The Peracid Oxidation of Dibenz[*a*,*h*]anthracene

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The peracetic and perbenzoic acid oxidation of dibenz[*a*,*h*]anthracene was examined. With perbenzoic acid a new anthrone, 7-keto-14-dihydrodibenz[*a*,*h*]anthracene, was obtained. This compound probably is formed by rearrangement of 7,14-epoxydibenz[*a*,*h*]anthracene. Evidence is presented for the formation of a 5,6 epoxide. The peracetic acid oxidation of the hydrocarbon gave a high yield of 2-phenylphenanthrene-3,2′-dicarboxylic acid as well as the 7,14-quinone and 5,6-quinone.

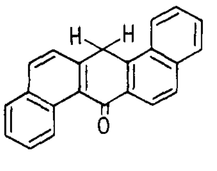
The oxidation of aromatic hydrocarbons has been studied extensively with a large variety of oxidizing agents; however, the peracid oxidation of these compounds has received scant attention. Perbenzoic acid has been used for the preparation of aromatic dicarboxylic acids,[1] and peracetic acid has been used in the oxidation of the hydrocarbons to their quinones.[2,3] The rate of oxidation of various aromatic hydrocarbons with perbenzoic acid has been examined,[4] but the products of these reactions were not investigated.

Our studies on the peracid oxidation were based on the possibility that epoxides may be formed as intermediates in these reactions. Some epoxides of aromatic hydrocarbons are known, *e.g.*, 7,12-dimethyl-7,12-epoxybenz[*a*]anthracene and 7,14-dimethyl-7,14-epoxydibenz[*a*,*h*]anthracene,[5] but these compounds were prepared by other methods.

The hydrocarbon chosen for this work was dibenz[*a*,*h*]anthracene. The products obtained from it by oxidation with osmium tetroxide,[6] chromic acid,[7] and ozone[8] have been characterized. Oxidation with these reagents occurs at the 7,14- and 5,6-positions.[6,7,8]

Results and Discussion

The perbenzoic acid oxidation of dibenz[*a*,*h*]anthracene gave a 7.3% yield of a compound with correct analysis for a new monooxygenated derivative of the hydrocarbon. This compound showed in its infrared absorption spectrum, a peak of 1650 cm.$^{-1}$ ascribed to conjugated carbonyl absorption, and the expected aromatic absorption at 1600 cm.$^{-1}$. Reductive acetylation of this compound with zinc dust and acetic acid–acetic anhydride gave a monoacetyoxy derivative of dibenz[*a*,*h*]anthracene. This compound was identical by melting point, mixture melting point, infrared absorption, and R_f with an authentic sample of 7-acetoxydibenz[*a*,*h*]anthracene synthesized by the previously described procedure.[9] Chromic acid oxidation of the unknown ketonic compound yielded dibenz[*a*,*h*]anthracene-7,14-dione. The latter compound also was identified by direct comparison with an authentic sample prepared by the chromic acid oxidation of the hydrocarbon.[7] The monocarbonyl compound, therefore, is the anthrone, 7-keto-14-dihydrodibenz[*a*,*h*]anthracene (I).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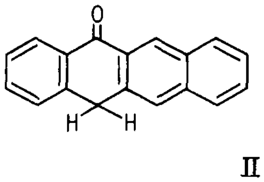
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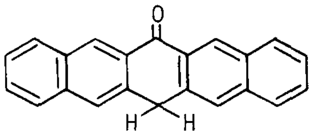
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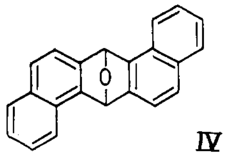
IV

Alkali hydrolysis of the acetate under a nitrogen atmosphere proceeded very slowly and gave a phenolic product in low yield. Lithium aluminum hydride cleavage of 7-acetoxydibenz[*a*,*h*]anthracene gave the corresponding phenol. However, this compound showed in its infrared spectrum, in addition to the hydroxyl peaks at 3450, 1090, 1020 (doublet) cm.$^{-1}$, a small carbonyl peak at 1650 cm.$^{-1}$. This peak is ascribed to isomerization of the phenol to the anthrone (I). This isomerization is well-known in other phenol–anthrone systems. Clar[10] has pointed out that in these phenols there is a variation in stability depending on the ring system. Thus, anthrone exists to the extent of 11% as the isomeric phenol, and the phenols of 6-keto-11-dihydronaphthacene (II) and 6-keto-13-dihydropentacene (III) are unstable and unknown, respectively.[10]

It is expected that ring strain would render transannular epoxides of unsubstituted polynuclear aromatic compounds unstable, and it seems reasonable to conclude that I is formed from the hydrocarbon by rearrangement of an intermediary transannular epoxide (IV). This epoxide could not be isolated in the present work, but it is known that transannular epoxides in less strained systems such as V and VI rearrange readily to phenolic (VII)[11] and carbonyl compounds (VIII),[12] respectively. Alternatively, it is possible that electrophilic substitution of perbenzoic acid occurs on the hydrocarbon. The resultant phenol may then isomerize to I.

