Anal. Calcd. for $C_3HF_7O_3S$: C, 14.4; H, 0.4; F, 53.2; S, 12.8; mol. wt., 250. Found: C, 15.0; H, 0.6; F, 52.8, 52.9; S, 13.6, 13.8; mol. wt., 258.9, 248.0.

The infrared spectrum showed strong bands at 3.34 μ (CH stretching) and 6.75 μ (asymmetrical SO stretching). The NMR spectrum was consistent with the proposed structure.

2-Hydroperfluoropropyl fluosulfonate from fluosulfonic acid. Method B. Hexafluoropropylene (50 g.) and fluosulfonic acid (25 g.) were charged into a platinum-lined pressure vessel (330-ml. capacity). The mixture was agitated for 3 hr. at 150° under autogenous pressure. The dark amber product was poured onto ice, washed twice with water, and distilled; yield 11.3 g. (19%), b.p. 75–76°. The product was identical with that obtained by Method A.

2,4-Dihydroperfluorobutyl fluosulfonate. 4-Hydroperfluoro-1-butene (20 g.) and fluosulfonic acid (11 g.) were heated for 8 hr. at 150° in a stainless steel pressure vessel (100 ml. capacity). The product was discharged and washed with ice water. Distillation of the water-insoluble material gave 2.06 g. of 2,4-dihydroperfluorobutyl fluosulfonate, b.p. 119.0–119.2°. The infrared spectrum was consistent with the proposed structure.

2-Hydroperfluoroheptyl fluosulfonate. Perfluoro-1-heptene (70 g.) and fluosulfonic acid (15 g.) were heated in a platinum-lined pressure vessel at 150° for 3 hr. The product was discharged and shaken with water. It was then filtered through anhydrous magnesium sulfate and dried over calcium sulfate. Distillation gave 35 g. of unchanged olefin and 2.2 g. of product, b.p. 53.5–54.5° (18 mm.). The yield based on unrecovered olefin was 5%. Infrared and NMR spectra were consistent with the proposed structure.

2,8-Dihydroperfluorooctyl fluosulfonate. 8-Hydroperfluoro-1-octene (4.3 g.) was allowed to react with 1.5 g. of fluosulfonic acid in a 6 × 3/8 in. platinum tube for 3 hr. at 200°. Distillation of the product gave 2.8 g. of unchanged olefin and 1.5 g. of fluosulfonate; b.p. 80–81° (8 mm.). Infrared and NMR spectra were consistent with the proposed structure.

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Evidence for 9-Methylene-10-acetoxy-10-methyl-9,10-dihydrophenanthrene as an Intermediate[1]

WILLIAM E. ADCOCK

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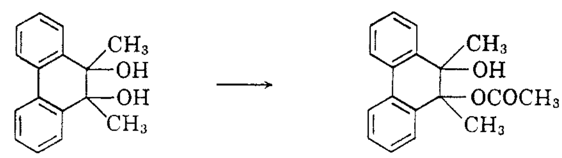
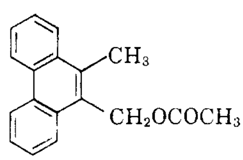
A recent report by Gardner and Sarrafizadeh R.[2] on the reaction of 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (I) with thionyl chloride and the mechanism offered by Hauptmann[3] for the formation of the product, 9-chloromethyl-10-methylphenanthrene, make it seem timely to report results obtained in this Laboratory in experiments carried out along similar lines. In the present work the diol was found to react with acetic anhydride in pyridine to give the monoacetate II in 34% yield. The structure of the monoacetate was confirmed by saponification, which regenerated the diol. At

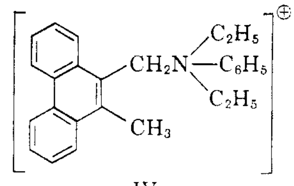


I II

higher temperatures (150°) in diethylaniline the diol reacted with acetic anhydride to give the monoacetate in only 8% yield; the chief product (29%) was 9-acetoxymethyl-10-methylphenanthrene (III). It was accompanied by a quaternary salt, isolated in a yield of 4% as the bisulfate IV.



III

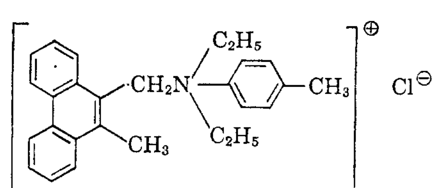


IV

$HSO_4^{\ominus}$

The structure of the acetoxymethyl compound was established by hydrolysis to the corresponding alcohol, which is known.[2] Treatment of the salt IV with silver perchlorate converted it into the perchlorate.

Confirmation of the above results was obtained when the diol I was allowed to react with acetic anhydride in diethyl-*p*-toluidine. The reaction mixture was heated under reflux (150–155°); again the major product was the acetoxymethyl compound III (42.5%). A quaternary salt was isolated in a yield of 5.0% as the chloride V.



