spectrum is the resemblance of the olefinic region (triplet due to one proton centered at δ 6.0 for V and 5.8 for VI) to that of neopine (VIII) (triplet, δ 5.5; actually, the X part of a deceptively simple ABX system[4]) and deoxycodeine D (IX)[5] (triplet, δ 5.65).

It is thus clear that anhydrometathebainol possesses the expected structure III and that the earlier observations on the nonidentity of dihydroanhydrometathebainol and dihydrodesoxymetacodeine were erroneous.

Experimental Section

Melting points were determined on a Kofler block. Ultraviolet spectra were determined in ethanol on a Cary 14 spectrophotometer, infrared spectra in chloroform solution on a Beckman IR7 spectrophotometer, and nmr spectra in deuteriochloroform on a Varian A60 or HA100 instrument. The optical rotatory dispersion was measured on a Cary 60 spectropolarimeter, the circular dichroism on the Jouan dichrograph of the University of Strasbourg.

Metathebainol (II). **A.** Metathebainone (2.99 g) dissolved in a minimum of ethanol was treated with 0.1 *N* HCl (100 ml) and Adams catalyst (50 mg). The mixture was hydrogenated at 46 psi for 18 hr, filtered, basified with ammonia and extracted with chloroform. Evaporation of the extracts afforded an oil which crystallized on contact with methanol. Crystallization from methanol afforded metathebainol (1.93 g, 64%), mp 76–80° (lit.[2] mp 87–88° for chloroform solvate, 92–93° for methanol solvate); no carbonyl stretching appeared in the infrared spectrum. In another experiment, hydrogenation was continued for 12 hr and gave crystalline metathebainol, contaminated with starting material, in 27% yield.

B. Metathebainone (3.0 g) in ethanol (35 ml) was treated with sodium borohydride (1.75 g) portionwise with stirring for 30 min. Stirring was continued for 6 hr, acetone was added to decompose excess borohydride, the solution was poured into water, acidified with acetic acid, and basified with ammonia. Extraction with chloroform afforded an oil (2.97 g) which did not crystallize, but was sufficiently pure for the next step. Its infrared spectrum was essentially identical with that of the product from the previous preparation.

Metathebainol diacetate (IV) was prepared from metathebainol by the method of Small and Meitzner:[2] mp 137–138° (lit.[2] mp 140°); λ_{max} 291, 242, 214 mμ (ϵ 2900, 11,000, 27,200).

Anhydrometathebainol (III).—The base was prepared by the method of Small and Meitzner.[2] Alternatively, II (1.0 g) and potassium hydroxide (0.25 g) in ethylene glycol (6.5 ml) were heated at 160° for 4 hr. The reaction mixture was worked up in the usual way, affording III as a crystalline solid (0.27 g) after crystallization from methanol, indefinite mp 70–100° (lit.[2] mp 106–107°). Thin layer chromatography on silica gel using cyclohexane–diethylamine (9:1) as eluent showed the presence of some impurities. Purification of the product by preparative thin layer chromatography in the same solvent system gave a sample mp 112–115° (softens at 70°) after crystallization from methanol.

Acetylanhydrometathebainol (VII) could not be prepared by the published method.[2] It was obtained by acetylation of crude III with pyridine–acetic anhydride at room temperature for 5 days. It had mp 174–176° after crystallization from methanol (lit.[2] mp 166°); uv bands were at λ_{max} 307 mμ (ϵ 13,800), 245 (infl) (46,000), 225 (infl) (11,300), 211 (20,000). Circular dichroism showed a broad, evidently complex, negative band, between ~240 and 340 mμ, with maximum, $\Delta\epsilon$ −11.3, at 281–288 mμ. Optical rotatory dispersion in methanol (*c* 0.04) showed $[\Phi]_{325}$ −18,100° (sh), $[\Phi]_{313}$ −19,700°, $[\Phi]_{297}$ ±0°, $[\Phi]_{\sim 270-260}$ +38,000°, $[\Phi]_{248}$ +45,900° $[\Phi]_{230}$ +3600°, $[\Phi]_{220}$ *ca.* +17,000°. The identity with an authentic sample prepared by Small and Meitzner was established by mixture melting point determination and comparison of infrared spectra.

