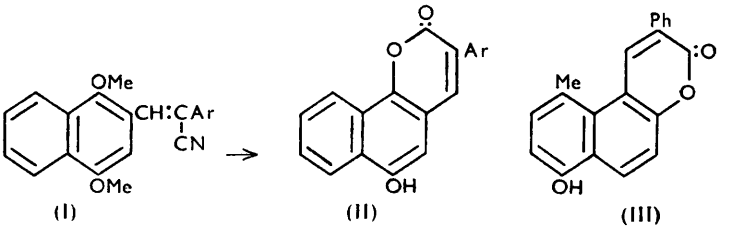
343. *Further Studies of Dihydroxynaphthalenes.*

By Ng. Ph. Buu-Hoï and Denise Lavit.

Syntheses are reported of several mono- and di-substituted derivatives of dihydroxy- and dimethoxy-naphthalenes (methyl homologues, allyl and benzyl derivatives, aldehydes, ketones), and the positions of the substituents are discussed. The conversion of dihydroxynaphthalenes into benzocoumarins and other heterocyclic sytems is investigated.

It was recently found that treatment of dimethoxynaphthalenes with dimethylformamide, and Wolff–Kishner reduction of the resulting dimethoxynaphthaldehydes, provided a convenient route to methyl-substituted dihydroxynaphthalenes.[1] This method has now been applied to the preparation of methyl-substituted 1 : 4- and 1 : 6-dihydroxynaphthalene. Formylation of 1 : 4-dimethoxynaphthalene readily gave 1 : 4-dimethoxy-2-naphthaldehyde, which Sah[2] claimed to have obtained by a Gattermann reaction from 1 : 4-dimethoxynaphthalene but whose properties differed considerably from those reported by that author. The constitution of our aldehyde was established, not only by the preparation therefrom of 1 : 4-dihydroxy-2-methylnaphthalene, but also by formation, with arylacetonitriles, of acrylonitriles (I), which gave 3-aryl-6-hydroxy-7 : 8-benzocoumarins (II) on demethylation with pyridine hydrochloride; this reaction proves the *ortho*-position of the aldehyde function in respect of a methoxy-group.



(I) (II) (III)

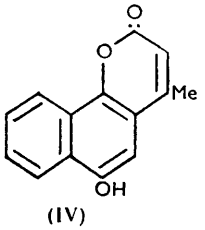
In the 1 : 6-dihydroxynaphthalene group, 1 : 6-dihydroxy-4-methylnaphthalene was prepared by demethylation of 4 : 7-dimethoxy-1-methylnaphthalene; formylation of this ether gave 2 : 5-dimethoxy-8-methyl-1-naphthaldehyde, in whose molecule the *ortho*-position of the formyl group was confirmed by conversion of its condensation product with benzyl cyanide into the benzocoumarin (III). Reduction of this aldehyde, followed by demethylation, led to 1 : 6-dihydroxy-4 : 5-dimethylnaphthalene, which was rapidly oxidised in air; an even greater autoxidability was encountered in the isomeric 4-ethyl-1 : 6-dihydroxynaphthalene, whose dimethyl ether was prepared by reduction of 1-acetyl-4 : 7-dimethoxynaphthalene.

In the 1 : 5-dihydroxynaphthalene series, the zinc chloride-catalysed reaction of benzyl chloride with its dimethyl ether yielded a mixture of 4-benzyl- and 4 : 8-dibenzyl-1 : 5-dimethoxynaphthalene; demethylation with pyridine hydrochloride, however, afforded the free dihydroxy-compound only from the disubstituted product, the monobenzyl derivative being converted into a compound containing more oxygen than that in

[1] Buu-Hoï and Lavit, *J.*, 1955, 2776.
[2] Sah, *Rec. Trav. chim.*, 1940, **59**, 1029, 1032, 1035.

the expected 4-benzyl-1 : 5-dihydroxynaphthalene. In the 2 : 7-dihydroxynaphthalene series, the constitution of 2 : 7-dimethoxy-1-naphthaldehyde was rigidly proved by oxidation to 2 : 7-dimethoxy-1-naphthoic acid; had the formyl group, by analogy with bromination of 2 : 7-dimethoxynaphthalene,[4] entered position 3, 3 : 6-dimethoxy-2-naphthoic acid would have resulted. The last named acid, first synthesised by Sunthankar and Gilman [5] by carboxylation of the lithio-derivative of 2 : 7-dimethoxynaphthalene, was now obtained by oxidation, with sodium hypobromite, of 2-acetyl-3 : 6-dimethoxynaphthalene, prepared by Friedel–Crafts acetylation of 2 : 7-dimethoxynaphthalene, proving thereby that formylation and Friedel–Crafts acylation follow different courses in this series. An attempt to prepare 2 : 7-dihydroxy-1 : 8-di-*n*-propylnaphthalene by dehydrogenation of the product of a Claisen rearrangement of 2 : 7-diallyloxynaphthalene was unsuccessful, because this rearrangement-product was highly autoxidisable and could not be obtained pure.