The progress of the perbenzoic acid oxidation was followed for 8 days by fluorescence and absorption spectroscopy of fractions separated by paper and thin

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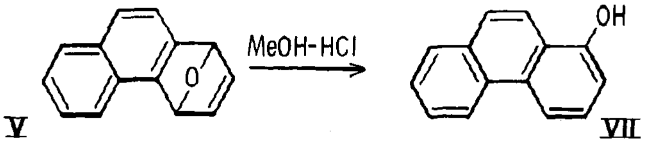
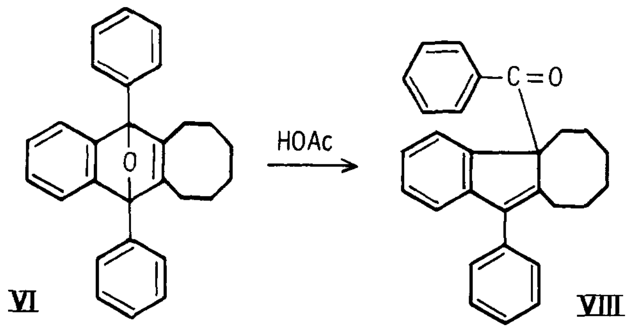


V VII



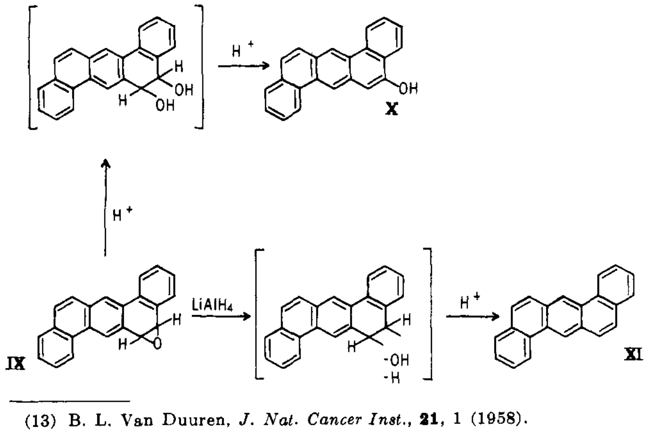
VI VIII

layer chromatography. Evidence was obtained in this manner for the presence of another epoxide intermediate. This material, obtained from the neutral fraction, was formed in minute amounts; it readily oxidized on exposure to air or light and could not be isolated.

This material showed in its fluorescence, excitation, and emission spectra close similarities to the corresponding spectra of 5,6-dihydro-5,6-dibenz[*a*,*h*]anthracenediacetate (Fig. 1). The absorption spectrum of the reaction intermediate, shown in curve 3 of Fig. 1, is also very similar to that of the diacetate, curve 1, Fig. 1. This compound has a closed-ring phenylphenanthrene chromophore which is distinctly different in its absorption spectrum from the open phenylphenanthrene chromophore, exemplified by the dimethyl ester of 2-phenylphenanthrene 3,2′-dicarboxylic acid, curve 2, Fig. 1.

Several chemical transformations were carried out on this material at the microgram level followed by spectroscopic examination of the products. The intermediates in this sequence were purified by paper chromatography[13,14] and were compared with the known compounds by R_f, ultraviolet absorption, fluorescence excitation, and emission maxima. The transformations carried out on this material, summarized in Chart I, led to the conclusion that the unknown material is the 5,6 epoxide (IX).