Acetyldihydroanhydrometathebainol (VI).—A solution of VII (0.425 g) in ethanol (20 ml) was shaken in an atmosphere of hydrogen in the presence of Adams catalyst (50 mg). Hydrogen uptake (35 ml; theoretical uptake for 1 mol = 32 ml) was complete in less than 1 hr. The solution was filtered and the filtrate was evaporated to dryness. The residual solid (0.44 g) was crystallized three times from hexane and had mp 115.5–116°. The solution of the compound in concentrated hydrochloric acid does not show the blue halochromism of II, III, and IV even on heating. Uv absorptions were at λ_{max} 288 mμ (ϵ 4000), 243 (10,400), 215 (29,900).

Anal. Calcd for $C_{20}H_{25}NO_3$; C, 73.24; H, 7.66; N, 4.17%. Found: C, 73.37; H, 7.70; N, 4.28%.

Wolff-Kishner Reduction of Metathebainone.—The preparation was carried out by the method of Small and Meitzner,[2] affording a crystalline solid, mp 51–69° (lit.[2] mp 72°), which rapidly darkened on exposure to air. It could be purified by preparative thin layer chromatography on silica gel using cyclohexane–diethylamine (9:1) as eluent and had mp 40–70° after crystallization from methanol. On standing over calcium chloride the solvent-free base was obtained as a glass. Acetylation with acetic anhydride in pyridine at room temperature for 2 days afforded the acetyl derivative, mp 114–115°, after crystallization from hexane. It was identical in every respect (mixture melting point determination and infrared spectrum) with VII.

Registry No.—III, 15448-36-9; VI, 15448-37-0; VII, 15448-38-1; morphine, 57-27-2.

Acknowledgment.—We are indebted to Drs. E. L. May and L. J. Sargent of this institute for kindly supplying a sample of acetylanhydrometathebainol originally prepared by Small and Meitzner, to Dr. E. Lustig, of the Food and Drug Administration, Washington, D. C., for measurement of the 100-Mc spectrum, to Mrs. K. Warren, National Heart Institute, for measurement of infrared spectra, and to Professor Guy Ourisson, Strasbourg, for measurement of the circular dichroism.

(4) T. Rüll, *Bull. Soc. Chim. Fr.*, 586 (1963).

(5) U. Weiss, unpublished results.

Synthesis of Murrayanine[1]

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Received September 7, 1967

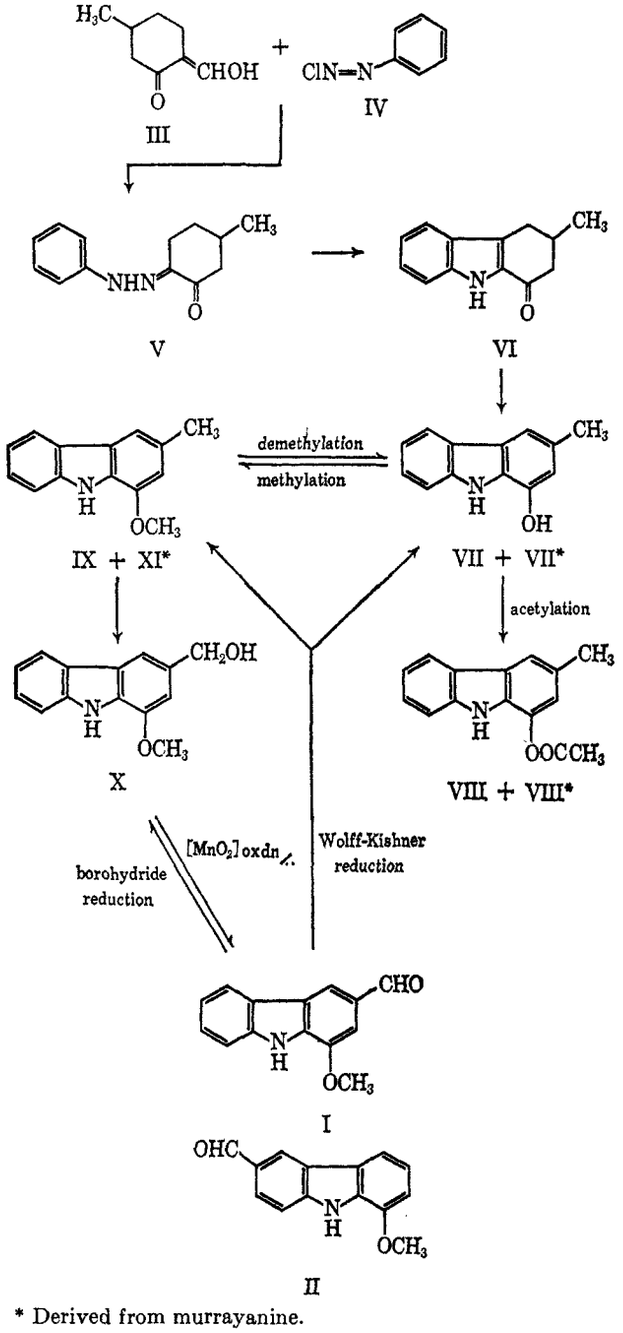
In a previous communication, the structure of murrayanine, $C_{14}H_{11}NO_2$, mp 168°, a simple carbazole derivative isolated from the stem bark of *Murraya koenigii* Spreng., was proposed as 1-methoxy-3-formylcarbazole (I) by Chakraborty, Barman, and Bose.[2a] From the spectral evidences (uv, ir, nmr) and the results of reactions, it was shown that murrayanine could be formulated either as 1-methoxy-3-formylcarbazole (I) or as 1-methoxy-6-formylcarbazole (II). The assignment of the formyl group at position 3 of the carbazole nucleus was made on the basis of nmr data of murrayanine. We, therefore, sought a confirmation of the previously proposed structure by synthesis. The present report relates to the synthesis of murrayanine and the preparation of compounds (VII and VIII) from natural murrayanine. The intermediate