2 : 7-Dimethoxy-1-naphthaldehyde and 2 : 7-dimethoxy-8-methyl-1-naphthaldehyde readily condensed with arylacetonitriles to give acrylonitriles, which were converted into 3-aryl-2′-hydroxy-5 : 6-benzocoumarins; similarly, coumarins were obtained by demethylation of the acrylonitriles derived from 2 : 6-dimethoxy- and 2 : 6-dimethoxy-5-methyl-1-naphthaldehyde. Although condensation of α- and β-naphthol with β-ketonic esters has frequently been used for the preparation of coumarins,[6] the behaviour of dihydroxynaphthalenes in this reaction has hitherto been investigated only in the case of 1 : 5-dihydroxynaphthalene.[7] It was now found that 1 : 4-dihydroxynaphthalene readily gave 6-hydroxy-4-methyl-7 : 8-benzocoumarin (IV) with ethyl acetoacetate; for 1 : 6-dihydroxy-



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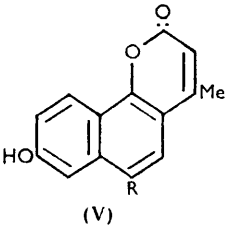

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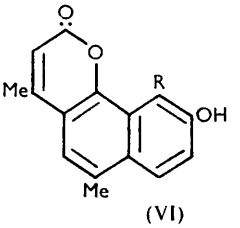
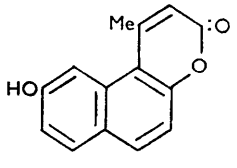


(VI)

naphthalene and its 4-methyl homologue, the condensation products can be formulated as 2′-hydroxy-4-methyl- (V; R = H) and 2′-hydroxy-4 : 6-dimethyl-7 : 8-benzocoumarin (V; R = Me), in view of the known higher reactivity of α-naphthol compared with the β-isomer.[8] The same argument is valid for assigning the structure of 3′-hydroxy-4 : 6-dimethyl-7 : 8-benzocoumarin (VI; R = H) to the condensation product of 1 : 7-dihydroxy-



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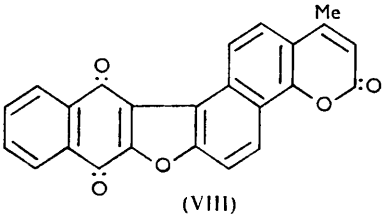

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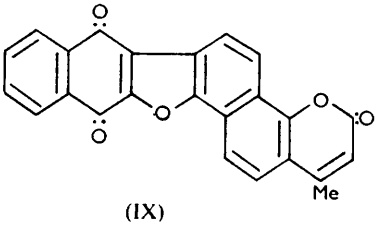

(IX)

4-methylnaphthalene. From the same viewpoint, an interesting difference was noted between 2 : 6- and 2 : 7-dihydroxynaphthalene, the former giving no condensation product with ethyl acetoacetate, whilst the latter gave 2′-hydroxy-4-methyl-5 : 6-benzocoumarin

[3] Buu-Hoï and Khenissi, *J.*, 1951, 2307.
[4] Ioffe and Fedorova, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 1079; Bell, personal communication.
[5] Sunthankar and Gilman, *J. Org. Chem.*, 1951, **16**, 8.
[6] Von Pechmann and Cohen, *Ber.*, 1884, **17**, 2187; Bartsch, *Ber.*, 1903, **36**, 1966; Bargellini, *Gazzetta*, 1925, **55**, 945; Baker, *J.*, 1925, **127**, 2349.
[7] Robinson and Weygand, *J.*, 1941, 386; Shamshurin, *J. Gen. Chem.* (*U.S.S.R.*), 1944, **14**, 885.
[8] Appel, *J.*, 1935, 1031.

