(XX) is dimorphic and melted first at 130°. Recrystallization from isopropyl ether did not raise the melting point.

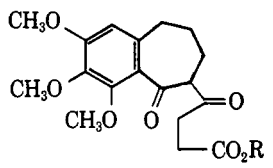
Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.9; H, 6.0.

The ultraviolet and infrared spectra and the chemical properties (*cf.* below) are in agreement with structure XX.

The aqueous bicarbonate washings, made acidic with 2 *N* hydrochloric acid, were extracted with methylene chloride. The organic layer was washed with water, dried, and distilled to dryness. The residue, crystallizing from ether, yielded 0.4 g., m.p. 165°, of the bicyclic diacid corresponding to the saponification of diester XIX. Recrystallization from isopropyl ether raised the melting point to 172°; λ_{max} 222 mμ (ε 19,600) and 271 mμ (ε 9300).

Anal. Calcd. for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33; O, 31.97. Found: C, 61.6; H, 6.3; O, 31.8.

Opening of the Enol Lactone Group of XX.—Opening of the enol lactone of XX can give rise either to the ester XXVII (R = CH_3) or to the corresponding acid XXVII (R = H) according to the amount of sodium hydroxide used in the reaction.



XXVII

A. Ester XXVII (R = CH_3).—To a solution of 1 g. of XX in 50 ml. of methanol containing 2 drops of phenolphthalein was added 3 ml. of 1 *N* sodium hydroxide which caused a change of the color of the indicator. Two more milliliters of 1 *N* sodium hydroxide was added and the stirred solution was kept for 30 min. at room temperature and then made acid with 1 *N* sulfuric acid. Water was added which precipitated crystals of the diketo ester XXVII (R = CH_3) which were filtered and dried; 0.8 g., m.p. 100° (prisms from ether).

Anal. Calcd. for $C_{19}H_{24}O_7$: C, 62.62; H, 6.64. Found: C, 62.7; H, 6.6.

Saponification of the preceding ester with aqueous methanolic potassium hydroxide (reflux for 30 min.) yielded the corresponding acid, m.p. 130°. The latter was obtained directly from the enol lactone as given below.

B. Acid XXVII (R = H).—Enol lactone XX (0.1 g.) was refluxed 0.5 hr. in a solution of methanol (2 ml.), water (0.1 ml.), and concentrated sodium hydroxide (0.1 ml.). After removing the methanol on the steam bath, the residue was diluted with water and extracted with methylene chloride. The alkaline aqueous layer, acidified with 7 *N* sulfuric acid, was extracted with ethyl acetate; the organic layer was washed with water, dried, and evaporated to dryness. The crystalline residue (needles) weighed 74 mg.; m.p. 130°; inflection at 240 mμ (ε 5900) and λ_{max} 319 mμ (ε 16,300). Titration of the acid with 0.1 *N* NaOH gave the theoretical value.

Anal. Calcd. for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33. Found: C, 61.6; H, 6.4.

Acknowledgment.—The authors gratefully acknowledge the encouragement given to them during this work by Professor L. Velluz, Director of Research at Roussel-Uclaf, to whom thanks are due for authorizing this publication.

Synthesis of Dehydrootobain*

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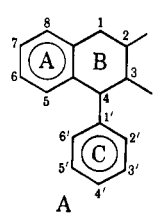
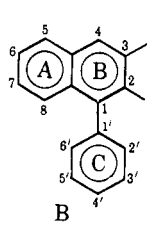
2,3-Dimethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**5**) has been synthesized from piperonal and is identical with dehydrootobain, a product obtained from the lignan otobain (**1**) by dehydrogenation with palladium–carbon. Dicyclohexylcarbodiimide is shown to be a useful reagent for conversion of phenylpropiolic acids to 1-phenylnaphthalene derivatives.

A natural product, first isolated in 1854 by Uricoechea[1] from the fruit of *Myristica otoba* and shown to have an empirical formula $C_{20}H_{20}O_4$ by Baughman and co-workers,[2] has since been characterized as a lignan and named otobain.[3] The constitution 5,6-methylenedioxy-2,3-dimethyl-4-(3′,4′-methylenedioxyphenyl)-1,-2,3,4-tetrahydronaphthalene (**1**) was proposed for otobain independently by two groups.[4,5] The proposed structure was based largely on interpretation of nuclear magnetic resonance spectra of otobain and derivatives, and the observation that the dehydrogenation product dehydrootobain, $C_{20}H_{16}O_4$, differed from the isomeric dehydroepigalbacin to which the structure 2,3-dimethyl-6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**2**) had been assigned.[6] Dehydroepigalbacin (**2**) had been obtained both by acid isomerization of galbacin (**3**) followed by dehydrogenation,[4,7] and by oxidative cyclization[5] of dipiperonylidene succinic anhydride (**4**). Within the lignan class of natural products[8] of which about 60 members are known to date, the oxygenation pattern in ring A of otobain was considered sufficiently unusual to merit substantiation by a synthesis of dehydrootobain (**5**).