V

The ultraviolet spectra (absolute alcohol) of the dihydrophenanthrene derivatives I and II exhibited maxima at 271 mμ (ε 1.73 × 10^4) and 272 mμ (ε 1.82 × 10^4), respectively. The absorption spectrum of 9,10-dihydrophenanthrene has a maximum at approximately 265 mμ (ε 1 × 10^4) and agrees in shape and intensity with that of biphenyl.[4] This similarity was also observed in the spectra of I and II. The maximum absorption of the phenanthrene derivatives III and IV was at 255 mμ (ε 2.63 × 10^4) and 256 mμ (ε 5.66 × 10^4), respectively. The general shape and intensity of absorption of the phenan-

(1) This work was supported in part by a grant from the office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

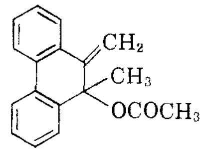
(2) P. D. Gardner and H. Sarrafizadeh R., *J. Am. Chem. Soc.*, **82**, 4287 (1960).

(3) S. Hauptmann, *Chem. Ber.*, **93**, 2604 (1960).

(4) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 1658 (1941).

threne derivatives agree with the data presented by Hauptmann.[3]

The production of compounds III, IV, and V might involve the intermediate formation of 9-methylene - 10 - acetoxy - 10 - methyl - 9,10 - dihydrophenanthrene (VI), which could be produced



VI

by dehydration of the monoacetate. Nucleophilic attack by acetate ion or an amine on the methylene carbon atom of VI with loss of acetate ion would give rise to the phenanthrene products. Attempts to dehydrate the monoacetate under mild conditions were not successful. Unchanged monoacetate was isolated when the compound was treated with acetyl chloride, although Shriner and Geipel[5] were able to dehydrate a similar tertiary alcohol at these conditions. The monoacetate was also recovered unchanged when treated with acetyl chloride in diethylaniline at steam-bath temperatures. It is probable that the higher reaction temperature afforded by the use of diethylaniline or diethyl-*p*-toluidine causes the dehydration of the monoacetate II, which gives rise to the intermediate VI.

If the monoacetate rather than the diol is allowed to react with acetic anhydride in diethylaniline, the salt IV is obtained in higher yield (36%). The loss of the acetate residue from the monoacetate in forming the salt lends support to the proposed methylene intermediate, which loses the acetate group upon rearrangement to the phenanthrene system. The mechanism suggested does not involve the formation of a carbonium ion.[3]

EXPERIMENTAL[6]

9-Acetoxy-10-hydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (II). To a solution of 5.00 g. (20.8 mmoles) of 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene,[2] m.p. 163–164°, in 20 ml. of dry pyridine was added 15 ml. (160 mmoles) of acetic anhydride, and the solution was heated under reflux (approximately 120°) for 12 hr. The reaction mixture was poured with stirring into a solution of 100 ml. of cold water and 25 ml. of acetic acid. The black oily residue that formed was extracted with six 50-ml. portions of ether. The combined ether extracts were shaken with a saturated sodium carbonate solution and then with three 25-ml. portions of water. After the ether solution had been dried over anhydrous magnesium sulfate, the solvent was distilled; the residual oil was dissolved in 10 ml. of absolute alcohol. Crystallization afforded 2.08 g. (35.4% yield) of colorless crystals melting at 122–123°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.58; H, 6.42. Found: C, 76.48; H, 6.37.

The diol (1.00 g., or 20.0%) was recovered from the reaction mixture.

Saponification of the monoacetate II by heating with aqueous potassium hydroxide in diethylene glycol dimethyl ether gave the diol I, m.p. 161–164°, in 70% yield. A mixture melting point with an authentic sample confirmed the structure.

Reaction of the diol I *with acetic anhydride in diethylaniline.* To a mixture of 9,10-dihydroxy-9,10-dimethyl-9-10-dihydrophenanthrene (4.85 g., 20.15 mmoles) and 20 ml. of diethylaniline was added 15 ml. (160 mmoles) of acetic anhydride, and the mixture was heated under reflux (approximately 150°) for 12.5 hr. The dark colored solution was shaken with 150 ml. of diethyl ether and washed with 30 ml. of water. The ether layer was shaken with 10-ml. portions of cold 10% sulfuric acid; a total of 100 ml. was necessary to remove the last traces of amine. Each fraction was made basic with a concentrated sodium hydroxide solution. At the point where 95% or more of the amine had been removed (fourth extraction), a colorless solid precipitated in the ether solution. Filtration gave the salt IV in 4.0% yield, m.p. 240–245°. An analytical sample (m.p. 231–233°) was prepared by recrystallizing the salt three times from methanol. A sodium fusion analysis gave a qualitative test for sulfur. The carbon-hydrogen analyses varied from the theoretical values by ±0.5.

