Naturally-occurring Compounds Related to Phenalenone. Part II.[1] The Synthesis of Haemocorin Aglycone†

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A synthesis of haemocorin aglycone (33; $R^1 = R^2 = H$) from 2,7-dibromo-3,6-dimethoxynaphthalene (24) is described. 2,3-Dihydro-4,9-dimethoxyphenalen-1-one (5) has also been prepared and some of its reactions have been investigated.

HAEMOCORIN is a red glycoside found in the bulbous roots of the Australian genus *Haemodorum corymbosum*. The structure of the derived aglycone [(**33**; $R^1 = R^2 = H$) or the tautomeric form (**34**; $R^1 = R^2 = H$)] was assigned on the basis of degradative studies, and comparison of the spectra of haemocorin with those of the aglycone monomethyl ethers A (**33**; $R^1 = Me$, $R^2 = H$) and B (**34**; $R^1 = H$, $R^2 = Me$) suggested that haemocorin should be represented as (**34**; $R^1 = H$, $R^2 = \beta$-cellobiose residue).[2] When it was first isolated haemocorin was the only plant product known with a structure based on the phenalenone nucleus. More recently, however, lachnanthocarpone (**14**; $R^1 = R^2 = H$), lachnanthoside [a bioside or diglycoside of the compound (**14**; $R^1 = OH$, $R^2 = H$)], and lachnanthofluorone (**35**) have been extracted from *Lachnanthes tinctoria*, another representative of the family Haemodoraceae.[3] All the other known naturally occurring derivatives of phenalenone (*e.g.* atrovenetin,[4] herqueinone,[4,5] norherqueinone,[4,5] and resistomycin [6]) are mould metabolites. Part I of this series described a synthesis of lachnanthocarpone. We now report a synthesis of the two dimethyl ethers of haemocorin aglycone, A (**33**; $R^1 = R^2 = Me$) and B (**34**; $R^1 = R^2 = Me$). Since the dimethyl ether A has previously been hydrolysed to the aglycone,[2b] the work described here completes a synthesis of haemocorin aglycone itself.

The previously described synthesis of lachnanthocarpone (**14**; $R^1 = R^2 = H$) [1] proceeded through the intermediate dihydrophenalenone (**13**; $R = H$). An obvious route to a phenalenone possessing the same pattern of oxygen and phenyl substitution as haemocorin aglycone was therefore to oxidise the dihydrophenalenone (**13**; $R = H$) to the enolic-α-diketone (**14**; $R^1 = OH$, $R^2 = Me$). In order to investigate the conditions required for such an oxidation, 2,3-dihydro-4,9-dimethoxyphenalenone (**5**) was synthesised as a model compound. 2,7-Dimethoxy-1-naphthaldehyde (**2**), prepared by Vilsmeier formylation of 2,7-dimethoxynaphthalene (**1**),[7] was treated with ethoxycarbonylmethylenetriphenylphosphorane in refluxing benzene. The resulting unsaturated ester (**3**) was hydrogenated to give ethyl β-(2,7-dimethoxy-1-naphthyl)propionate (**4**;

† Preliminary communication, B. Laundon and G. A. Morrison, *Chem. Comm.*, 1968, 1557.

[1] Part I, B. Laundon and G. A. Morrison, *J. Chem. Soc.* (*C*), 1971, **36**; *Tetrahedron Letters*, 1970, 2301.

[2] R. G. Cooke and W. Segal, *Austral. J. Chem.*, 1955, **8**, (*a*) p. 107; (*b*) p. 413; (*c*) R. G. Cooke, B. L. Johnson, and W. Segal, *ibid.*, 1958, **11**, 230.

[3] U. Weiss and J. M. Edwards, (*a*) *Tetrahedron Letters*, 1969, 4325; (*b*) *Phytochemistry*, 1970, **9**, 1653.

[4] D. H. R. Barton, P. de Mayo, G. A. Morrison, W. H. Schaeppi, and H. Raistrick, *Chem. and Ind.*, 1956, 551; D. H. R. Barton, P. de Mayo, G. A. Morrison, and H. Raistrick, *Tetrahedron*, 1959, **6**, 48; G. A. Morrison, I. C. Paul, and G. A. Sim, *Proc. Chem. Soc.*, 1962, 352; I. C. Paul and G. A. Sim, *J. Chem. Soc.*, 1965, 1097.