An attractive method for the preparation of 1-phenylnaphthalenes, particularly those where functional groups are required at C-2 and C-3, consists of treating suitably substituted phenylpropiolic acids with acetic anhydride. This reaction was first observed by



A



B

* Submitted in honor of Professor Louis F. Fieser by R. S. (Research Fellow, Harvard University, 1953).

(1) E. Uricoechea, *Ann.*, **91**, 369 (1854).

(2) W. F. Baughman, G. S. Jamieson, and D. H. Brauns, *J. Am. Chem. Soc.*, **43**, 199 (1921).

(3) R. Stevenson, *Chem. Ind.* (London), 270 (1962).

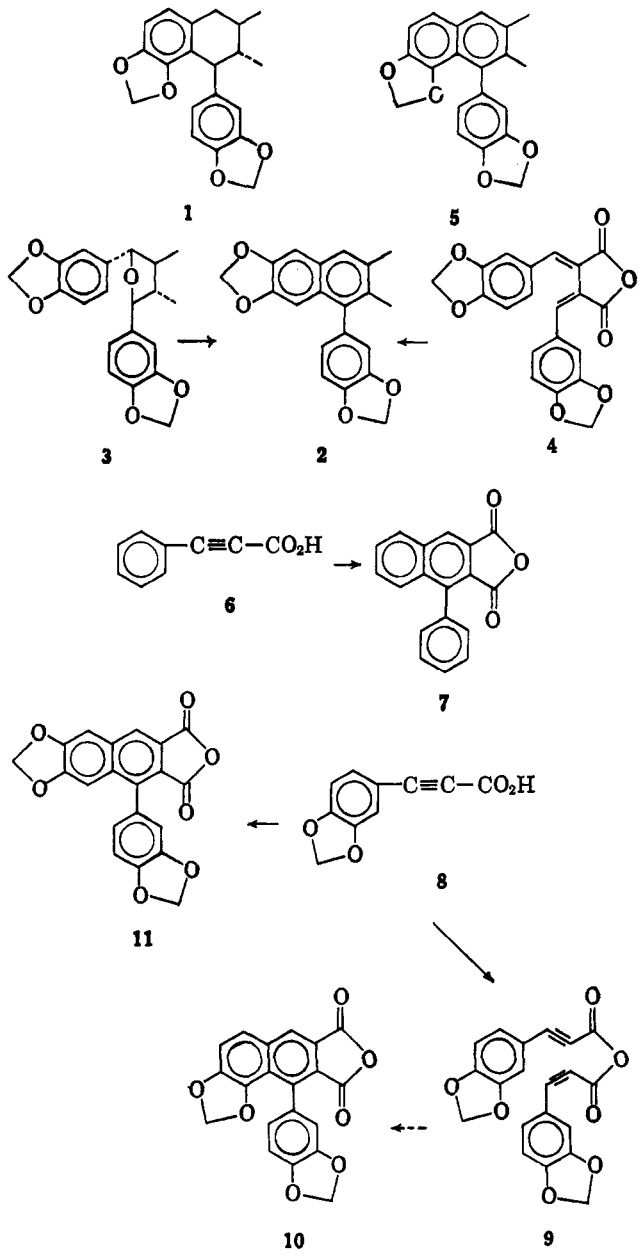
(4) N. S. Bhacca and R. Stevenson, *J. Org. Chem.*, **28**, 1638 (1963).

(5) T. Gilchrist, R. Hodges, and A. L. Porte, *J. Chem. Soc.*, 1780 (1962).

(6) The systematic name given to otobain, a phenyltetralin, is in accordance with lignan nomenclature in which the carbon atom bearing the C-ring phenyl group is regarded as C-4 [*i.e.*, as in A]. The lignan dehydrogenation products and synthetic phenylnaphthalenes herein described are named as 1-phenylnaphthalenes [*i.e.*, as in B].

(7) G. K. Hughes and E. Ritchie, *Australian J. Chem.*, **7**, 104 (1956).