(1) When this synthesis was complete we received a personal communication from Dr. D. J. Crum informing us that he has also synthesized murrayanine. Since then we came across his communication (*Chem. Commun.*, 417, 1966) which shows that his method and approach are different from ours. A short communication on our results appeared in *Sci. Cult.* (Calcutta), **32**, 590 (1966). The paper was presented at the Joint Convention of the Chemical Research Committee, C. S. I. R., and the Society of Biological Chemists of India, held at Delhi on Dec 25–27, 1966.

(2) (a) D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Tetrahedron*, **21**, 681 (1965); (b) B. H. Brown and P. G. Philpott, *J. Chem. Soc.*, 7185 (1965), and references therein.

compounds (VII–X) obtained during synthesis have also been derived from natural murrayanine.

Recent reports[2b] show that the Japp–Klingemann reaction provides a convenient method for the synthesis of the hydrazones required for indole synthesis by the Fischer method. The hydrazone necessary for the present synthesis was obtained by the condensation of 2-hydroxymethylene-5-methylcyclohexanone (III) with phenyldiazonium chloride (IV) under Japp–Klingemann condition.[3] The resulting 4-methylcyclohexane-1,2-dione-1-phenylhydrazone (V), was cyclized to 1-oxo-3-methyl-1,2,3,4-tetrahydrocarbazole (VI), using a mixture of acetic acid and concentrated hydrochloric acid as the condensing agent. The dehydrogenation of 1-oxo-3-methyl-1,2,3,4-tetrahydrocarbazole (VI) with



* Derived from murrayanine.

(3) D. P. Chakraborty, K. C. Das, and B. K. Chowdhury, *Chem. Ind.* (London), 1684 (1966).

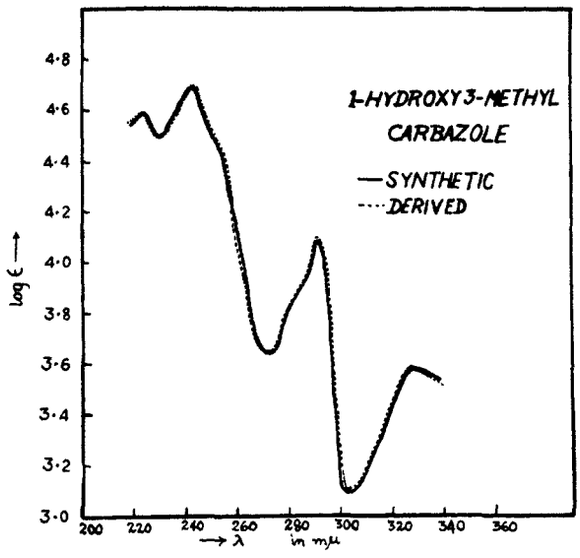


Figure 1.