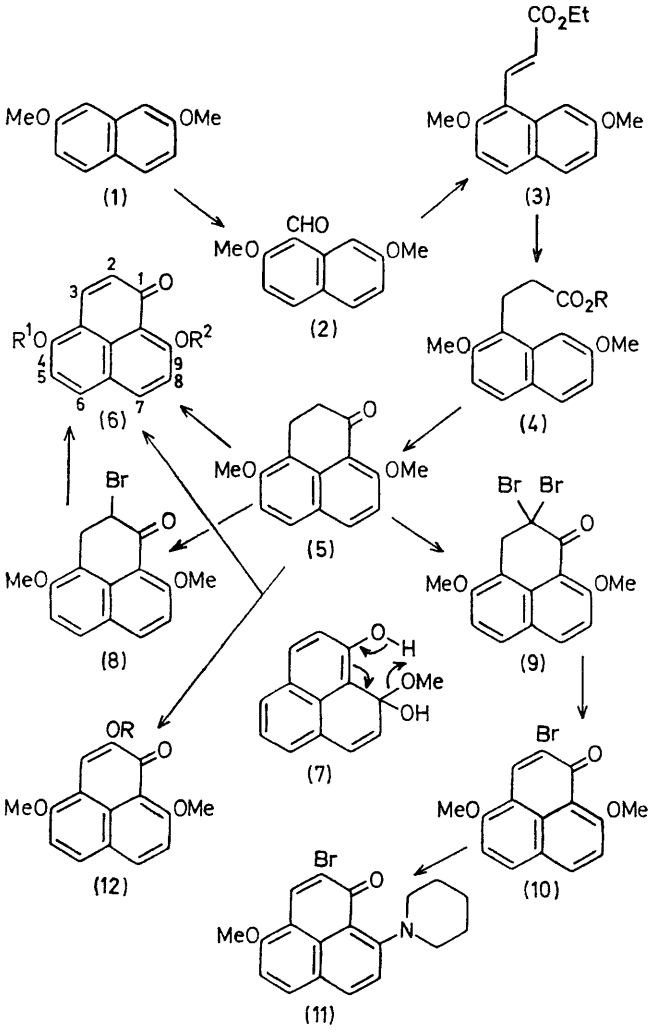
[5] J. S. Brooks and G. A. Morrison, *Tetrahedron Letters*, 1970, 963.

[6] H. Brockmann, E. Meyer, K. Schrempp, R. Reiners, and T. Reschke, *Chem. Ber.*, 1969, **102**, 1224; N. A. Bailey, C. P. Falshaw, W. D. Ollis, M. Watanabe, M. M. Dhar, A. W. Khan, and V. C. Vora, *Chem. Comm.*, 1968, 374.

[7] Ng. Ph. Buu-Hoï and D. Lavit, *J. Chem. Soc.*, 1955, 2776.

R = Et), which was subsequently saponified to afford the naphthylpropionic acid (4; R = H). Cyclisation of the acid (4; R = H) with polyphosphoric acid gave 2,3-dihydro-4,9-dimethoxyphenalenone (5) in an overall yield of 65% from the aldehyde (2).

Conversion of the dihydrophenalenone (5) into 2-hydroxy-4,9-dimethoxyphenalenone (12; R = H) was



attempted by a number of different methods. Direct oxidation with selenium dioxide gave 9-hydroxy-4-methoxyphenalenone (6; R^1 = Me, R^2 = H) as the only identifiable product. The same product was obtained when the dihydrophenalenone (5) was treated successively with *p*-nitrosodimethylaniline and ethanolic hydrochloric acid under conditions which have been employed successfully to convert other dihydrophenalenones into the corresponding 2-hydroxyphenalenones.[2c,8] In both cases demethylation probably occurred during the acid conditions of the work-up. That the hydroxy-group in the product was attached to C-9 followed from the appearance of an n.m.r. signal at τ −6·38, indicative of a strongly hydrogen-bonded hydroxy-group. Since both methoxy-groups in the dihydrophenalenone (5) bear the same vinylogous relationship to the carbonyl group, the exclusive isolation of the 9-hydroxy-derivative (6; R^1 = Me, R^2 = H) rather than a mixture containing some of the alternative demethylation product (6; R^1 = H, R^2 = Me) is of interest. The specificity may be due to the fact that intramolecular proton transfer is possible only in the intermediate (7) leading to the 9-hydroxy-compound.