(8) General reviews of lignans include (a) H. M. Hearon and W. S. MacGregor, *Chem. Rev.*, **55**, 957 (1955); (b) K. Freudenberg and K. Weinges, *Tetrahedron*, **15**, 115 (1961); (c) M. S. Adjangba, *Bull. soc. chim. France*, 2344 (1963).



Michael and Bucher,[9] who obtained 1-phenylnaphthalene-2,3-dicarboxylic anhydride (**7**) from phenylpropiolic acid (**6**). The interesting early history of this reaction has been reviewed[10] and the general synthetic utility well demonstrated, particularly by the work of Baddar and co-workers.[11] With regard to a synthetic route to dehydrootobain, the specific problem is in effecting cyclization of the intermediate anhydride (**9**) derived from piperonylpropiolic acid (**8**) in the manner desired to yield **10**. It has been shown by Haworth and Kelly,[12] however, that treatment of **8** with acetic anhydride yields the product **11** in which cyclization has occurred in the expected but undesired sense. Despite a subsequent claim,[13] without experimental detail, that the isomer **10** can be "obtained in very small amount," we were able to isolate only **11** by Haworth's procedure.[12]

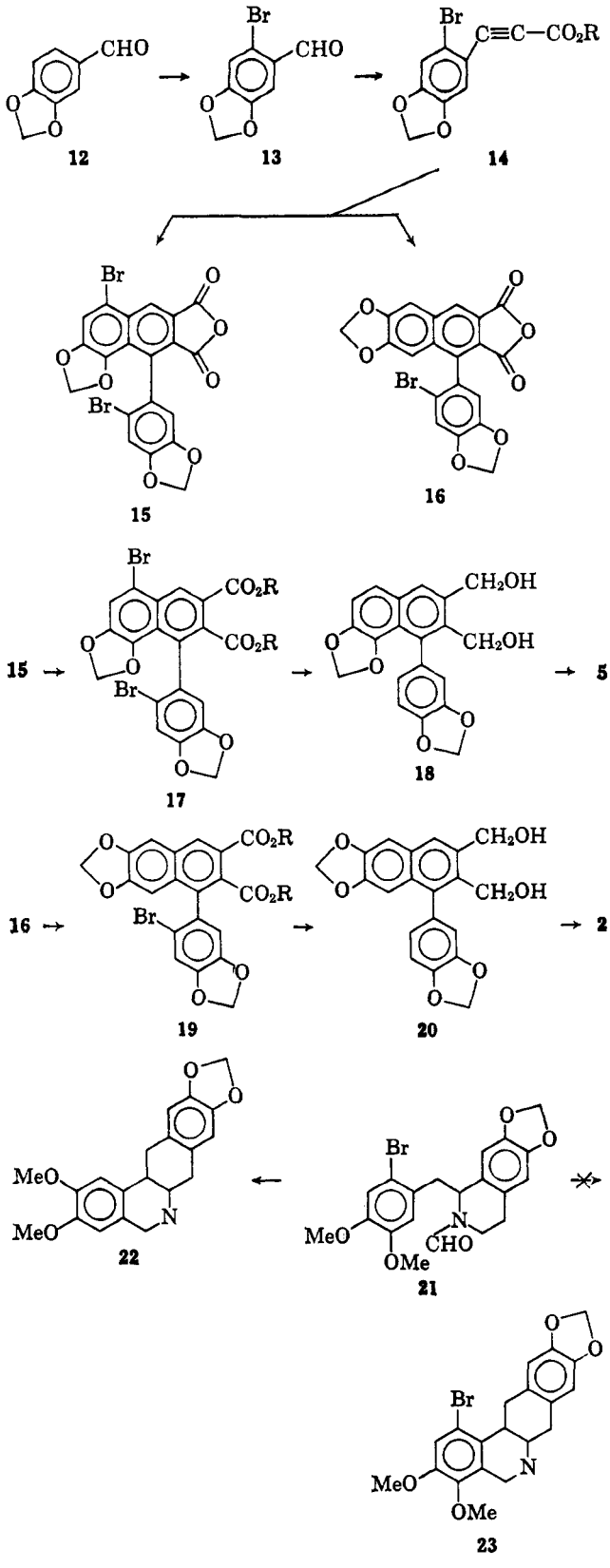
(9) A. Michael and J. E. Bucher, *Ber.*, **28**, 2511 (1895).
(10) A. W. Johnson, "Acetylenic Compounds," Vol. II, Edward Arnold Ltd., London, 1950, p. 77.
(11) F. G. Baddar, *J. Chem. Soc.*, 224 (1947), and subsequent papers in series.
(12) R. D. Haworth and W. Kelly, *ibid.*, 745 (1936).
(13) F. G. Baddar, H. A. Fahim, and M. A. Galaby, *ibid.*, 465 (1955).