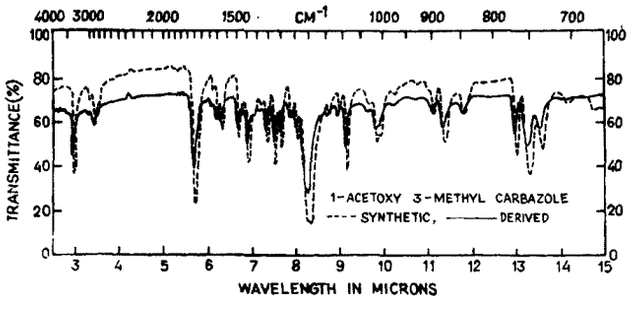


Figure 2.

Pd–C (10%)[4,5] in a sealed tube under evacuated condition instead of chloranil[6,7] furnished 1-hydroxy-3-methylcarbazole (VIII). This was found to be identical (melting point, mixture melting point, and superimposible uv spectrum, Figure 1) with the phenol (VII-derived) obtained by demethylation of the Wolff–Kishner reduction product (IX-derived) of murrayanine.

The phenol (VII-derived) was also obtained from the alkaline fraction of the Wolff–Kishner reduction product of murrayanine. 1-Acetoxy-3-methylcarbazole (VIII), obtained by acetylation of phenol VII with pyridine and acetic anhydride, was identical with the phenol acetate derived from murrayanine (melting point, mixture melting point, and superimposible ir spectrum, Figure 2). Phenol VII on methylation with diazomethane in the presence of methanol furnished 1-methoxy-3-methylcarbazole (IX) identical with the Wolff–Kishner reduction product of murrayanine (IX-derived). This eventually confirms the structure of the Wolff–Kishner reduction product of murrayanine as 1-methoxy-3-methylcarbazole. The conversion of 1-methoxy-3-methylcarbazole into 1-methoxy-3-formylcarbazole would now accomplish the desired synthesis of murrayanine. For this purpose, compound IX was brominated with N-bromosuccinimide[8] in the pres-

(4) J. A. Cummins and M. L. Tomlinson, *J. Chem. Soc.*, 3475 (1955).
(5) R. H. Shapiro in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, p 371.
(6) N. Campbell and B. M. Barclay, *Chem. Rev.*, **40**, 359 (1947).
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(8) H. Schmidt and P. Karrer, *Helv. Chim. Acta.*, **29**, 573 (1946).

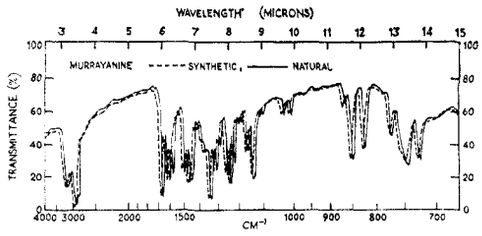

Figure 3.

ence of traces of benzoyl peroxide and the resulting 1-methoxy-3-bromomethylcarbazole was hydrolyzed *in situ* with caustic potash to 1-methoxy-3-hydroxymethylcarbazole (X). Compound X was found to be identical with the borohydride reduction product of murrayanine reported previously[1] (mp and mmp 127°). The benzylic alcohol X was oxidized with manganese dioxide[9] in carbon tetrachloride to 1-methoxy-3-formylcarbazole (I-synthetic), which was found to be identical with natural murrayanine in all respects (melting point, mixture melting point, uv spectrum, and superimposible ir spectrum, Figure 3).

Experimental Section

All melting points were determined on a Kofler block. The alumina used was of Brockmann grade as prepared by Sarabhai-Merck Co. of India. Petroleum ether refers to the fraction boiling between 40 and 60°.

4-Methylcyclohexane-1,2-dione 1-Phenylhydrazone (V).—2-Hydroxymethylene-5-methylcyclohexanone[3] (3.5 g) in methanol (36 ml) was added to an aqueous solution of sodium acetate (5.5 g in 19 ml of water). To this solution was added a solution of phenyl diazonium-chloride (prepared from 2.7 g of aniline) during 25 min under mechanical agitation when the crystals of 4-methylcyclohexane-1,2-dione 1-phenylhydrazone was obtained. On recrystallization from ethanol the compound V, mp 209°, was obtained in 75% yield.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.36; H, 7.19; N, 13.08.