Anal. Calcd. for $C_{26}H_{29}NO_4S$: C, 69.16; H, 6.46; N, 3.10. Found: C, 68.61; H, 6.60; N. 3.04.

A perchlorate salt (m.p. 272–274°) was prepared by treatment of the bisulfate with silver perchlorate in nitromethane.

Anal. Calcd. for $C_{26}H_{28}ClNO_4$: Cl, 7.81. Found: Cl, 7.66.

The ether was shaken with three 10-ml. portions of a saturated sodium bicarbonate solution and then with two 10-ml. portions of water. After the ether solution had been dried over anhydrous magnesium sulfate, the solvent was distilled; the residual gummy solid, recrystallized three times from absolute ethanol, gave 1.53 g. (28.7% yield) of 9-acetoxymethyl-10-methylphenanthrene, m.p. 129–131° (lit.[3] 132.5°).

Hydrolysis of 9-acetoxymethyl-10-methylphenanthrene by heating under reflux with methanolic potassium hydroxide gave 10-methyl-9-phenanthrylcarbinol in 80% yield, m.p. 169.5–171° (lit.[2] 170–171°).

Evaporation of solvent from the filtrate of the first alcohol recrystallization of the acetoxymethyl compound gave a solid which had a melting point range of 95–115°. The material, when subjected to chromatography on a column of neutralized alumina, gave 0.383g. (6.7% yield) of 9-acetoxy-10-hydroxy-9,10-dimethyl-9,10-dihydrophenanthrene melting at 120–121° and 0.235 g. (4.8% yield) of unchanged 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene. Also 0.727 g. of a mixture, melting at 90–118°, was eluted from the column.

Reaction of the diol I *with acetic anhydride in diethyl-p-toluidine.* To a mixture of 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (2.86 g., 11.90 mmoles) and 11.7 ml. of diethyl-*p*-toluidine was added 4.47 ml. (47.60 mmoles) of acetic anhydride, and the mixture was heated under reflux for 15 hr. Isolation of the products as described in the preceding experiment gave 0.242 g. (5.0% yield) of the salt V, m.p. 221–223°.

Anal. Calcd. for $C_{27}H_{30}ClN$: C, 80.27; H, 7.49; N, 3.47. Found: C, 80.60; H, 7.72; N, 3.46.

The acetoxymethyl compound III was isolated in a yield of 42.5%.

Reaction of the monoacetate II *with succinic anhydride in diethylaniline.* To a mixture of 9-acetoxy-10-hydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (1.00 g., 3.54 mmoles) and 4.13 ml. of diethylaniline was added 1.416 g. (14.16 mmoles) of succinic anhydride, and the mixture was heated under reflux (approximately 180°) for 13 hr. The quaternary bisulfate IV (0.4407 g., 36% yield), m.p. 231–233°, was iso-

(5) R. L. Shriner and L. Geipel, *J. Am. Chem. Soc.*, **79**, 227 (1957).

(6) Melting points are corrected values. The microanalyses were performed by Mr. Josef Nemeth, Miss Mary Ann Weatherford, and Mr. Gary D. Callahan.

lated as described previously. A mixture of the salt and that obtained in a preceding experiment melted at 229–231°.

The ether solution yielded an oil (0.371 g.) which could not be induced to crystallize.

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The Alkaloids of *Liriodendron tulipifera* L. The Structure and Synthesis of the Unnamed Yellow Alkaloid and the Isolation of *d*-Glaucine

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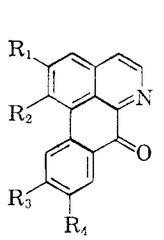
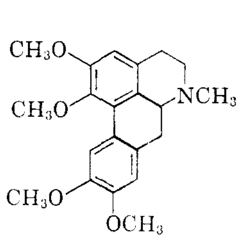
Buchanan and Dickey[1] have traced the color of the heartwood of the yellow poplar (*Liriodendron tulipifera* L.) to two yellow alkaloids, liriodenine and an unnamed base. Although liriodenine was degraded to benzo[*g*]quinoline-5,10-dione, the authors were unable to propose a satisfactory structure for the alkaloid. We have shown[2] that liriodenine must be I from the data which had been presented and biogenetic considerations. This conclusion was substantiated by synthesis.

In the same paper we suggested that the second unnamed base should be a tetramethoxy analogue of liriodenine and by synthesis it is now shown to be II. Nitropapaveraldine[3] prepared either by a total synthesis or in two steps from papaverine, was reduced to the amine and its diazonium derivative subjected to Pschorr cyclization conditions. The resulting 1,2,9,10-tetramethoxydibenz[*de,g*]-quinoline-7-one (II) had physical properties identical in all respects with those recorded by Buchanan and Dickey[1] for the unnamed yellow base.