This led us to examine the action of acetic anhydride on 2-bromo-4,5-methylenedioxyphenylpropiolic acid (**14**, R = H) in the expectation that the bromine atom would serve as a suitable blocking group and consequently furnish **15**. Bromination of piperonal (**12**) readily gave 6-bromopiperonal[14] (**13**) which was conveniently converted in one step to ethyl 2-bromo-4,5-methylenedioxyphenylpropiolate (**14**, R = C_2H_5) by treatment with triethyl phosphonoiodoacetate under the general conditions devised by Wadsworth and Emmons[15] for synthesis of propiolate esters. The corresponding 2-bromo-4,5-methylenedioxyphenylpropiolic acid (**14**, R = H), obtained by alkaline hydrolysis of the ester, was heated with acetic anhydride under conditions whereby **8** was successfully converted to **11**; the product, however, was a mixture whose infrared spectrum showed that acetylenic derivatives were still present and from which no identifiable crystalline compounds were obtained. The unpromising nature of this product led us to seek an alternative method of obtaining the required dibromo anhydride (**15**).

We have found that piperonylpropiolic acid (**8**) undergoes anhydride formation and ring closure to yield **11** in excellent yield under very mild conditions, namely, treatment with N,N-dicyclohexylcarbodiimide in dimethoxyethane solution below 0°. When the bromopropiolic acid analog (**14**, R = H) was subjected to these conditions two products, anhydrides A and B, were isolated each in about 20% yield. Anhydride A is a dibromo anhydride, $C_{20}H_8O_7Br_2$, which we formulate as the required 5-bromo-7,8-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride (**15**) and anhydride B is a monobromo anhydride, $C_{20}H_9O_7Br$, which we regard as 6,7-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride (**16**).

The infrared spectrum of the dibromo anhydride (**15**) showed typical absorption bands for methylenedioxy and anhydride groups and confirmed the absence of acetylenic groups. Alkaline hydrolysis of **15** gave the dicarboxylic acid (**17**, R = H) from which it could be regenerated on heating. The corresponding dimethyl ester $C_{22}H_{14}O_8Br_2$ (**17**, R = CH_3) was obtained from the acid by diazomethane treatment. The nuclear magnetic resonance spectrum of the dimethyl ester, consisting of singlet peaks of correct intensity at δ 3.65 and 3.94 (two methyl groups as carbomethoxyls), 5.83 and 5.96 (two methylenedioxy groups), and 6.73, 6.98, 7.54, and 8.90 (four aromatic protons), confirmed the assigned structure. Reduction of the ester (**17**, R = CH_3) with lithium aluminum hydride–aluminum chloride in ether solution yielded the diol, 2,3-bishydroxymethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**18**), debromination occurring concomitantly with carbomethoxyl reduction. Less reproducible results were obtained in the absence of aluminum chloride. The synthesis of dehydrootobain was then completed by hydrogenolysis of the diol using 10% palladium–carbon as catalyst to give 2,3-dimethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**5**), identical with the product obtained by dehydrogenation of otobain.

(14) A. Oelker, *Ber.*, **24**, 2592 (1891).
(15) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).



Alkaline hydrolysis of anhydride B (**16**) and esterification of the product with diazomethane gave the dimethyl ester (**19**, R = CH_3), reduction of which with lithium aluminum hydride yielded the diol (**20**); the absence of bromine in this diol was confirmed by a negative Beilstein test. Subsequent hydrogenolysis of **20** gave 2,3-dimethyl-6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**2**), identical with dehydroepigalbacin.

The ring closure involved in the conversion of **14** to **16** is particularly noteworthy in that it requires the extrusion of the protecting bromine atom (presumably as Br^+) as an alternative to cyclization at the unsubstituted *ortho* position (**14** → **15**). This is reminiscent of the Bischler–Napieralski reaction of the formamide (**21**), which yielded the bromine-free product (**22**) rather than the expected product (**23**) on treatment with phosphorus oxychloride followed by zinc dust reduction.[16]

Experimental

Melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra were measured on a Perkin-Elmer Infracord spectrometer, using potassium bromide disk samples. Nuclear magnetic resonance spectra were determined in deuteriochloroform solution with tetramethylsilane as an internal reference.