Another approach to the oxidation of the model dihydrophenalenone (5) involved its conversion by treatment with trimethylanilinium tribromide [9] (1 equiv.) into the α-bromo-ketone (8), an unstable compound which was immediately treated with dimethyl sulphoxide and sodium hydrogen carbonate under the conditions of the Kornblum oxidation.[10] Once again, however, the only product isolated (after work-up with hydrochloric acid) was 9-hydroxy-4-methoxyphenalenone (6; R^1 = Me, R^2 = H).

The reaction of 2-bromophenalenone with piperidine can be controlled to give 2-piperidinophenalenone,[11] hydrolysis of which could give 2-hydroxyphenalenone. Accordingly, the dihydrophenalenone (5) was converted into 2-bromo-4,9-dimethoxyphenalenone (10) by treatment with trimethylanilinium tribromide [9] (2 equiv.), followed by dehydrobromination, with sodium methoxide, of the unstable αα-dibromo-ketone (9) which resulted. Treatment of the 2-bromophenalenone (10) with piperidine, however, gave a product in which a methoxy-group, and not the bromine atom had been replaced by the piperidino-group. By analogy with the hydrolytic demethylation of 4,9-dimethoxyphenalenone already discussed, this compound is represented by structure (11).

The dihydrophenalenone (5) was finally oxidised by direct oxygenation of its solution in t-butyl alcohol containing potassium t-butoxide.[12] The 2-hydroxy-4,9-dimethoxyphenalenone (12; R = H) obtained was characterised as its acetate (12; R = Ac); the reaction also gave 9-hydroxy-4-methoxyphenalenone (6; R^1 = Me, R^2 = H).

Having successfully completed the model sequence, we subjected the intermediate (13; R = H) [1] to the conditions established for the oxygenation of the dihydrophenalenone (5). However, although sufficient oxygen was consumed by the ketone (13; R = H), none of the required oxidation product was isolated. Treatment with *p*-nitrosodimethylaniline, followed by hydrolysis of the presumed azomethine intermediate, similarly failed to give any of the required 2-hydroxyphenalenone (14; R^1 = OH, R^2 = Me); attempted Kornblum oxidation [10] of the α-bromo-ketone (13; R = Br), obtained

[8] N. G. Buu-Hoï and P. Cagniant, *Rev. Sci.*, 1942, **86**, 176; *Compt. rend.*, 1942, **214**, 315.

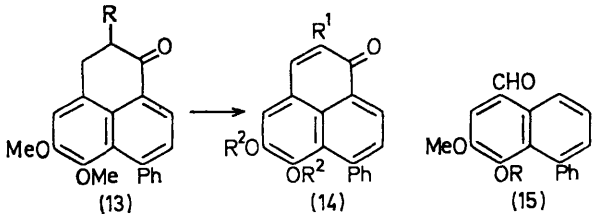
[9] W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, 1963, **19**, 861.

[10] L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 303.

[11] D. B. Capps, N. H. Cromwell, and S. E. Palmer, *J. Amer. Chem. Soc.*, 1951, **73**, 1226; *cf.* N. H. Cromwell, *ibid.*, 1959, **81**, 4702.

[12] *Cf.* E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1962, 1578.

by treatment of the compound (13; R = H) with trimethylanilinium tribromide (1 equiv.), gave a mixture of the phenalenone (14; R^1 = H, R^2 = Me) (identical with lachnanthocarpone orange dimethyl ether) [1] and its bromo-derivative (14; R^1 = Br, R^2 = Me), which were separated by preparative t.l.c.