(VII). 1-Hydroxy-5-methoxynaphthalene readily gave 1′-methoxy-4-methyl-7 : 8-benzocoumarin, which underwent demethylation with pyridine hydrochloride to the 1′-hydroxy-compound previously described by Robinson and Weygand.[7]

Condensation of 2 : 3-dichloro-1 : 4-naphthaquinone with 2′- and 1′-hydroxy-4-methyl-7 : 8-benzocoumarin in the presence of pyridine afforded 4′-methylcoumarino(7′ : 8′-4 : 3)- (VIII) and 4′-methylcoumarino(7′ : 8′-1 : 2)-brasan-5 : 10-quinone (IX) respectively; these high-melting compounds belong to a new type of complex oxygen-heterocyclic system.

Experimental

1 : 4-*Dimethoxy-2-naphthaldehyde*.—1 : 4-Dimethoxynaphthalene (91 g.; b. p. 175°/18 mm.) was prepared by methylation of 1 : 4-dihydroxynaphthalene (100 g.) with dimethyl sulphate (181 g.) and 10% aqueous potassium hydroxide (77 g.). A mixture of this dimethyl ether (50 g.), dimethylformamide (25 g.), dry toluene (50 c.c.), and phosphorus oxychloride (47 g.) was refluxed for 10 hr. with frequent shaking; on cooling, concentrated aqueous sodium acetate was added, and the mixture refluxed for 30 min. The aldehyde was then taken up in benzene, the benzene solution washed with dilute hydrochloric acid, then with water, and dried (Na_2SO_4), the solvent removed, and the residue fractionated *in vacuo*. 1 : 4-*Dimethoxy-2-naphthaldehyde* (25 g.), b. p. 199—200°/16 mm., formed stable, pale yellow needles, m. p. 117° (from ethanol), giving a red halochromy in sulphuric acid (Found : C, 72·2; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%). The product obtained by Sah [2] from a Gattermann reaction with 1 : 4-dimethoxynaphthalene, and considered to be 1 : 4-dimethoxy-2-naphthaldehyde, melted between 60° and 65° and darkened rapidly in the air; it was probably a mixture containing demethylation products of the aldehyde sought. 1 : 4-*Dimethoxy-2-naphthaldehyde thiosemicarbazone* formed yellowish prisms, m. p. 252° (decomp. >225°), from acetic acid (Found : C, 57·8; H, 5·0. $C_{14}H_{15}O_2N_3S$ requires C, 58·1; H, 5·2%).

1 : 4-*Dihydroxy-2-methylnaphthalene*.—A mixture of the foregoing aldehyde (28 g.), 95% hydrazine hydrate (12 g.), and diethylene glycol (150 c.c.) was heated until dissolution occurred; potassium hydroxide (12 g.) was then added, and heating renewed for a further 30 min. at 190—200°, with removal of water. After cooling, water was added, and the reduction product was taken up in benzene, washed first with dilute hydrochloric acid, then with water, dried (Na_2SO_4), and fractionated *in vacuo*; 1 : 4-dimethoxy-2-methylnaphthalene (21 g.) b. p. 170—171°/14 mm., n_D^{24} 1·6086, gave a picrate which crystallised as red prisms, m. p. 91°, from ethanol. A mixture of this dimethyl ether (2 g.) and pyridine hydrochloride (12 g.) was refluxed for 10 min., water was added after cooling, and the demethylation product was taken up in ether; the ethereal solution was washed with a little cold water and dried (Na_2SO_4), and the residue from evaporation of the solvent recrystallised from toluene. 1 : 4-Dihydroxy-2-methylnaphthalene formed colourless needles, m. p. 175°, becoming grey in the air. The m. p. recorded [9] varies from 160° to 177—178°. The procedure described here provides a convenient method for preparing this biologically important substance.

6-*Hydroxy-4-methyl-7 : 8-benzocoumarin* (IV).—A cooled solution of 1 : 4-dihydroxynaphthalene (4 g.) and ethyl acetoacetate (10 g.) in ethanol (40 c.c.) was saturated with hydrogen chloride, and the mixture kept for 4 hr.; the precipitated *product* was collected, dried, and recrystallised from toluene, giving yellow prisms (3·2 g.), m. p. 206° (Found : C, 74·0; H, 4·6. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

β-(1 : 4-*Dimethoxy-2-naphthyl*)-α-*phenylacrylonitrile* (I; Ar = Ph).—A solution of 1 : 4-dimethoxy-2-naphthaldehyde (5 g.) and benzyl cyanide (2·7 g.) in warm ethanol (100 c.c.) was shaken with a few drops of 20% aqueous sodium hydroxide, and the mixture kept for 30 min.; the oil obtained on dilution with water solidified to a crystalline mass (6 g.). Recrystallisation from ethanol afforded pale yellow needles, m. p. 120°, giving a red halochromy in sulphuric acid (Found : C, 81·9; H, 5·5. $C_{21}H_{17}O_2N$ requires C, 80·0; H, 5·4%). Similar *acrylonitriles* are listed in Table 1.