6-Bromopiperonal (13).—A solution of bromine (10 ml.) and iodine (1 g.) in carbon disulfide (20 ml.) was added dropwise over 30 min. to a stirred solution of piperonal (20 g.) in carbon disulfide (50 ml.) at room temperature. After the mixture had been stirred for 24 hr., it was evaporated under reduced pressure to give a residual red-brown solid which on two recrystallizations from ethanol yielded 6-bromopiperonal as needles (12 g.), m.p. 127–129°, lit.[14] m.p. 129–130°.

Ethyl 2-Bromo-4,5-methylenedioxyphenylpropiolate (14, R = C_2H_5).—Triethyl phosphonoacetate (8.4 g., Aldrich Chemical Co.) was added dropwise to a stirred suspension of 50% sodium hydride (1.8 g.) in dry dimethoxyethane (40 ml.), and the temperature was maintained below 10°. When hydrogen evolution had ceased, a solution of iodine (9.5 g.) in dry dimethoxyethane (30 ml.) was added dropwise with stirring and cooling below 10°. After the mixture had been stirred for 30 min., 50% sodium hydride (3.6 g.) was added in one batch, the temperature was allowed to rise to 25°, and stirring was continued until gas evolution ceased. A solution of 6-bromopiperonal (8.55 g.) in dry dimethoxyethane (100 ml.) was then added with stirring over 15 min., the mixture was stirred at 35–40° until no further evolution of gas (*ca.* 3 hr.), cooled below 10°, and water (300 ml.) was added. The precipitate of crude ester (7.1–8.5 g.) was collected after standing overnight at 3° and washed with water, and a small portion was crystallized twice from isopropyl ether to give ethyl 2-bromo-4,5-methylenedioxyphenylpropiolate as yellow needles, m.p. 100–101°, λ (μ) 4.53 (C≡C), 5.90 (ester), and 10.70 (methylenedioxy).

Anal. Calcd. for $C_{12}H_9BrO_4$: C, 48.51; H, 3.06; Br, 26.89. Found: C, 48.52; H, 3.44; Br, 27.08.

2-Bromo-4,5-methylenedioxyphenylpropiolic Acid (14, R = H).—The crude ester from the previous experiment was dissolved in hot methanol (50 ml.), and a solution of potassium hydroxide (1 g.) in hot methanol (25 ml.) was added. The mixture was maintained at *ca.* 65° for a few minutes, cooled to 5°, and filtered. The precipitate was washed with ether and triturated with water (100 ml.), and the mixture was acidified by dropwise addition of concentrated hydrochloric acid. Filtration gave 2-bromo-4,5-methylenedioxyphenylpropiolic acid as a white powder (5.85 g.), m.p. 181–183° dec., λ (μ) 4.54 (C≡C), 5.96 (-CO_2H), and 10.71 (methylenedioxy).

Anal. Calcd. for $C_{10}H_5BrO_4$: C, 44.8; H, 1.86. Found: C, 45.13; H, 2.38.

Recrystallization (from methanol or isopropyl ether) caused a general lowering and divergence of melting point, and inconsistent microanalyses were obtained. Isolation of a further quantity of acid, from the filtrate from which crude ester was removed, increased the total yield to 88%.

Treatment of 2-Bromo-4,5-methylenedioxyphenylpropiolic Acid with N,N-Dicyclohexylcarbodiimide.—A solution of dicyclohexylcarbodiimide (2.0 g.) in dimethoxyethane (10 ml.) at −12° was added to a solution of the bromomethylenedioxyphenylpropiolic acid (3.61 g.) in dimethoxyethane at the same temperature. It was noted after a few minutes that a crystalline precipitate had formed and the solution had darkened in color. The mixture was kept in a refrigerator for 24 hr. and filtered, and the precipitate (1.25 g., identified as N,N-dicyclohexylurea

(16) R. D. Haworth and W. H. Perkin, *J. Chem. Soc.*, 1448 (1925).

by melting point and infrared spectrum) was washed with dimethoxyethane. The filtrate and washings were evaporated under reduced pressure to give a residual brown glass. The infrared spectrum of this revealed the presence of minor amounts of unchanged diimide and propiolic acid in addition to anhydride formation. The brown glass was worked up by two methods.

(a) A solution of the brown glass was dissolved in benzene and chromatographed on silica gel. The first fractions eluted were identified as unchanged bromomethylenedioxyphenylpropiolic acid. Subsequent fractions were obtained as bright yellow eluates and showed strong carbonyl absorption in the anhydride region. These were combined (1.5 g.) and crystallized from acetone containing a little acetic anhydride to yield **anhydride A** as yellow needles (450 mg.), identified as **5-bromo-7,8-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride** (**15**), m.p. 255–258°, λ (μ) 5.45 and 5.63 (anhydride), and 10.77 (methylenedioxy), C≡C absent.