The conversion of the dihydrophenalenone (13; R = H) into the hydroxyphenalenone (14; R^1 = OH, R^2 = Me) was not pursued further, since an alternative approach to the synthesis of haemocorin aglycone, which was investigated concurrently, proved to be more viable. However, the following attempt to utilise an earlier intermediate in the lachnanthocarpone synthesis was made. The aldehyde (15; R = Me) [1] was treated with methoxyacetyl chloride under the conditions of the Friedel–Crafts reaction, in the hope of achieving acylation at C-8. Intramolecular condensation of the resulting keto-aldehyde would then have given haemocorin aglycone dimethyl ether B (34; R^1 = R^2 = Me). The only product isolated, however, was the phenol (15; R = H); that it was the 4-methoxy-group which was demethylated followed from the observation that the remaining methoxy-group gave rise to an n.m.r. signal at τ 6·02. The 4-methoxy-group of the aldehyde (15; R = Me) is shielded by the *peri*-phenyl group and gives a signal at abnormally high field (τ 6·74).

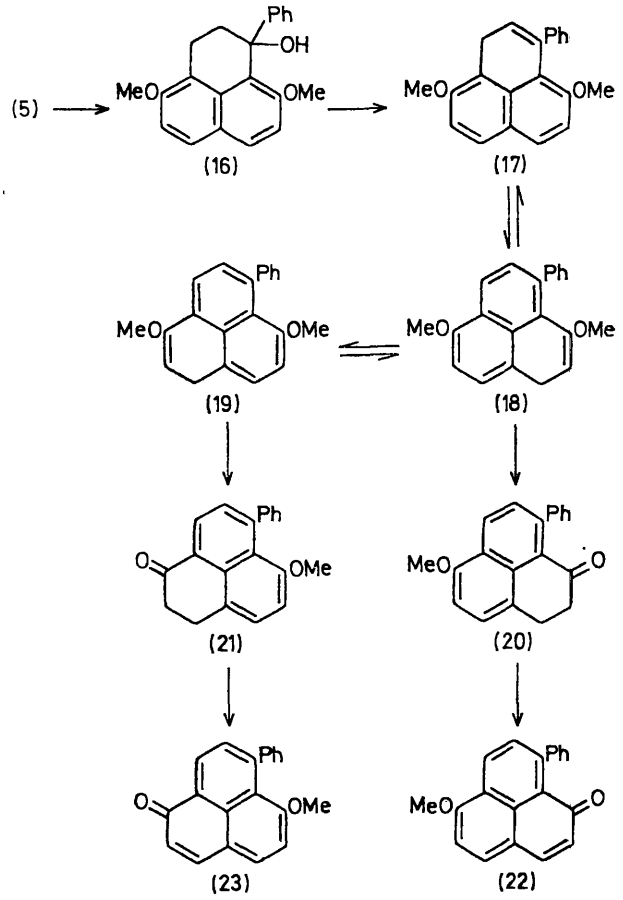
The synthetic route to haemocorin aglycone which ultimately proved successful involved the naphthalene (26; R^1 = R^2 = OMe) as an intermediate containing all the oxygen functions of the natural product in the form of methoxy-groups. The principles underlying the synthesis are best explained by describing the model reactions carried out to test the feasibility of the route.

As a model for compound (26; R^1 = R^2 = OMe), 2,7-dimethoxynaphthalene (1) was chosen. It was converted into 2,3-dihydro-4,9-dimethoxyphenalenone (5) as already described, and then into the carbinol (16) by means of a Grignard reaction with phenylmagnesium bromide. The carbinol (16) was not isolated, but was dehydrated with dilute hydrochloric acid, and the product was treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to give a mixture of the phenalenones (22) and (23). These were separated chromatographically and distinguished by their n.m.r. spectra; the methoxy-group of compound (23) absorbs at higher field (τ 6·45) than that of its isomer (22) (τ 5·99) as a result of strong shielding by the *peri*-phenyl substituent.

[13] For an account of the tautomerism of phenalenes, see D. H. Reid, *Quart. Rev.*, 1965, **19**, 274.

[14] R. G. Cooke, B. L. Johnson, and W. R. Owen, *Austral. J. Chem.*, 1960, **13**, 256.