6-*Hydroxy-3-phenyl-7 : 8-benzocoumarin* (II; Ar = Ph).—The foregoing nitrile (5·5 g.) was treated with boiling pyridine hydrochloride (35 g.) for 10 min., water added on cooling, and the mixture refluxed for 5 min.; the precipitate formed yellow needles (3·6 g.), m. p. 272° (from ethanol–toluene), whose solutions gave a strong green fluorescence (Found : C, 79·0; H, 4·1. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%). Similar *coumarins* are listed in Table 2.

[9] Fries and Lohmann, *Ber.*, 1921, **54**, 2912; Sah, *loc. cit.*; MacCorquodale *et al.*, *J. Biol. Chem.*, 1939, **131**, 357; Giral, *Anales. Fis. Quim.*, 1933, **31**, 861.

TABLE 1. αβ-*Disubstituted acrylonitriles.*[a]

	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
α-*p*-Chlorophenyl-β-(1 : 4-dimethoxy-2-naphthyl)-	140°	$C_{21}H_{16}O_2NCl$	71·9	4·8	72·0	4·6
α-*o*-Chlorophenyl-β-(1 : 4-dimethoxy-2-naphthyl)-	123	$C_{21}H_{16}O_2NCl$	71·8	4·9	72·0	4·6
α-*p*-Bromophenyl-β-(1 : 4-dimethoxy-2-naphthyl)-	144	$C_{21}H_{16}O_2NBr$	63·8	4·0	63·9	4·1
β-(1 : 4-Dimethoxy-3-methyl-2-naphthyl)-α-phenyl-[b] ...	149	$C_{22}H_{19}O_2N$	79·9	5·8	80·2	5·8
β-(2 : 7-Dimethoxy-1-naphthyl)-α-phenyl-	116	$C_{21}H_{17}O_2N$	79·8	5·5	80·0	5·4
α-*p*-Chlorophenyl-β-(2 : 7-dimethoxy-1-naphthyl)-	141	$C_{21}H_{16}O_2NCl$	72·2	4·5	72·0	4·6
α-*p*-Bromophenyl-β-(2 : 7-dimethoxy-1-naphthyl)-	161	$C_{21}H_{16}O_2NBr$	63·6	4·0	63·9	4·1
β-(2 : 7-Dimethoxy-8-methyl-1-naphthyl)-α-phenyl- ...	117	$C_{22}H_{19}O_2N$	80·4	5·7	80·2	5·8
β-(2 : 6-Dimethoxy-1-naphthyl)-α-phenyl-	128	$C_{27}H_{17}O_2N$	79·9	5·4	80·0	5·4
α-*p*-Chlorophenyl-β-(2 : 6-dimethoxy-1-naphthyl)-	157	$C_{21}H_{16}O_2NCl$	71·9	4·8	72·0	4·6
β-(2 : 6-Dimethoxy-5-methyl-1-naphthyl)-α-phenyl- ...	132	$C_{22}H_{19}O_2N$	80·0	6·0	80·2	5·8
α-*p*-Chlorophenyl-β-(2 : 8-dimethoxy-5-methyl-1-naphthyl)-	190	$C_{22}H_{18}O_2NCl$	72·2	4·8	72·5	5·0
β-(2 : 5-Dimethoxy-8-methyl-1-naphthyl)-α-phenyl- ...	139	$C_{22}H_{19}O_2N$	80·0	5·8	80·2	5·8
β-(1-Methoxy-4-methyl-2-naphthyl)-α-phenyl-	86	$C_{21}H_{17}ON$	84·2	5·8	84·3	5·7

[a] All substances were crystallised from ethanol; the halochromy in sulphuric acid varied from red to brown, except for the last substance which gave a green colour.