Anal. Calcd. for $C_{20}H_8Br_2O_7$: C, 46.18; H, 1.55; Br, 30.73. Found: C, 46.23; H, 1.46; Br, 30.18.

The mother liquors from this crystallization on concentration yielded **crude anhydride B** as pale yellow crystals, m.p. 210–258°.

(b) The brown glass was crystallized from benzene to give **crude anhydride A** as yellow crystals, m.p. 230–242°. The mother liquors were then chromatographed on silica gel, and the eluted fractions were examined by thin layer chromatography.[17] This showed that both anhydrides A and B were present in all fractions, but that later fractions were preponderantly anhydride B. These later fractions were combined, crystallized from benzene–acetone containing a little acetic anhydride to give **anhydride B** as pale yellow crystals, identified as **6,7-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride** (**16**), m.p. 263–266°, λ (μ) 5.45 and 5.63 (anhydride), 10.71 and 10.83 (methylenedioxy).

Anal. Calcd. for $C_{20}H_9BrO_7$: C, 54.45; H, 2.06; Br, 18.11. Found: C, 54.48; H, 2.14; Br, 18.37.

5-Bromo-7,8-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic Acid Dimethyl Ester (**17**, R = CH_3).—Anhydride A (1.0 g.) was added to a solution of potassium hydroxide (1.0 g.) in methanol (30 ml.) and the mixture was heated under reflux for 15 min., cooled, diluted with water (20 ml.), and acidified with concentrated hydrochloric acid. Filtration gave the dicarboxylic acid (**17**, R = H) as a pale yellow solid (0.9 g.). On determining the melting point, the compound frothed and turned yellow at 160–180°, crystallized on addition of a drop of acetone, and remelted at 240–250° dec. A solution of the dicarboxylic acid (900 mg.) was dissolved in dimethoxyethane (15 ml.) and treated with an excess of diazomethane in ether at −12°. The mixture was allowed to reach room temperature over 30 min., then evaporated to give a glass which crystallized from methanol–acetone to give **5-bromo-7,8-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)-naphthalene-2,3-dicarboxylic acid dimethyl ester** as needles, m.p. 185–186°, λ (μ) 5.80 (ester), 6.18, 6.70, 6.81, 7.05, 8.91, 9.61, and 10.72.

Anal. Calcd. for $C_{22}H_{14}Br_2O_8$: C, 46.66; H, 2.49; Br, 28.22. Found: C, 46.38; H, 2.47; Br, 28.45.

2,3-Bishydroxymethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**18**).—To a stirred suspension of lithium aluminum hydride (450 mg.) and aluminum chloride (450 mg.) in dry ether (30 ml.) was added a solution of the preceding dibromophenylnaphthalene dimethyl ester (450 mg.) in dimethoxyethane (15 ml.). The mixture was stirred overnight at room temperature, treated consecutively with ethyl acetate, water, and dilute hydrochloric acid, then extracted with ether (three 50-ml. portions). The washed and dried ($MgSO_4$) extract was evaporated to give a solid (272 mg.) which was crystallized twice from methanol to yield **2,3-bishydroxymethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene** as prisms, m.p. 200–203°, λ (μ) 3.0, 6.10, 6.26, 6.38, 6.66, 6.72, 8.09, 9.61, and 10.68.

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.18; H, 4.58. Found: C, 68.52; H, 4.59.

(17) These were routinely performed using microscope slides bearing a silica gel layer and ethyl acetate–petroleum ether (1:1) containing a few drops of acetic anhydride as developing solvent. The anhydrides A and B had the same R_f values but were distinguishable by the observation that the former showed a yellow spot in both visible and ultraviolet light, whereas the latter was barely apparent in visible, but showed as a dark spot in ultraviolet light.

Dehydrootobain (**5**).—A solution of the preceding diol (110 mg.) in ethyl acetate (10 ml.) was stirred in a hydrogen atmosphere with 10% palladium–carbon catalyst (20 mg.). When uptake was complete (2 hr.) the mixture was filtered and evaporated to yield a gum which was dissolved in benzene and chromatographed on alumina (Spence, type H). Elution with light petroleum gave a solid (43 mg.) which was recrystallized from chloroform–methanol to give **2,3-dimethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene** as needles, m.p. 184–185°, undepressed by an authentic specimen of dehydrootobain (m.p. 185–187°) and with identical infrared spectrum.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 75.08; H, 5.24.