Compounds (22) and (23) are formed by dehydrogenration of the dihydrophenalenones (20) and (21), respectively, and these in turn are formed by hydrolysis of the enol ethers (18) and (19) under the acid conditions employed in the dehydration of the carbinol (16). The enol ethers (18) and (19) are tautomers of the phenalene (17) initially formed by dehydration of the carbinol (16), and as such are in equilibrium with it.[13]

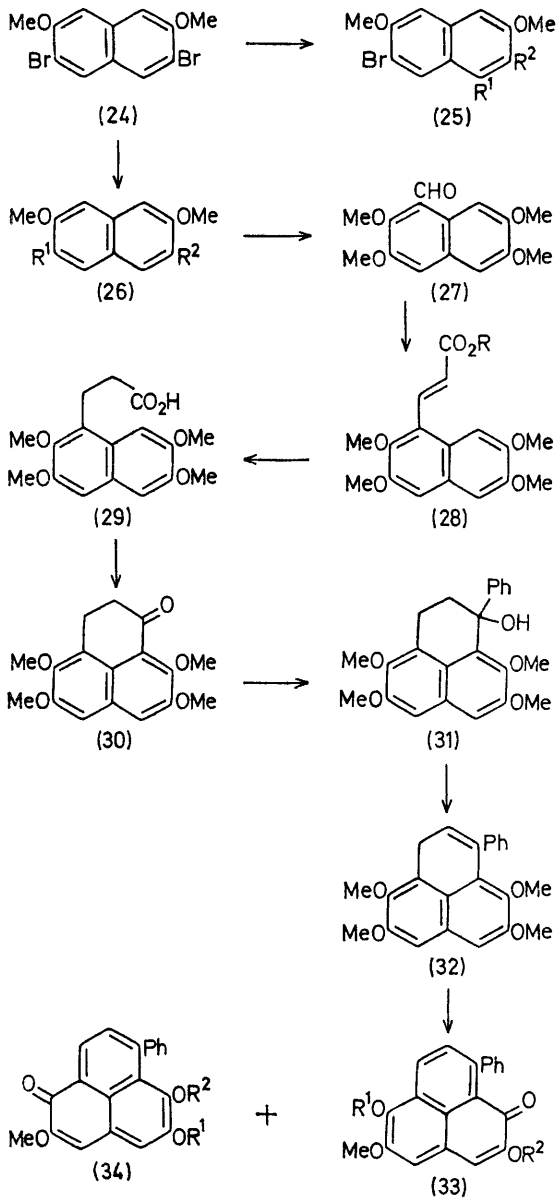


In order to apply the foregoing reaction sequence to a synthesis of haemocorin aglycone it was necessary to prepare 2,3,6,7-tetramethoxynaphthalene (26; R^1 = R^2 = OMe). A convenient precursor for this was 2,7-dibromo-3,6-dimethoxynaphthalene (24).[14] Attempts at direct displacement of the bromine atoms in this compound by alkoxy-groups [15] were unsuccessful. Treatment with sodium methoxide in dimethyl sulphoxide gave only 2,7-dimethoxynaphthalene (1), in a yield of 78%. Partial and selective dehalogenation of polyhalogenobenzenes by treatment with a solution of potassium t-butoxide in t-butyl alcohol and dimethyl sulphoxide have been reported;[16] the present reaction, like those earlier examples, probably proceeds through an aryl anion formed by direct attack of the anion derived from

[15] *Cf.* D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, 1960, **82**, 6412; M. R. V. Sahyun and D. J. Cram, *Org. Synth.*, 1965, **45**, 89.

[16] J. F. Bunnett and R. R. Victor, *J. Amer. Chem. Soc.*, 1968, **90**, 810.

dimethyl sulphoxide on the bromine atom. A different reaction occurred when the dibromo-compound (24) was treated at room temperature with potassium t-butoxide in dimethyl sulphoxide. The major product, obtained in a yield of 34% after purification, was assigned structure (25; R^1 = SMe, R^2 = OH) or (25; R^1 = OH, R^2 = SMe) on the basis of the analytical figures and spectra afforded by it and by its derived monoacetate. Analogous products have been obtained by similar treatment of other aromatic halides, and their mechanism of formation has been discussed.[17] The present example is remarkable for its specificity and for the relatively high yield of product.