[b] This nitrile was prepared from benzyl cyanide and the formylation product of 1 : 4-dimethoxy-2-methylnaphthalene; this aldehyde was characterised as its *thiosemicarbazone*, pale yellow needles, m. p. 223° (decomp. >205°) (from ethanol) (Found: C, 59·1; H, 5·5. $C_{15}H_{17}O_2N_3S$ requires C, 59·4; H, 5·6%).

TABLE 2. 3-*Substituted benzocoumarins.*[a]

Benzocoumarins	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
3-*p*-Chlorophenyl-6-hydroxy-7 : 8-[b]	306°	$C_{19}H_{11}O_3Cl$	70·7	3·2	70·6	3·4
3-*o*-Chlorophenyl-6-hydroxy-7 : 8-	299	$C_{19}H_{11}O_3Cl$	70·2	3·3	70·6	3·4
3-*p*-Bromophenyl-6-hydroxy-7 : 8-	324	$C_{19}H_{11}O_3Br$	62·4	3·1	62·1	3·0
6-Hydroxy-5-methyl-3-phenyl-7 : 8-	240	$C_{20}H_{14}O_3$	79·1	4·5	79·4	4·6
6-Methyl-3-phenyl-7 : 8-	164	$C_{20}H_{14}O_2$	83·6	5·1	83·9	4·9
2′-Hydroxy-3-phenyl-5 : 6-	258	$C_{19}H_{12}O_3$	78·9	4·4	79·2	4·2
3-*p*-Chlorophenyl-2′-hydroxy-5 : 6-	288	$C_{19}H_{11}O_3Cl$	70·3	3·3	70·6	3·4
3-*p*-Bromophenyl-2′-hydroxy-5 : 6-	307	$C_{19}H_{11}O_3Br$	61·9	3·2	62·1	3·0
2′-Hydroxy-1′-methyl-3-phenyl-5 : 6-	261	$C_{20}H_{14}O_3$	79·3	4·5	79·4	4·6
3′-Hydroxy-3-phenyl-5 : 6-	261	$C_{19}H_{12}O_3$	79·3	4·1	79·2	4·2
3-*p*-Chlorophenyl-3′-hydroxy-5 : 6-	277	$C_{19}H_{11}O_3Cl$	70·3	3·2	70·6	3·4
3′-Hydroxy-4′-methyl-3-phenyl-5 : 6-	299	$C_{20}H_{14}O_3$	79·3	4·5	79·4	4·6
3-*p*-Chlorophenyl-1′-hydroxy-4′-methyl-5 : 6-	335	$C_{20}H_{13}O_3Cl$	71·0	4·0	71·2	3·9
4′-Hydroxy-1′-methyl-3-phenyl-5 : 6-	254	$C_{20}H_{14}O_3$	79·1	4·6	79·4	4·6

[a] All substances were crystallised from ethanol–toluene or acetic acid, forming pale yellow or grey-tinged needles, soluble in aqueous alkalis to yellow solutions; the toluene solutions showed strong fluorescence.

[b] The structures of this and the four following substances resemble that of naphthotocopherol, a cyclisation product of α-phylloquinol possessing both vitamin E and vitamin K activities (Tishler, Fieser, and Wendler, *J. Amer. Chem. Soc.*, 1940, **62**, 1982).

1 : 6-*Dihydroxy*-4-*methylnaphthalene*.—A mixture of 1 : 6-dimethoxy-4-methylnaphthalene[10] (3 g.) and pyridine hydrochloride (18 g.) was refluxed for 8 min., and water (40 c.c.) was added after cooling; the demethylation-product was taken up in ether, the ethereal solution washed with water and dried (Na_2SO_4), and the residue quickly crystallised twice from benzene (charcoal). The *dihydroxy-compound* (1·8 g.) formed grey-tinged, autoxidisable needles, m. p. 132°, giving yellow alkaline solutions (Found: C, 75·6; H, 5·7. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·7%). After a brief boiling of its pyridine (5 c.c.) solution with 2 : 3-dichloro-1 : 4-naphthaquinone, this compound (0·25 g.) yielded a *brasanquinone*,[11] as sublimable, brown-red needles (0·3 g.; from nitrobenzene), m. p. >350°, giving a turquoise-blue halochromy in sulphuric acid (Found: C, 76·8; H, 3·9. $C_{21}H_{12}O_4$ requires C, 76·8; H, 3·7%).