Further elution with benzene gave a pale yellow gum (68 mg.) which crystallized from methanol to give a product,[18] m.p. 131–132°, λ (μ) 2.92, 6.10, 6.25, 6.73, 8.10, 8.82, 9.56, and 10.70.

6,7-Methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)-naphthalene-2,3-dicarboxylic Acid Dimethyl Ester (**19**, R = CH_3).—The anhydride B (100 mg.) was heated under reflux for 1.25 hr. with a solution of potassium hydroxide (50 mg.) in methanol (15 ml.) and the mixture was concentrated under reduced pressure to 3 ml., diluted with water (10 ml.), and acidified by dropwise addition of concentrated hydrochloric acid. The resultant precipitate (91 mg.) was collected, washed with water, and dried to give the dicarboxylic acid (**19**, R = H), m.p. 140–156° (frothing), with resolidification at 180° and remelting at 261–265°.

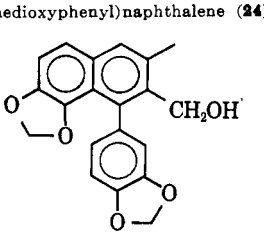
A solution of excess diazomethane in ether was added to the dicarboxylic acid (90 mg.) in dimethoxyethane (2 ml.) at −12°, the mixture was allowed to reach room temperature over 15 min., then evaporated to give the crude dimethyl ester, m.p. 220–228°. Recrystallization from methanol–acetone gave **6,7-methylenedioxy-1-(2′-bromo-4′,5′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic acid dimethyl ester** as small needles, m.p. 227–228°, λ (μ) 5.76, 5.83, 6.10, 6.20, 6.68, 6.75, 8.08, 8.91, 9.70, and 10.84.

Anal. Calcd. for $C_{22}H_{15}O_8Br$: C, 54.21; H, 3.10; Br, 16.40. Found: C, 53.92; H, 3.23; Br, 16.29.

2,3-Dimethyl-6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**Dehydroepigalbacin, 2**).—To a stirred suspension of lithium aluminum hydride (260 mg.) and aluminum chloride (250 mg.) in ether (10 ml.) was added a solution of the dimethyl ester (**19**, R = CH_3, 260 mg.) in dimethoxyethane (10 ml.). The mixture was stirred overnight at room temperature and worked up in the usual way, and the product was crystallized from methanol to give the crude diol (**20**), m.p. 170–175°, which gave a negative Beilstein test. A solution of the crude diol (160 mg.) in ethyl acetate (15 ml.) was hydrogenated using 10% palladium–carbon catalyst (30 mg.). The product (63 mg., m.p. 161–165° after one crystallization from chloroform–methanol) was dissolved in benzene and chromatographed on alumina (Spence H). Elution with benzene–petroleum ether (1:4) gave a solid which on crystallization from chloroform–methanol gave dehydroepigalbacin as needles, m.p. 174–175°, undepressed by an authentic specimen, m.p. 173–173.5°, and with identical infrared spectrum in carbon tetrachloride solution.

Treatment of 3,4-Methylenedioxyphenylpropiolic Acid with N,N-Dicyclohexylcarbodiimide.—To a solution of the acid (252 mg.) in dimethoxyethane (5 ml.) at −18° was added a solution of dicyclohexylcarbodiimide (136 mg.) in the same solvent (5 ml.). After standing at this temperature for 18 hr., the mixture was filtered to remove dicyclohexylurea; the filtrate was evaporated to yield a gummy solid (294 mg.) which on trituration with ether

(18) This is presumed to be 3-methyl-2-hydroxymethyl-7,8-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene (**24**). The proton magnetic resonance spectrum includes signals at δ 4.50 characteristic of a $PhCH_2OH$ system and at 2.63 (J = 1 c.p.s.) characteristic of the $PhCH_3$ system coupled to an adjacent proton.



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yielded yellow crystals of **6,7-methylenedioxy-1-(3′,4′-methylenedioxyphenyl)naphthalene-2,3-dicarboxylic anhydride**, m.p. 220–228°, with infrared spectrum identical with an authentic specimen.

Acknowledgment.—The award of a research grant (G-14528) from the National Science Foundation is gratefully acknowledged.