CHART I



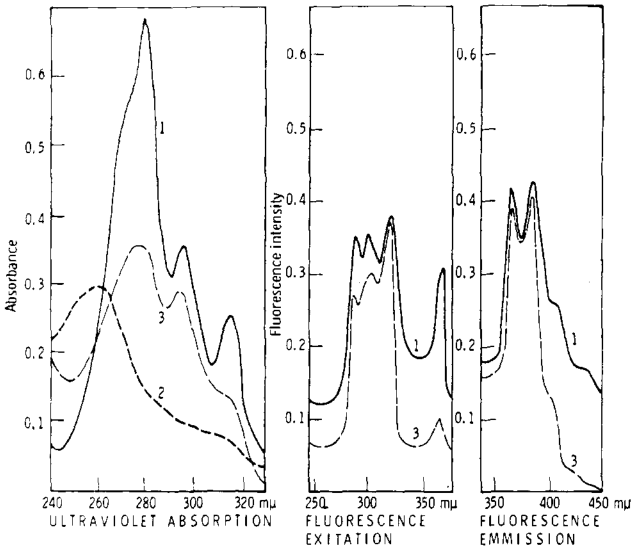


Fig. 1.—Absorption and fluorescence spectra of epoxide intermediate and model compounds: (1) 5,6-Dihydro-5,6-dibenz[*a*,*h*]anthracenediacetate, 1.10 × 10^{-5} moles/l. in cyclohexane; (2) 2-phenylphenanthrene-3,2′-dicarboxylic acid dimethyl ester, 0.43 × 10^{-5} moles/l. in dioxane; (3) neutral product from peracid oxidation, in cyclohexane.

Treatment of IX with acid yielded an alkali-soluble material which was acidified and extracted with benzene. This product showed in its fluorescence excitation and emission maxima a dibenzanthracene chromophore and on paper chromatography showed zero R_f. This indicated the phenol (X), which is probably formed *via* the dihydrodiol (shown in brackets in Chart I) since it is known that the dihydrodiol readily loses a molecule of water to form the phenol by treatment with acid or by heat. Treatment of IX with lithium aluminum hydride followed by treatment with acid gave dibenz[*a*,*h*]anthracene (XI) as major product. The hydrocarbon was identified by R_f[13] and fluorescence excitation and emission spectra.[15]

From these reactions it was possible to determine that the 5,6 epoxide is formed in an approximate yield of 0.04% after 72 hours of reaction. One-half of the weight of the original hydrocarbon was recovered after this reaction time, and this was taken into account in the estimation of yield.

When the perbenzoic acid oxidation of the hydrocarbon was allowed to proceed for 30 days a series of phenolic products was obtained. It was noticeable that 2-phenylphenanthren-3,2′-dicarboxylic acid, obtained in the peracetic acid oxidation described below, was not obtained in the perbenzoic acid oxidation.

The peracetic acid oxidation of dibenz[*a*,*h*]anthracene gave a 60–80% yield of 2-phenylphenanthrene-3,2′-dicarboxylic acid. This acid has been prepared before in low yield from dibenz[*a*,*h*]anthracene-5,6-dione[16,17] and *via* ozonization of the hydrocarbon.[8] By-products in the peracetic acid oxidation were the 7,14-quinone and 5,6-quinone identified by comparison with authentic samples.

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Experimental

Capillary melting points were measured in a Thomas–Hoover apparatus and are uncorrected; fluorescence spectra were measured with a Farrand recording spectrofluorimeter; infrared spectra were measured with a Perkin-Elmer Model 221 grating-prism (sodium chloride) spectrophotometer, and absorption spectra were measured in a Beckman D. U. spectrophotometer equipped with a recording unit. All thin layer chromatograms were run on sprayed silica gel plates[18] (layer thickness, 200 μ), with benzene–cyclohexane (3:1) as solvent. Paper chromatograms were run with hexane saturated with N,N-dimethylformamide as solvent on Whatman No. 1 filter paper.[13]

Perbenzoic Acid Oxidation. 7-Keto-14-dihydrodibenz[*a,h*]-anthracene (I).—The hydrocarbon, 10.0 g. (0.035 mole) in 1 l. of chloroform, was stirred at 4° with 11.31 g. of perbenzoic acid (0.082 mole) in 190 ml. of dry chloroform under nitrogen. After 24 hr. the reaction mixture was extracted with small portions of a cold saturated solution of sodium bicarbonate. The organic layer was dried over anhydrous sodium sulfate and distilled to one-half the original volume *in vacuo*. On standing, unchanged hydrocarbon crystallized, 5.8 g. The chloroform solution left after removal of the hydrocarbon was evaporated *in vacuo* to 30 ml. This solution was chromatographed on a Florisil (150 g.) column. An additional 0.5 g. of hydrocarbon was eluted with petroleum ether (b.p. 30–60°). The petroleum ether–ether (1:1) eluate was evaporated to a small volume in *vacuo*. On standing, pale yellow crystals settled. This product, 268 mg. (7.3% yield), was recrystallized three times from ether, m.p. 233–234.5°; ultraviolet absorption, $\lambda_{\max}^{\text{chloroform}}$ in mμ ($\epsilon_{\max}$): 298 (8400), 313 (8500), 342 (7700); infrared absorption in potassium bromide pellet: 3070 (aromatic CH), 1650 (carbonyl), 1600 cm.$^{-1}$ (aromatic C═C).