2 : 5-*Dimethoxy*-8-*methyl*-1-*naphthaldehyde*.—A mixture of 1 : 6-dimethoxy-4-methylnaphthalene (16·5 g.), dimethylformamide (8 g.), phosphorus oxychloride (14·5 g.), and toluene (5 c.c.) was refluxed for 6 hr., and the mixture worked up in the usual way. Distillation *in vacuo* gave a mixture (16 g.) boiling at 227—229°/17 mm., which yielded on fractional recrystallisation

[10] Buu-Hoï and Lavit, *Bull. Soc. chim. France*, 1955, 1419.
[11] Buu-Hoï, *J.*, 1952, 489.

from ethanol: (*a*) 2 : 5-*dimethoxy*-8-*methyl*-1-*naphthaldehyde* (8 g.), pale yellow prisms, m. p. 98° (Found: C, 73·3; H, 5·9. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%) [*thiosemicarbazone*, yellowish needles, m. p. 276° (decomp. >250°), from acetic acid (Found: C, 59·1; H, 5·4. $C_{15}H_{17}O_2N_3S$ requires C, 59·4; H, 5·6%)], and (*b*) an isomeric *aldehyde* (0·6 g.), possibly 1 : 6-dimethoxy-4-methyl-2-naphthaldehyde, pale yellow needles, m. p. 90°, showing a depression of m. p. on admixture with the main product (Found: C, 72·8; H, 6·0%).

1 : 6-*Dihydroxy*-4 : 5-*dimethylnaphthalene*.—2 : 5-Dimethoxy-8-methyl-1-naphthaldehyde (5 g.) yielded on the usual Wolff–Kishner reduction 1 : 6-*dimethoxy*-4 : 5-*dimethylnaphthalene* (4 g.), pale yellow oil, b. p. 187—188°/17 mm., $n_D^{26\cdot5}$ 1·5995, which solidified to prisms, m. p. 48° (Found: C, 77·7; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%), giving a picrate, deep orange needles, m. p. 96° (from ethanol). 1 : 6-*Dihydroxy*-4 : 5-*dimethylnaphthalene*, obtained on demethylation, formed readily autoxidisable, grey-tinged needles, m. p. 153—154°, from benzene (Found: C, 76·3; H, 6·3. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

1-*Acetyl*-4 : 7-*dimethoxynaphthalene*.—To a cooled solution of 1 : 6-dimethoxynaphthalene (26·5 g.) and acetyl chloride (13 g.) in dry nitrobenzene (125 c.c.), aluminium chloride (21 g.) was added in portions with stirring, and the mixture kept overnight at room temperature. After decomposition with water and steam-distillation of the solvent, the product was worked up in the usual way, and gave a *ketone*, b. p. 232—235°/20 mm., crystallising as colourless needles (20 g.), m. p. 67°, from ethanol (Found: C, 72·9; H, 6·3. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

2-(4 : 7-*Dimethoxy*-1-*naphthyl*)*cinchoninic Acid*.—A solution of the foregoing ketone (3 g.), isatin (2·1 g.), and potassium hydroxide (2·2 g.) in ethanol (50 c.c.) was refluxed for 24 hr.; water was then added, the neutral impurities were removed by ether-extraction and the aqueous layer was acidified with acetic acid. The *cinchoninic acid* (95% yield) formed yellowish needles, m. p. 226°, from ethanol (Found: C, 73·4; H, 4·9. $C_{22}H_{17}O_4N$ requires C, 73·5; H, 4·7%). Thermal decarboxylation afforded 2-(4 : 7-*dimethoxy*-1-*naphthyl*)*quinoline*, colourless prisms, m. p. 121° (from ethanol) (Found: C, 79·7; H, 5·7. $C_{21}H_{17}O_2N$ requires C, 80·0; H, 5·4%).

4-*Ethyl*-1 : 6-*dimethoxynaphthalene*.—Wolff–Kishner reduction of 1-acetyl-4 : 7-dimethoxynaphthalene (13 g.) gave a very poor yield of 4-*ethyl*-1 : 6-*dimethoxynaphthalene* (2·5 g.) as a pale yellow oil, b. p. 196—197°/20 mm., n_D^{26} 1·6040 (Found: C, 77·7; H, 7·4. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%); demethylation afforded an alkali-soluble, viscous yellow oil, which rapidly became a black resin on exposure to the air.

