluble in benzene) the compound was obtained as bright yellow, heavy prismatic needles, m. p. 164.5–165°.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.79; H, 4.39. Found: C, 67.93; H, 3.97.

In one experiment cyclization of the oxalyl derivative with concentrated sulfuric acid at 20° was tried. The material was largely sulfonated and the water-insoluble product was found to contain a considerable amount of the aromatic anhydride (see Table I), which was obtained pure after five crystallizations from benzene.

6,7 - Dimethoxy - 3,4 - dihydronaphthalene - 1,2-dicarboxylic Anhydride.—The potassium salt separated as an oil and this was washed and converted into the free oxalyl derivative which, for cyclization, was heated for twenty minutes on the steam-bath with 70% sulfuric acid. The product separated as a bright red, crystalline solid and was washed with 60% acid and with water; yield crude (m. p. 180–186°) 56%. The anhydride is moderately soluble in benzene and gives a pure yellow solution; the recrystallized material forms bright red needles from this solvent, m. p. 192.5–193.

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.59; H, 4.65. Found: C, 64.79; H, 4.67.

When the ester condensation was interrupted after three and one-half hours, the anhydride obtained from the cyclization of the potassium salt which separated corresponded

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[11] Ruzicka and Waldmann, *Helv. Chim. Acta*, **15**, 907 (1932).

to a 43% yield. Treatment of the material from the ether mother liquor with 70% sulfuric acid gave 6,7-dimethoxy-1-tetralone,[8] m. p. 99.5–100° (purified) in 34% yield. This undoubtedly came from unreacted anisylbutyric ester.

6 - Methoxy - 7 - methyl - 3,4 - dihydronaphthalene - 1,2-dicarboxylic Acid.—In the ester condensation the red-orange ethereal solution deposited no salt and the crude oxalyl compound was obtained by adding cold dilute sulfuric acid and extracting with ether. For cyclization the oil was heated with 78% sulfuric acid at 70–80° for thirty minutes, giving very nearly pure anhydride in 82% yield. After two crystallizations from benzene (moderately soluble) the substance melted constantly at 189.8–190.3° and formed thin, yellow diamond-shaped plates. The cyclization was also accomplished by heating nearly to boiling for a few minutes with a solution of zinc chloride in glacial phosphoric acid.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.82; H, 4.96. Found: C, 69.07; H, 5.17.

6 - Methoxy - 3,4 - dihydronaphthalene - 1,2 - dicarboxylic Anhydride.—The oxalyl derivative prepared from ethyl γ-(*m*-methoxyphenyl)-butyrate[8] on cyclization with 75% sulfuric acid at 80° for fifteen minutes gave a mixture of the unsaturated and aromatic anhydrides. A fairly sharp separation was accomplished with ether, in which the dihydro compound alone dissolves easily. The aromatic anhydride, described in Table I, was identified by comparison with a sample obtained by sulfur dehydrogenation of the dihydro derivative. The latter, purified by repeated crystallization from benzene–ligroin, formed yellow needles, m. p. 164–165°.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.79; H, 4.39. Found: C, 67.83; H, 4.49.

9 - Methoxy - 3,4 - dihydrophenanthrene - 1,2 - dicarboxylic Anhydride.—The potassium derivative of the oxalyl ester largely separated as a solid after two hours of refluxing, and after standing for six hours longer the salt was collected, washed and decomposed with cold acid. The crude product, a pale yellow oil, was stirred with 84% sulfuric acid on the steam-bath for fifteen minutes, when conversion to an orange solid was complete. Washed with 84% acid and with water, this melted in the range 185–205° and proved to be a mixture of the unsaturated and the aromatic anhydrides. The latter is the less soluble of the two and was obtained pure after repeated crystallization from benzene (Table I); the former was isolated by fractional crystallization from glacial acetic acid (readily soluble). It forms reddish orange needles, m. p. 194–197°, which separate in a brilliant condition but become opaque on drying.

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.83; H, 4.32. Found: C, 73.07; H, 4.42.

Aromatic Anhydrides.—The substances isolated as by-products in the cyclization experiments are listed in Table I. They can be obtained also by heating the unsaturated anhydrides with the calculated amount of sulfur in a bath at 240–250° for fifteen to twenty minutes, followed by distillation at diminished pressure and crystallization. Benzene was found to be a good solvent in each case.

Diels–Alder Reaction.—The addition products listed in Table II were prepared as follows (or with double the quantities). About 25 g. of fresh butadiene was distilled into a mixture of 10 g. of the appropriate unsaturated anhydride and 15 cc. of dioxane contained in a Pyrex tube and cooled in a bath of solid carbon dioxide with the eutectic mixture of chloroform and carbon tetrachloride (equal parts), and the tube was sealed and heated at 160–180° for thirteen to fifteen hours. After opening the tube in the same cooling mixture the excess butadiene was evaporated by gentle warming and the product was obtained as a clean solid free from polymer by distillation in high vacuum in 75–85% yield. This material invariably contained a small amount of a colored impurity having the properties of the aromatic anhydride corresponding to the starting material and evidently arising by a dehydrogenation or disproportionation in the course of the reaction. This is considerably less soluble in benzene–ligroin than the addition product and can be eliminated by crystallization, but a more convenient method is based upon the greater resistance of the addition product to hydrolysis. The crude material is crystallized once from a concentrated benzene–ligroin solution and shaken with warm dilute aqueous-alcoholic alkali until the yellow or orange material has been hydrolyzed and dissolved and the largely unattacked addition product is left in a completely colorless condition. Crystallization from benzene–ligroin then gives pure material.