Anal. Calcd. for $C_{22}H_{14}O$: C, 89.87; H, 4.80. Found: C, 89.66; H, 4.57.

The mother liquors from the crystallization of the anthrone were evaporated to dryness; 1.9 g. of a brown crystalline residue was left. This material on thin layer chromatography showed the presence of at least eight components. Two of these were identified by melting point and mixture melting point as the 5,6- and 7,14-quinones; 0.5 g. (13.5% yield) of the 7,14-quinone, m.p. 252° (lit.[7] m.p. 244–249°), was obtained from the mixture. The 5,6-quinone, m.p. 318° (lit.[17] m.p. 327–329°), was obtained in less than 1% yield.

7-Acetoxydibenz[*a,h*]anthracene.—The anthrone (I), 75 mg., was refluxed with 12 ml. of acetic acid–acetic anhydride (1:1) for 2 hr. in the presence of 10 mg. of zinc dust. The solvent was removed, and the residue was washed once with 10 ml. of water. The water-insoluble residue was crystallized from ether, m.p. 227–228° (lit.[9] m.p. 235°).

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.79; H, 4.80. Found: C, 85.58; H, 4.73.

An authentic sample of 7-acetoxydibenz[*a,h*]anthracene was prepared by aluminum reduction of the 7,14-quinone in concentrated sulfuric acid followed by acetylation.[9,19] The two samples were proved identical by their infrared spectra, their melting points, and the mixture melting point. Ultraviolet absorption, in chloroform, $\lambda_{\max}^{\text{chloroform}}$ in mμ ($\epsilon_{\max}$): 287 (81,000), 297 (99,000), 325 (11,900), 338 (13,000), 353 (12,200); fluorescence excitation max. (emission at 400 mμ): 300, 325, 335, 351 mμ; fluorescence emission max. (excitation at 300 mμ): 399, 420, 445 (sh), 475 (sh) mμ.

Lithium aluminum hydride reduction of the acetate, in ether, gave a low yield of an unstable phenolic product, m.p. 234–240° dec., which showed both hydroxyl, 3450, 1090, and 1020 (doublet) cm.$^{-1}$, and carbonyl absorption, 1650 cm.$^{-1}$, in the infrared spectrum. The hydrolysis was complete since there was no evidence of ester carbonyl which occurs in the acetate at 1760 cm.$^{-1}$. Because of its instability, satisfactory analytical data could not be obtained on this product.

Oxidation of I to Dibenz[*a,h*]anthracene-7,14-dione.—I, 15 mg., was dissolved in benzene, 1 ml., and stirred at room temperature with 1 ml. of chromic acid in sulfuric acid for 4 days. The product was extracted with benzene, washed with water, and crystallized from benzene. Red needles, 12.3 mg. (83% yield), m.p. 250–252°, were obtained. This product gave no depression of melting point upon admixture with an authentic sample of the 7,14-quinone, m.p. 252°, prepared by chromic acid oxidation of dibenz[*a,h*]anthracene.[7]

5,6-Epoxydibenz[*a,h*]anthracene (IX).—Dibenz[*a,h*]anthracene, 100 mg. (3.5×10^{-4} mole) in 20 ml. of dry chloroform, was mixed with 87.4 mg. (6.4×10^{-4} mole) of perbenzoic acid in 2 ml. of chloroform at 4° and stirred for 72 hr. under dry nitrogen. The progress of the reaction was followed by thin layer chromatography of aliquots of the reaction mixture. At the end of 72 hr. an optimal yield of a fluorescent spot was obtained (together with several other products), which showed in its fluorescence excitation and emission spectra, and its ultraviolet absorption spectrum (Fig. 1) close agreement with the corresponding spectra of 5,6-dihydro-5,6-dibenz[*a,h*]anthracenediacetate.