III

I. $R_1R_2 = OCH_2O$; $R_3 = R_4 = H$
II. $R_1 = R_2 = R_3 = R_4 = OCH_3$

III.

It was our opinion that these yellow bases could have been derived oxidatively from co-occurring aporphines—*e.g.* roemerine or glaucine or their nor compounds. As a corollary we would expect compounds like I and II to be of wide occurrence as minor alkaloids in Magnoliaceous plants.

A sample of yellow poplar heartwood was worked up for alkaloid in a manner essentially the same as previously described.[1] Chromatography of the crude material resulted in the isolation of *d*-glaucine (III) as a major component of the mixture. The isolation of this aporphine can be considered to support but not to prove our hypothesis for the origin of the yellow bases.

EXPERIMENTAL

All melting points are uncorrected. The alumina used for chromatography was Woelm neutral activity III.

Nitropapaveraldine. 1,2'-Nitro-4',5'-dimethoxybenzyl-6,7-dimethoxy-3,4-dihydroisoquinoline[4] (0.5 g.) in acetic acid was heated with chromic oxide (0.5 g.) until an exothermic reaction began. After the solution had cooled, it was diluted with water and extracted with methylene chloride. The solution was concentrated to dryness and the residue in methylene chloride was filtered through a plug of alumina to furnish 1,2'-nitro-4,5-dimethoxybenzoyl-6,7-dimethoxy-3,4-dihydroisoquinoline (250 mg.), m.p. 168–172° from methylene chloride–methanol.

Anal. Calcd. for $C_{20}H_{20}O_7N_2$: C, 60.0; H, 5.0. Found: C, 60.3; H, 5.0.

The above benzoyl derivative (100 mg.) was boiled in methanol containing several drops of 2*N* potassium hydroxide for 15 min. After the solution had cooled the resulting nitropapaveraldine (40 mg.) m.p. 207° dec. was filtered off.

Anal. Calcd. for $C_{20}H_{18}O_7N_2$: C, 60.3; H, 4.6. Found: C, 60.2; H, 4.5.

1,2,9,10-Tetramethoxydibenz[de,g]quinoline-7-one. Nitropapaveraldine (567 mg.) suspended in ethanol was shaken overnight in an atmosphere of hydrogen in the presence of Raney nickel. The catalyst was filtered off and the ethanol removed *in vacuo* after the addition of a few drops of hydrochloric acid. The resultant hydrochloride (524 mg.) in dilute sulfuric acid (5 ml.) and methanol (5 ml.) was diazotized then heated on a steam bath for 0.5 hr. After dilution with water, treatment with base and extraction with chloroform, the crude product (355 mg.) was chromatographed using chloroform as an eluant. From the slower running eluate (187 mg.) the desired product (II) was obtained (86 mg.), m.p. 227–229° after crystallization from chloroform and then methanol; $\lambda_{max}^{C_2H_5OH}$ 242 mμ (ϵ 33,000, 272 (34,000), 355 (9,770) and a plateau at 376–382 (8,010). The infrared spectrum (potassium bromide disc) checked with the published curve[1] of the unnamed yellow base in all thirty-four peaks and shoulders of the fingerprint region.

Isolation of d-glaucine. Yellow poplar heartwood (8.26 kg.) was extracted three times with benzene:alcohol (10:1). The combined extracts were concentrated *in vacuo* to about 2 l. A precipitate was filtered off, then the solution was extracted, after the addition of benzene (1 l.), twice with 0.5% tartaric acid (each 600 ml.). The acid extracts were washed with benzene, made basic, and the precipitate extracted into methylene chloride. This was dried, and its concentrate passed over alumina (40 cm. × 4.5 cm. diam. column) to yield a pale tan eluate (26.07 g.) and a yellow eluate (9 g.). Rechromatography of the first fraction furnished a colorless oil (22.9 g.) a portion (5 g.) of which gave *d*-glaucine hydrochloride (2.8 g.) upon treatment with dilute acid. It had m.p. 245–246° dec. from either water or methanol.

Anal. Calcd. for $C_{21}H_{25}O_4N \cdot HCl \cdot H_2O$: C, 61.7; H, 7.0. $C_{21}H_{25}O_4N \cdot HCl . 0.25H_2O$: C, 63.7; H, 6.8; OCH_3, 31.4.

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(1) M. A. Buchanan and E. E. Dickey, *J. Org. Chem.*, **25**, 1389 (1960).

(2) W. I. Taylor, *Tetrahedron, in press.*

(3) R. Pschorr, *Ber.*, **37**, 1936 (1904).

(4) R. K. Callow, J. M. Gulland, and R. D. Haworth, *J. Chem. Soc.*, 658 (1929).