1-Oxo-3-methyl-1,2,3,4-tetrahydrocarbazole (VI).—4-Methylcyclohexane-1,2-dione 1-phenylhydrazone (2.4 g) was boiled with glacial acetic acid (19 ml) and concentrated hydrochloric acid (4.5 ml) for 5 min and then diluted with ice water (70 ml). The solid obtained was filtered, washed with water, dried, and crystallized from benzene when colorless needles, mp 197°, of VI were obtained in 77% yield: $\lambda_{max}^{ethanol}$ 237 mμ (log ε 4.26) and 308 mμ (log ε 4.36); ν_{max}^{KBr} 3257 (–NH–), 1639 (carbonyl), 1562 and 1527 (aromatic system), 1379 (C-methyl) and 925, 869, and 813 cm^{-1} (substituted benzene ring).

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.38; H, 6.58; N, 7.03. Found: C, 78.29; H, 6.78; N, 6.92.

1-Hydroxy-3-methylcarbazole (VII).—1-Oxo-3-methyl-1,2,3,4-tetrahydrocarbazole (1.5 g) was dehydrogenated with Pd–C (10%, 0.75 g) at 250–270° for 4 hr in a sealed, evacuated tube in the presence of dry alcohol (0.5 ml). The reaction product was cooled and filtered. The semisolid mass left after the removal of the solvent from the filtrate was dissolved in ether from which the phenolic fraction was separated by extraction with aqueous sodium hydroxide solution (5%). The alkaline solution was acidified with 10% hydrochloric acid and was extracted with ether. On removal of ether and chromatography over silica gel (10 g) a pale brown crystalline product, mp 155–156°, was obtained from the benzene eluent. On recrystallization from benzene–petroleum ether, almost colorless needles, mp 158°, were obtained in 45% yield: $\lambda_{max}^{ethanol}$ 224 mμ (log ε 4.59), 242 (4.69), 292 (4.09), and 330 (3.58); ν_{max}^{KBr} 3400 (–NH–), 3279 (hump, bonded hydroxyl), 1613 and 1587 (aromatic system), 1389 (C-methyl), and 980 and 854 cm^{-1} (substituted aromatic ring).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.01; H, 5.72; N, 6.80.

(9) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

1-Acetoxy-3-methylcarbazole (VIII).—A solution of 1-hydroxy-3-methylcarbazole (300 mg) in pyridine (1 ml) after heating with acetic anhydride (1 ml) on a water bath for 1 hr was poured into ice water from which the acetate separated. It was filtered. The crude acetate on repeated crystallization from benzene–petroleum ether mixture gave 260 mg of colorless needles: mp 154°; $\lambda_{max}^{ethanol}$ 238 mμ (log ε 4.62), 248 (4.40), 257 (4.15), 292 (4.12) and 328 (3.38); ν_{max}^{KBr} 3400 (–NH–), 1762 (acetoxy), 1626, and 1587 (aromatic system), 1370 (C-methyl) and 900 and 885 cm^{-1} (substituted benzene ring).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.50; H, 5.33; N, 6.05.

1-Hydroxy-3-methylcarbazole from Murrayanine (VII-Derived). A.—Murrayanine on Wolff–Kishner reduction furnished a neutral oily product as reported previously.[1] The alkaline aqueous fraction of the Wolff–Kishner reduction product furnished on acidification a solid, mp 140–145°. This product, on chromatography over silica gel and subsequent crystallization from benzene–petroleum ether, furnished almost colorless needles, mp 158°. This was found to be identical with 1-hydroxy-3-methylcarbazole by mmp 158° and a superimposible uv spectrum (Figure 1).

B.—The Wolff–Kishner reduction product of murrayanine (200 mg) was demethylated with HBr (48%; 1 ml) and glacial acetic acid (2.8 ml). The demethylated product on chromatography through silica gel and on crystallization from benzene–petroleum ether mixture melted at 158° (100 mg) alone or when mixed with 1-hydroxy-3-methylcarbazole (VII). The uv spectrum of the demethylated product was superimposible with that of 1-hydroxy-3-methylcarbazole.

1-Acetoxy-3-methylcarbazole Derived from Murrayanine (VIII-Derived).—The phenol derived from murrayanine was acetylated as was the synthetic phenol (VII) to an acetate which had a melting point and mixture melting point (154°) identical with the synthetic sample. The ir spectra of the synthetic 1-acetoxy-3-methylcarbazole (VIII) and that of the phenol acetate derived from murrayanine were superimposible (Figure 2).