2′-*Hydroxy*-4-*methyl*-7 : 8-*benzocoumarin* (V; R = H).—Obtained in 80% yield from 1 : 6-dihydroxynaphthalene (4 g.) and ethyl acetoacetate (10 g.) in ethanol (40 c.c.) saturated with hydrogen chloride, this *coumarin* formed colourless, sublimable needles, m. p. 260° (nitrobenzene), soluble in aqueous alkali with a greenish-yellow colour (Found: C, 74·0; H, 4·6. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

4′-*Methylcoumarino*(7′ : 8′-4 : 3)*brasan*-5 : 10-*quinone* (VIII).—A solution of the foregoing coumarin (0·3 g.) and 2 : 3-dichloro-1 : 4-naphthaquinone (0·3 g.) in dry pyridine (5 c.c.) was refluxed for 30 min.; the precipitated *product* was washed with benzene, and recrystallised as brown needles, m. p. >350° (nitrobenzene), giving a deep violet halochromy in sulphuric acid (Found: C, 75·6; H, 2·9. $C_{24}H_{12}O_5$ requires C, 75·8; H, 3·2%).

2′-*Hydroxy*-4 : 6-*dimethyl*-7 : 8-*benzocoumarin* (V; R = Me).—Prepared from 1 : 6-dihydroxy-4-methylnaphthalene (1 g.) and ethyl acetoacetate (2·5 g.) in ethanol (10 c.c.), this *coumarin* (1·2 g.) formed yellowish, sublimable needles, m. p. 323°, from nitrobenzene (Found: C, 74·7; H, 5·1. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%).

3′-*Hydroxy*-4 : 6-*dimethyl*-7 : 8-*benzocoumarin* (VI; R = H).—This *coumarin* (0·6 g.), prepared from 1 : 7-dihydroxy-4-methylnaphthalene (0·75 g.) and ethyl acetoacetate (2 g.), formed yellowish leaflets, m. p. 321°, from nitrobenzene (Found: C, 74·8; H, 4·8%); 3′-*hydroxy*-4 : 6 : 4′-*trimethyl*-7 : 8-*benzocoumarin* (VI; R = Me), obtained from 1 : 7-dihydroxy-4 : 8-dimethylnaphthalene (0·75 g.), formed pale yellow, sublimable needles (0·5 g.), m. p. 315°, from nitrobenzene (Found: C, 75·3; H, 5·2. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

Benzylation of 1 : 5-*Dimethoxynaphthalene*.—A solution of this dimethyl ether (50 g.) and benzyl chloride (34 g.) in dry chloroform (500 c.c.) was refluxed with finely powdered zinc chloride (15 g.) for 6 hr., water was added, and the chloroform layer was washed with aqueous sodium hydroxide, then with water, and dried (Na_2SO_4). Fractionation *in vacuo* of the residue from evaporation of the solvent yielded: (*a*) 4-*benzyl*-1 : 5-*dimethoxynaphthalene* (22 g.), b. p. 253—255°/14 mm., which crystallised as colourless needles, m. p. 115°, from ethanol (Found: C, 81·8; H, 6·3. $C_{19}H_{18}O_2$ requires C, 82·1; H, 6·5%); demethylation with pyridine hydrochloride gave a solid which crystallised from acetic acid as yellowish needles, m. p. 161°, which contained more oxygen than the expected 4-benzyl-1 : 5-dihydroxynaphthalene; (*b*)

4 : 8-*dibenzyl*-1 : 5-*dimethoxynaphthalene*, b. p. 310—312°/20 mm., crystallising as colourless leaflets (3 g.), m. p. 234°, from benzene (Found : C, 84·9; H, 6·3. $C_{26}H_{24}O_2$ requires C, 84·8; H, 6·5%); demethylation afforded **4 : 8-*dibenzyl*-1 : 5-*dihydroxynaphthalene***, an autoxidisable compound which formed colourless needles, m. p. 198°, from aqueous acetic acid (Found : C, 84·2; H, 5·7. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

1′-*Methoxy*-4-*methyl*-7 : 8-*benzocoumarin*.—A water-cooled solution of 1-hydroxy-5-methoxynaphthalene (4 g.) and ethyl acetoacetate (10 g.) in ethanol (40 c.c.) was saturated with hydrogen chloride for 2 hr., then left overnight. The precipitate obtained was washed with ethanol, and gave on recrystallisation grey-tinged prisms, m. p. 190° (from toluene) (Found : C, 75·1; H, 5·2. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). Demethylation with pyridine hydrochloride yielded 1′-hydroxy-4-methyl-7 : 8-benzocoumarin,[7] m. p. 302—303°.