Several attempts were made to obtain this product in crystalline form but its instability and the low yield in which it was formed precluded its isolation. The nature of this material was examined by the following transformations. (1) An aliquot of material was purified by thin layer chromatography followed by elution with benzene. The benzene was removed *in vacuo*, the residue was dissolved in ether and treated with 0.1 mg. of lithium aluminum hydride dissolved in ether. The complex was destroyed with 5 ml. of 10% aqueous hydrochloric acid, and this solution was refluxed for 1 hr. The product was extracted with benzene and chromatographed on paper. The R_f was identical with that of dibenz[*a,h*]anthracene which was applied as marker, R_f 0.91. The eluted spot dissolved in benzene showed fluorescence excitation and emission and ultraviolet absorption spectra identical with that of dibenz[*a,h*]anthracene.[15] (2) A second aliquot from the 72-hr. reaction mixture, also purified by thin layer chromatography, was dissolved in benzene and refluxed with 15% hydrochloric acid for 2 hr. The benzene extract of the reaction product was purified by paper chromatography and showed R_f 0. The spot was eluted with benzene. The fluorescence excitation and emission maxima were identical with that of 5-hydroxydibenz[*a,h*]anthracene.

5-Hydroxydibenz[*a,h*]anthracene (X). (1) **Acid Dehydration of 5,6-Dihydro-5,6-dibenz[*a,h*]anthracenediol.**—The diol (20 mg.), m.p. 203.5–204.5°, prepared by the osmium tetroxide oxidation of the hydrocarbon,[6] was refluxed with 4 ml. of a concentrated hydrochloric acid–glacial acetic acid mixture (1:1). The mixture was diluted with water, the insoluble product was filtered off and recrystallized from benzene. White needles, m.p. 218–225°, were obtained. This product was not pure as was shown by the appearance of several spots on a paper chromatogram.

(2) **Vacuum Sublimation of 5,6-dihydro-5,6-dibenz[*a,h*]-anthracenediol.**—Vacuum sublimation of the diol at 180° (0.1 mm.) yielded the pure phenol, m.p. 225°, R_f 0; fluorescence excitation max. (emission at 400 mμ): 298, 318, 335 and 352 mμ; fluorescence emission max. (excitation at 300 mμ): 398, 420 mμ.

Anal. Calcd. for $C_{22}H_{14}O$: C, 89.79; H, 4.76. Found: C, 89.92; H, 4.59.

Peracetic Acid Oxidation of Dibenz[*a,h*]anthracene.—A suspension of the hydrocarbon, 2.0 g. (0.0071 mole) in 75 ml. of chloroform, was cooled to 4° and 10.0 g. of 40% peracetic acid (0.05 mole, saturated with sodium acetate) was added. The mixture was stirred at 4°; after stirring for 8 hr. a clear solution was obtained, and then a cream-colored precipitate gradually settled. Stirring was continued for 8 days at 4°. The solution was taken to dryness under a stream of nitrogen at room temperature. The residue was suspended in 200 ml. of benzene, 200 ml. of cold 10% aqueous potassium hydroxide was added, and the mixture was stirred under nitrogen for 30 min. The aqueous and organic layers in the filtrate were separated. The neutral (organic layer) and acid (aqueous layer) fractions were worked up separately. Acidification of the aqueous layer gave a tan precipitate. This product was filtered off and dried to give 2.1 g. (87% yield) of a crystalline solid, m.p. above 300°. The acid was purified by repeated recrystallization from acetone to give tan crystals, m.p. 309–311° (lit.[8] m.p. 317–318°). The acid was converted to its dimethyl ester by treatment with diazomethane, and this product was chromatographed on activated alumina. The benzene–ether (1:1) eluate gave a crystalline solid which was purified by recrystallization from ether–petroleum ether, m.p. 148–149° (lit.[8] m.p. 146.5–147.5°). This ester, when chromatographed on paper, gave an R_f 0.20 (R_f of DBA marker 0.40);

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ultraviolet absorption, $\lambda_{max}^{dioxane}$ in mμ (ϵ_{max}): 260 (66,062), 310, sh (13,668), 340 (1594), 357 (1640); infrared absorption (potassium bromide pellet): 3050, 3020, 2987, 2950 (C—H), 1730 cm.$^{-1}$ (C=O); fluorescence in cyclohexane, excitation max. (emission at 390 mμ): 312, 340, 360 mμ; emission max. (excitation at 320 mμ): 365, 385 mμ. Column chromatography of the neutral fraction on Florisil gave the 7,14-quinone and 5,6-quinone, m.p. 252° and 318°, respectively, unchanged upon admixture with authentic materials.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.54; H, 4.67.