The 6-methyl-7-methoxy derivative was converted into the dipotassium salt of the corresponding acid by re-

TABLE I

-1,2-DICARBOXYLIC ANHYDRIDES

Compound	Cryst. form	M. p., °C.	Analyses % C Calcd.	Analyses % C Found	Analyses % H Calcd.	Analyses % H Found
7-Methoxynaphthalene-	Yellow needles	194–195	68.39	68.57	3.54	3.55
6-Methoxy-7-methyl-	Yellow prisms	215–215.5	69.39	69.63	4.17	4.31
6-Methoxynaphthalene-	Yellow micro needles	210–210.5	68.39	68.67	3.54	3.77
9-Methoxyphenanthrene-	Orange-yellow needles	251–252	73.35	73.07	3.63	3.60

TABLE II

-1,4,9,10,11,12-HEXAHYDROPHENANTHRENE-11,12-DICARBOXYLIC ANHYDRIDES

Substituent	Cryst. form (all colorless)	M. p., °C.	Analyses % C Calcd.	Analyses % C Found	Analyses % H Calcd.	Analyses % H Found
6-Methoxy-	Diamond-shaped prisms	126.5–127	71.81	72.21	5.67	5.88
6,7-Dimethoxy-	Prisms	138.6–138.8	68.79	68.44	5.77	5.61
6-Methyl-7-methoxy-	Prisms	152–152.5	72.43	72.38	6.11	6.11

TABLE III

-1,2,3,4,9,10,11,12-OCTAHYDROPHENANTHRENE-11,12-DICARBOXYLIC ANHYDRIDES

Substituent	Cryst. form (all colorless)	M. p., °C.	Analyses: % C Calcd.	% C Found	% H Calcd.	% H Found
6-Methoxy-	Needles or prisms	159–159.5	71.28	71.48	6.33	6.65
6,7-Dimethoxy-	Prismatic clusters	146.5–147	68.31	68.30	6.38	6.53
6-Methyl-7-methoxy-	Needles	149.5–150	71.95	71.78	6.73	6.81

fluxing with 4 *N* potassium hydroxide until dissolved and adding stronger alkali, and the dry salt (iridescent leaflets) was heated slowly in a bath from 350 to 420°, applying suction. The small amount of yellow oil which distilled was heated with selenium at 300° and the extracted product, **2-methoxy-3-methylphenanthrene**, after sublimation and crystallization from methyl alcohol, melted at 132–132.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.49; H, 6.31. Found: C, 86.55; H, 6.54.

The picrate formed orange needles, m. p. 142.5–143°, from benzene–ligroin.

Anal. Calcd. for $C_{22}H_{17}O_8N_3$: N, 9.31. Found: N, 9.25.

2,3 - Dimethyl - 6 - methoxy - 1,4,11,12,13,14 - hexahydrochrysene-13,14-dicarboxylic anhydride, obtained by heating the corresponding unsaturated anhydride with 2,3-dimethylbutadiene at 100° for two days, formed colorless prisms, m. p. 181–182°, from benzene–ligroin.

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.48; H, 6.13. Found: C, 76.48; H, 6.13.

Octahydrophenanthrene Anhydrides.—The three addition products listed in Table II were converted into the saturated compounds of Table III by hydrogenation in glacial acetic acid solution in the presence of Adams catalyst at atmospheric pressure. The absorption of gas was complete in five to ten minutes (3-g. samples) and the products were obtained in nearly quantitative yield. Benzene–ligroin was used for recrystallization.

Dimethyl 6,7-dimethoxy-1,2,3,4,9,10,11,12-octahydrophenanthrene-11,12-dicarboxylate, obtained by converting the anhydride into the free acid and esterifying with diazomethane, formed colorless microcrystals, m. p. 134.5–135.5°.

Anal. Calcd. for $C_{20}H_{26}O_6$: C, 66.26; H, 7.24. Found: C, 66.32; H, 7.56.

Demethylation.—The ethers of Table III were demethylated by refluxing 1 g. of the material with 10 cc. each of glacial acetic acid and 48% hydrobromic acid for three to five hours. On dilution with water the product separated as an oil which became crystalline after standing for several hours; average yield 80%.

6 - Hydroxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride crystallized from benzene as colorless prismatic needles, m. p. 160–160.5°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.56; H, 5.92. Found: C, 70.69; H, 5.66.

6,7 - Dihydroxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride formed small round crystal clusters, m. p. 147.5–148.5°, from benzene. It is very soluble in alcohol, moderately soluble in hot benzene, slightly soluble in hot water.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.64; H, 5.59. Found: C, 66.69; H, 5.58.

The diacetyl derivative, prepared with the use of acetic anhydride and sodium acetate, formed colorless iridescent plates from alcohol, m. p. 151.5–152°.

Anal. Calcd. for $C_{20}H_{20}O_7$: C, 64.48; H, 5.43. Found: C, 64.63; H, 5.55.

The dibenzoyl derivative was prepared by boiling the substance in pyridine solution with benzoyl chloride for five minutes, adding water, and treating the precipitated oil with alkali, when it at once solidified. Crystallized from alcohol, it formed clusters of short needles, m. p. 175–175.5°.

Anal. Calcd. for $C_{30}H_{24}O_7$: C, 72.55; H, 4.88. Found: C, 72.65; H, 4.93.

6 - Methyl - 7 - methoxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene-11,12-dicarboxylic anhydride formed colorless microcrystals from benzene–ligroin, m. p. 134.5–135.5°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.30; H, 6.33. Found: C, 71.30; H, 6.33.

Summary

Hydroxyl or methoxyl derivatives of phenanthrene-1,2-dicarboxylic anhydride and of octahydrophenanthrene-11,12-dicarboxylic anhydride which are of interest in the study of oestrogenic activity are described in this paper.

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