4′-*Methylcoumarino*(7′ : 8′-1 : 2)*brasan*-5 : 10-*quinone* (IX), prepared by boiling for 5 min. a solution of 1′-hydroxy-4-methyl-7 : 8-benzocoumarin and 2 : 3-dichloro-1 : 4-naphthaquinone, formed brown-red prisms, m. p. > 350° (from nitrobenzene), giving a brown-violet halochromy with sulphuric acid (Found : C, 75·5; H, 3·0%).

2-*Acetyl*-3 : 6-*dimethoxynaphthalene*.—To an ice-cooled solution of 2 : 7-dimethoxynaphthalene (23 g.) and acetyl chloride (10 g.) in nitrobenzene (200 c.c.), aluminium chloride (18 g.) was added in portions with stirring, and the mixture left overnight at room temperature, then worked up in the usual way. The *ketone* (6·5 g.), b. p. 210—211°/12 mm., formed colourless needles, m. p. 65°, from light petroleum (Found : C, 72·8; H, 6·3%). It condensed with veratraldehyde in ethanol containing a few drops of aqueous sodium hydroxide, to give **3 : 6-*dimethoxy*-2-(3 : 4-*dimethoxycinnamoyl*)*naphthalene***, pale yellow needles, m. p. 109° (from ethanol) (blood-red halochromy in sulphuric acid) (Found : C, 72·9; H, 5·7. $C_{23}H_{22}O_5$ requires C, 73·0; H, 5·8%).

2-(3 : 6-*Dimethoxy*-2-*naphthyl*)*cinchoninic Acid*.—This *acid*, obtained by heating for 48 hr. a solution of 2-acetyl-3 : 6-dimethoxynaphthalene (2 g.), isatin (1·4 g.), and potassium hydroxide (1·5 g.) in ethanol (30 c.c.), formed pale yellow needles (0·5 g.), m. p. 230°, from ethanol (Found : C, 73·2; H, 4·8%).

3 : 6-*Dimethoxy*-2-*naphthoic Acid*.—To an aqueous solution of sodium hypobromite (prepared from 1·2 c.c. of bromine and 2·8 g. of sodium hydroxide in 13 c.c. of iced water), a solution of 2-acetyl-3 : 6-dimethoxynaphthalene (2 g.) in dioxan (5 c.c.) was added, and the mixture shaken for 1 hr.; the aqueous layer was then decanted, treated with a few c.c. of aqueous sodium hydrogen sulphite, and acidified with hydrochloric acid. 3 : 6-Dimethoxy-2-naphthoic acid [5] formed colourless needles (1 g.), m. p. 185°, from benzene. 2 : 7-Dimethoxy-1-naphthoic acid, prepared in poor yield by oxidation of the corresponding aldehyde (5 g.) with silver oxide (4 g.) in water at 60°, formed colourless prisms, m. p. 122°, from ligroin. Adams *et al.*[12] gave m. p. 112—113°.

Derivatives of **2 : 7-*Dihydroxynaphthalene***.—(*a*) A solution of 2 : 7-dihydroxynaphthalene (20 g.) and allyl bromide (34 g.) in acetone (200 c.c.) was refluxed with potassium carbonate (38 g.) for 3 hr., and the mixture poured into water. The supernatant oil was decanted, the allyl bromide in excess was evaporated, and the solid mass obtained recrystallised from ethanol, giving **2 : 7-*diallyloxynaphthalene*** (8 g.) as colourless needles, m. p. 62° (Found : C, 79·9; H, 6·7. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%); the picrate formed orange needles, m. p. 77°. Claisen rearrangement of this product, by boiling its diethylaniline solution for 1 hr., yielded an oil which darkened rapidly in the air and from which no solid derivative could be prepared.

(*b*) **2′-*Hydroxy*-4-*methyl*-5 : 6-*benzocoumarin*** (VII), prepared by keeping for 48 hr. a solution of 2 : 7-dihydroxynaphthalene (4 g.) and ethyl acetoacetate (10 g.) in ethanol (40 c.c.) saturated with hydrogen chloride, formed grey-tinged needles (1·2 g.), m. p. 277°, from nitrobenzene (Found : C, 74·0; H, 4·2%). No coumarin was obtained under the same conditions with 2 : 6-dihydroxynaphthalene.

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Department of Organic Chemistry,
The Radium Institute, University of Paris. [*Received, December 19th*, 1955.]

[12] Adams, Miller, McGrew, and Anderson, *J. Amer. Chem. Soc.*, 1942, **64**, 1795.