Replacement of the bromine atoms of compound (24) with oxygen functions was finally achieved by treatment of the compound with an excess of n-butyl-lithium, and treatment of the resulting dilithio-derivative with methyl borate, water, and hydrogen peroxide.[18] In this way a mixture of the dihydric phenol (26; $R^1 = R^2$ = OH) and the phenol (26; R^1 = H, R^2 = OH) was obtained. The latter probably arose as a result of protonation of the intermediate aryl carbanion by methanol present in the methyl borate. The products were separated by chromatography and each was characterised by acetylation and by methylation.

The tetramethyl ether (26; $R^1 = R^2$ = OMe) obtained by methylation of the dihydric phenol (26; $R^1 = R^2$ = OH) was formylated in good yield (Vilsmeier) and the resulting aldehyde (27) was converted into the unsaturated acid (28; R = H) by condensation with ethoxycarbonylmethylenetriphenylphosphorane followed by saponification of the ester produced. Hydrogenation gave the naphthylpropionic acid (29), which was cyclised smoothly with polyphosphoric acid to 2,3-dihydro-4,5,8,9-tetramethoxyphenalenone (30).

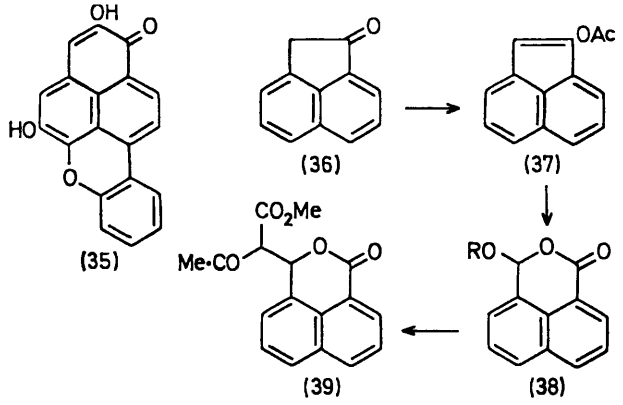
Reaction between the dihydrophenalenone (30) and phenylmagnesium bromide gave the stable carbinol (31), which had to be heated for 10 min. with aqueous methanolic hydrochloric acid in order to dehydrate it to the phenalene (32). The position of the styrenoid double bond was clear from the n.m.r. spectrum, which exhibited a triplet at τ 4·08 (C-2 vinyl proton) and a doublet at 6·10 (3-H_2). The stability of this phenalene to the acid conditions of the dehydration was unexpected, since the model phenalene (17) isomerised quickly with only a small amount of acid present. Isomerisation was, however, achieved by prolonging the dehydration conditions for a further 1 hr. The crude product from this reaction was dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, and a mixture of the dimethyl ethers A (33; $R^1 = R^2$ = Me) and B (34; $R^1 = R^2$ = Me) of haemocorin aglycone was obtained. These compounds were separated by preparative t.l.c. and identified by direct comparison with authentic specimens derived from a natural source. The n.m.r. spectra of the two dimethyl ethers were in good agreement with their assigned structures; only dimethyl ether B (34; $R^1 = R^2$ = Me), which contains one methoxy-group in a *peri*-relationship to the phenyl substituent showed a methoxy-signal at unusually high field (τ 6·75). Since hydrolysis of dimethyl ether A (33; $R^1 = R^2$ = Me) to haemocorin aglycone (34; $R^1 = R^2$ = H) has already been reported,[2b] the synthesis of the former completes the total synthesis of haemocorin aglycone.

Treatment of the phenalene (32), the dimethyl ether A (33; $R^1 = R^2$ = Me), or the dimethyl ether B (34; $R^1 = R^2$ = Me) with aqueous methanolic hydrochloric acid for prolonged periods under the conditions used to dehydrate the carbinol (31) gave a small amount of a purple phenol, which was obtained in a homogeneous

[17] D. J. Cram and A. C. Day, *J. Org. Chem.*, 1966, **31**, 1227; M. Kise, T. Asari, N. Furukawa, and S. Oae, *Chem. and Ind.*, 1967, 276.