Characterization and Synthesis of a Monocyclic Eleven-Carbon Acid Isolated from a California Petroleum*,[1]

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A C_{11} monocyclic acid has been isolated from a California petroleum by methods involving fractional distillation, a sequence of gas chromatographies, and crystallization of the amide. The structure, deduced largely from application of physical methods, was established by comparison with a synthetic sample as *trans*-2,2,6-trimethylcyclohexylacetic acid. Both *cis* and *trans* isomers of this structure were synthesized from ionone. Interesting features of the n.m.r. spectra of these isomers are discussed, as are certain unexpected features of the mass spectrum. 5-Cyclopentylhexanamide was synthesized, and its mass spectrum was determined for comparison purposes.

Although the acidic components of petroleum, commonly termed naphthenic acids, have been the subject of intensive investigation by several highly competent chemists,[2] the number of component acids that have been identified remains small. Lochte and co-workers[2] succeeded in isolating and identifying several acyclic and monocyclic acids containing less than ten carbon atoms; however, in the range of greatest abundance of naphthenic acids, the C_{10} to C_{20} level, the only acids identified, other than normal isomers, are the two C_{10} isomers, *cis*- and *trans*-2,2,6-trimethylcyclohexanecarboxylic acid. The chief deterrent to these investigations has been the formidable task of separating the remarkably complex mixture which comprises the naphthenic acids. The two C_{10} acids just cited were separated by virtue of the severe hindrance at the carboxyl group.

A current surge of interest in the nature of components of petroleum appears to be especially concerned with theories of the origin of petroleum. The evolution of petroleum, more or less directly, from plants has received considerable support, especially by recent reports[3] of the isolation of isoprenoid hydrocarbons from petroleum. It has been suggested that a major source of the petroleum hydrocarbons consists of carboxylic acids[4]; however, in the molecular weight range above ten carbons only the normal fatty acids had been isolated prior to our current investigations. We have reported[5] the separation and identification of acyclic isoprenoid acids at the C_{14}, C_{15}, C_{19}, and C_{20} molecular weights. The present report is concerned primarily with isolation and identification of a cyclic C_{11} acid which also proves to have an isoprenoid structure.

The acids used for this investigation were extracted, prior to cracking, from middle distillates of a San Joaquin Valley naphthenic-type crude.[6] A sample of these acids which had been separated from phenols by esterification of the acids, followed by saponification, showed a significant absorption in the ultraviolet [λ_{max} 197 mμ (ϵ 2920) based on an average mol. wt. of 214]; however, this is probably owing to aromatic acids rather than alkenoic acids. There is an additional smaller maximum or shoulder at about 223 mμ ($\epsilon \sim 700$), which is characteristic of aromatic acids; furthermore, the acids recovered after vigorous oxidation with potassium permanganate showed an ultraviolet absorption similar to that observed before oxidation. There were present no significant amounts of severely hindered acids. Direct acid-catalyzed esterification for 4 hr. at 30°, with a large excess of methanol, left only 4% of acids unesterified, and a second esterification of the surviving acids in refluxing methanol left only 0.5% of the original acids unesterified. Gas chromatography of the esters from the second esterification gave a tracing very similar to that obtained from the esters from the first esterification. The presence of significant quantities of acid-sensitive molecules was contraindicated by examination of samples of methyl esters prepared by acid-catalyzed esterification, from the silver salt and methyl iodide, or by use of diazomethane. Gas chromatography, and in some instances rechromatography of collected fractions, failed to reveal significant differences in these lots of esters.

Gas chromatography of the methyl naphthenates on various partitioning agents gave a continuum extending over 0.5 hr. or longer, with only a few broad peaks projecting in the region representing esters with more than ten carbons. Separation was improved somewhat and waiting for elution of higher molecular weight material was eliminated by gas chromatography of cuts from a rather rough fractional distillation. The complexity of the mixture is illustrated by gas chromatography (Figure 1) of the fraction of b.p. 130–135° (13 mm.). When cut C, Figure 1, was rechro-

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(2) The earlier investigations of naphthenic acids, as well as the modern investigations at the University of Texas, are described by H. L. Lochte and E. R. Littmann, "The Petroleum Acids and Bases," Chemical Publishing Co., New York, N. Y., 1955.

(3) (a) R. A. Dean and E. V. Whitehead, *Tetrahedron Letters*, **No. 21**, 768 (1961); (b) J. G. Bendoraitis, B. L. Brown, and L. S. Hepner, Sixth World Petroleum Congress, Frankfort, section V, Paper 15, June 1963; (c) J. J. Cummins and W. E. Robinson, *J. Chem. Eng. Data*, **9**, 304 (1964).

(4) J. E. Cooper and E. E. Bray, *Geochim. Cosmochim. Acta*, **27**, 1113 (1963).

(5) J. Cason and D. W. Graham, *Tetrahedron*, in press.

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