1-Methoxy-3-methylcarbazole (IX).—1-Hydroxy-3-methylcarbazole (350 mg) in methanol (25 ml) was treated with an ethereal solution of diazomethane and kept overnight in a refrigerator. After removal of the solvent, an oily product was obtained. This on distillation at 125–130° (0.05 mm) yielded a colorless oil (280 mg). This was found to be identical, by paper chromatography and uv spectral measurements, with the Wolff–Kishner reduction product of murrayanine (R_f 0.73, alcohol–water–acetic acid, 27:21:2): $\lambda_{max}^{ethanol}$ 226 mμ (log ε 4.4), 243 (4.5), 252 (4.4 hump), 281 (3.7), 290 (3.8) and 330 (3.5).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.73; H, 6.28; N, 6.56.

1-Methoxy-3-hydroxymethylcarbazole (X).—To a cold solution of 1-methoxy-3-methylcarbazole (400 mg) in carbon tetrachloride (50 ml) were added N-bromosuccinimide (338 mg) and a trace amount of benzoyl peroxide. The mixture was kept at room temperature for 4 hr and then refluxed for 15 min. The reaction mixture was then filtered and the residue obtained after removal of the solvent was hydrolyzed with 5% alcoholic KOH (10 ml). The hydrolyzed product was taken up with ether and the brownish semisolid mass obtained after working up the ether extract was chromatographed over alumina (8 g). A solid product, mp 119–121°, was obtained from benzene–ether (1:1) eluent. This product on repeated recrystallization from benzene–petroleum ether yielded 40 mg of a colorless product, mp 127°, identical with the sodium borohydride reduction product of murrayanine (X): mp, mmp 127°; $\lambda_{max}^{ethanol}$ 225 mμ (log ε 4.40), 242 (4.57), 252 (4.50), 2.90 (3.96) and 330 (3.55).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.90; H, 5.87; N, 6.10.

1-Methoxy-3-formylcarbazole (I-Synthetic).—To a solution of 1-methoxy-3-hydroxymethylcarbazole (100 mg) in dry CCl_4 (50 ml) was added active MnO_2 (1 g). The mixture was stirred for 6 hr and then filtered. The filtrate on removal of the solvent gave an oily product. This was dissolved in minimum amount of benzene and chromatographed over alumina (5 g). Several fractions collected with benzene as eluent gave on removal of the solvent a colorless solid, mp 160–162°. This was further purified by sublimation at 160° (0.05 mm) and subsequent crystallization from benzene–petroleum ether mixture when colorless needles (50 mg) were obtained. The compound melted at 168° alone or when mixed with natural murrayanine: $\lambda_{max}^{ethanol}$ 238 mμ (log ε 4.45), 247 (4.30), 274 (4.58), 289 (4.55) and 335 (4.15); ν_{max}^{Nujol}

3150 (-NH-), 1660 (aromatic aldehyde), 1620, 1600, 1575 (aromatic residue), and 850, 824, 773, 745, and 725 cm^{-1} (substituted benzene derivatives).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.35; H, 4.70; N, 6.00.

Registry No.—I, 723-97-7; V, 15562-11-5; VI, 14961-29-6; VII, 14960-81-7; VIII, 14961-28-5; IX, 4532-33-6; X, 3909-78-2.

Acknowledgments.—The authors' thanks are extended to Dr. D. M. Bose, Director, Dr. A. Sen, Head of the Department of Chemistry, Bose Institute, and Dr. P. K. Bose, Emeritus Scientist, for their interest in the work. Thanks are also due Dr. D. N. Roy, Department of Chemistry, University of Connecticut, Storrs, Conn., and Dr. S. C. Pakrashi, I. I. E. M., Calcutta 32, for some ir spectra. The research grant by the C. S. I. R. India is gratefully acknowledged.

Intramolecular Diels–Alder Reactions. V. Synthesis of Dehydro-β-peltatin Methyl Ether[1a]

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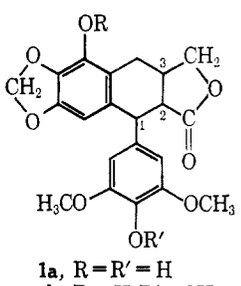
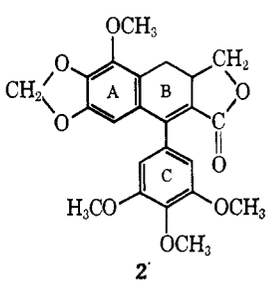
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Received October 30, 1967

During the period 1947–1953, Hartwell, *et al.*,[2] reported the isolation from podophyllin of the tumor-necrotizing agents α- and β-peltatin and structural investigations on them. The structures proposed (**1a** and **1b**, respectively) were based on (1) oxidative degradations, (2) analogy of spectral characteristics and chemical transformations with those found in the podophyllotoxin system, and (3) conversion of both peltatins into the same permethyl ether (**1c**). These studies clearly established the carbon skeleton of the peltatins and the locations of the phenolic, methoxy, and methylenedioxy substituents thereon. The stereochemistries at C-1, C-2, and C-3[3] as well as the orientation of the lactone ring (*i.e.*, as shown, or alternatively with the carbonyl and methylene moieties reversed) were still open to question. The research presented here serves to establish unequivocally the orientation of the lactone ring.