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Osage Orange Pigments. XIII. Isolation of Three New Pigments from the Root Bark[1,2]

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Three new pigments, characterized as substituted polyhydroxyxanthones, have been isolated from the root bark of the osage orange (*Maclura pomifera* Raf.). These are macluraxanthone (I, bright yellow), $C_{23}H_{22}O_6$; osajaxanthone (II, lemon yellow), $C_{18}H_{14}O_5$; and alvaxananthone (III, yellow), $C_{23}H_{24}O_6$. On standing in air, III decomposed readily but was stable indefinitely in the form of its triacetate or trimethyl ether. I showed insecticidal activity against the tropical termite; both I and III were effective fish poisons and were toxic to mosquito larvae.

Wolfrom and co-workers[4] have described the isolation and complete structure determination of two isoflavone pigments, osajin and pomiferin, obtained from the fruit of the osage orange (*Maclura pomifera* Raf.). Subsequently,[1] the syntheses of dihydroisoosajin and dihydroisopomiferin were reported. The vivid orange color of the root bark of this tree invited further investigation[5] and we report herein the isolation of three new yellow pigments from this source; osajin and pomiferin were not encountered. These three new pigments were found to be polyhydroxyxanthones; they have accordingly been designated macluraxanthone (I), $C_{23}H_{22}O_6$; osajaxanthone (II), $C_{18}H_{14}O_5$; and alvaxanthone (III),[6] $C_{23}H_{24}O_6$. The average yields of the pigments were found to be I, 0.45%; II, 0.02%; and III, 0.15%. However, yields were variable and in some samples of root bark no II or III were encountered; one sample of root bark gave only 0.36% I and 1.42% III. The isolation and separation of I and II were first effected by column chromatography on silicic acid but later work utilized more convenient solution methods and it was on applying such methods that III was found. The beautifully crystalline, yellow pigments were accompanied by large amounts of dark red resins. Although I and II are isolated in admixture and are separable by the chromatographic method, they were separated more conveniently through the 1:1 pyridine complex formed selectively by I. Macluraxanthone (I) and osajaxanthone (II) were stable in the air but alvaxanthone (III) was not; it could, however, be kept indefinitely in the form of its yellow triacetate or yellow trimethyl ether.

All three pigments were methoxyl free and optically inactive. Their acidity was entirely phenolic. All three contained the γ-pyrone ring as indicated by the Perkin test and all gave a deep green ferric chloride-alcohol color test. Macluraxanthone (I) and alvaxanthone (III) formed lead salts, diagnostic of a catechol grouping, while osajaxanthone (II) did not. Macluraxanthone and osajaxanthone showed positive Wilson[7] boric acid tests while alvaxanthone showed a negative reaction. This would indicate the presence in I and II (but not in III) of an auxochrome (presumably a hydroxyl) on the second carbon atom from a carbonyl group. Neither I nor III yielded formic acid on mild alkaline treatment and, therefore, were not isoflavones.

Alvaxanthone (III) formed a bright yellow triacetate under mild or stringent acetylation conditions. Alcoholic ferric chloride gave only a very faint green color with the triacetate; this color deepened on standing during a period of 30 min. Methylation under mild or severe conditions yielded a light yellow trimethyl ether. It was found advisable to convert alvaxanthone to the triacetate or trimethyl ether immediately on isolation to prevent loss due to the decomposition of the pigment.

The similarity of the ultraviolet spectra of macluraxanthone, osajaxanthone, alvaxanthone, and the dimethyl ether and diacetate of alvaxanthone (Table I) showed that all three pigments probably possess the same basic nucleus. A survey of the ultraviolet spectra of the various classes of naturally occurring plant pigments showed that the spectra of our pigments were similar only to xanthones.[8,9] Especially striking is the correspondence between macluraxanthone (I) and jacareubin,[10] and between alvaxanthone and di-

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[1] Preceding paper in this series: M. L. Wolfrom and B. S. Wildi, *J. Am. Chem. Soc.*, **73**, 235 (1951).

[2] Preliminary communication, M. L. Wolfrom, J. H. Looker, E. E. Dickey, P. McWain, and A. Thompson, Abstracts, 119th National Meeting of the American Chemical Society, Boston, Mass., April, 1951, p. 16M.

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