1a, R = R′ = H
b, R = H, R′ = CH_3
c, R = R′ = CH_3



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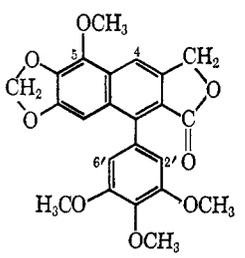

3

The ethyl ester of *trans*-2-methoxy-3,4-methylenedioxycinnamic acid (of established isomeric structure)[4] was reduced by means of lithium aluminum hydride to *trans*-2-methoxy-3,4-methylenedioxycinnamyl alcohol. The crude, open-chain ester formed from this alcohol and 3,4,5-trimethoxyphenylpropiolyl chloride was cyclized by means of refluxing acetic anhydride to a single product, **2**. Dehydrogenation of **2** by means of Pd–C in cymene or by means of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene afforded **3**, identical with the product obtained from dehydrogenation of β-peltatin-B methyl ether **1c** (derived directly from podophyllin). The identity of these products assures that cyclization of the open-chain ester did occur into ring A (where only a single position for cyclization was available) rather than into ring C and, thus, establishes the orientation of the lactone ring as that shown in formulas **1**–**3**. Cyclization into ring A is consistent with expectations for an intramolecular Diels–Alder reaction and with previous results on other *trans*-cinnamyl phenylpropiolates which reacted under similar conditions.[5,6]

It might be noted that the nmr signal for the proton on C-4 in the 1-phenylnaphthalene lignan lactone **3** falls at δ 8.17. The appearance of this singlet at such a low field is ascribed to the deshielding influence of the *peri* methoxy group at C-5. Dudek[7] has observed similar downfield shifts of signals for *peri* protons in naphthalenes which bear an OH, OCH_3, or NH_2 substituent in an α position. In an earlier paper[6] the presence or absence of a singlet at $\delta > 8.0$ was of diagnostic pertinence to the direction of cyclization in the intramolecular Diels–Alder reaction. In those examples, however, one was concerned only with the respective presence or absence of an aromatic hydrogen atom in a position *ortho* to the carbonyl group of the lactonic moiety. In no case was it possible to obtain a cyclized product bearing a methoxy or methylenedioxy group in a position *peri* to an aromatic hydrogen atom. In the present case, on the other hand, either direction of cyclization should give a product with a low-field singlet in its spectrum.

(1) (a) This investigation was supported by Research Grant No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service. (b) Research Associate, 1966–1967.

(2) (a) J. L. Hartwell, *J. Amer. Chem. Soc.*, **69**, 2918 (1947); (b) J. L. Hartwell and W. E. Detty, *ibid.*, **70**, 2833 (1948); (c) *ibid.*, **72**, 246 (1950); (d) J. L. Hartwell, A. W. Schrecker, and G. Y. Greenberg, *ibid.*, **74**, 6285 (1952); (e) A. W. Schrecker and J. L. Hartwell, *ibid.*, **75**, 5924 (1953).

(3) The numbering used in this paper is consistent with *Chemical Abstracts* practice but does not follow that used by Hartwell, *et al.*,[2] and by some other workers in the lignan field.

(4) See the Experimental Section for evidence on aspects of both positional and geometric isomerism in this starting material.

(5) L. H. Klemm, D. H. Lee, K. W. Gopinath, and C. E. Klopfenstein, *J. Org. Chem.*, **31**, 2376 (1966). *Cf.* L. H. Klemm and K. W. Gopinath, *J. Heterocycl. Chem.*, **2**, 225 (1965).

(6) L. H. Klemm, K. W. Gopinath, D. H. Lee, F. W. Kelly, E. Trod, and T. M. McGuire, *Tetrahedron*, **22**, 1797 (1966).

(7) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).