[18] *Cf.* M. F. Hawthorn, *J. Org. Chem.*, 1957, **22**, 1001.

state by chromatography. Spectroscopic and microanalytical evidence established this compound to be a hydroxy-dimethoxy-phenalenone. Methylation with diazomethane gave a mixture of dimethyl ethers A (**33**; $R^1 = R^2 = Me$) and B (**34**; $R^1 = R^2 = Me$), and acetylation gave a mixture of two acetates, which were separated chromatographically. The purple phenol therefore has structure (**33**; $R^1 = H$, $R^2 = Me$) or the tautomeric form (**34**; $R^1 = Me$, $R^2 = H$). The acetate methyl group of one of the derived acetates gives rise to an n.m.r. signal at unusually high field (τ 8·53), and on this basis the acetate is assigned the structure (**34**; $R^1 = Me$, $R^2 = Ac$) in which the acetate protons are strongly shielded by the *peri*-phenyl substituent; the second derived acetate, which exhibits a signal at τ 7·50 attributable to the acetate methyl group, has the structure (**33**; $R^1 = Ac$, $R^2 = Me$).



The purple phenol is designated haemocorin aglycone monomethyl ether C, since of the three possible monoethyl ethers of the aglycone it is the only one not previously described. The others have already been named monomethyl ether A (**33**; $R^1 = Me$, $R^2 = H$) and monomethyl ether B (**34**; $R^1 = H$, $R^2 = Me$)[2]. The ready demethylation of dimethyl ethers A and B to give monomethyl ether C under mild acid conditions is unexceptional, since the ether grouping which is affected is vinylogously β to the conjugated carbonyl group. However, conversion of the phenalene (**32**) into monomethyl ether C (**33**; $R^1 = H$, $R^2 = Me$) must involve a dehydrogenation step.

In connection with the work already described, certain reactions were carried out with acenaphthenone (**36**) as starting material. Details are given in the Experimental section for the preparation of 1-acetoxyacenaphthylene (**37**), ozonolysis of which gave the lactol (**38**; R = H), previously prepared[19] by treatment of acenaphthenequinone with concentrated potassium hydroxide solution at 130°. When the derived methyl ether (**38**; R = Me)[20] was treated with methyl acetoacetate in the presence of sodium methoxide the major product was the β-keto-ester (**39**), arising by nucleophilic attack at the acetal carbon atom. There are good analogies for the course followed by this reaction,[21] and the structure assigned to the product is fully supported by its i.r. and n.m.r. spectra.

[19] C. Graebe and E. Gfeller, *Annalen*, 1893, **276**, 1.
[20] J. Zink, *Monatsh.*, 1901, **22**, 986.

EXPERIMENTAL

M.p.s were measured with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Unicam SP 200 spectrophotometer or a Perkin-Elmer 125 instrument for Nujol mulls unless otherwise stated. U.v. spectra were recorded with a Unicam SP 800 spectrophotometer, for solutions in 95% ethanol. N.m.r. spectra were measured with a Varian A 60 instrument for solutions in deuteriochloroform unless specified otherwise. Mass spectra were recorded with an A.E.I. MS 902 spectrometer. T.l.c. was carried out with plates coated with Merck kieselgel G.

2,7-Dimethoxy-1-naphthaldehyde (2) [7] had m.p. 97—98° (lit.,[7] 98°), $\lambda_{max.}$ 230, 267, and 353 nm (log ε 4·19, 3·44, and 3·60), $\nu_{max.}$ 1596, 1620, and 1665 (aldehyde C=O) cm.$^{-1}$, τ 3·03 (1H, d, *J* 9 Hz, C-3 H), 2·99 (1H, dd, J_o 9, J_m 3 Hz, C-6 H), 2·41 (1H, d, *J* 9 Hz, C-5 H), 2·13 (1H, d, *J* 9 Hz, C-4 H), 1·12 (1H, d, *J* 3 Hz, C-8 H), and −0·81 (1H, s, ·CHO).

Ethyl β-(2,7-*Dimethoxy*-1-*naphthyl*)-trans-*acrylate* (**3**).—A solution of 2,7-dimethoxy-1-naphthaldehyde (2·16 g.) and ethoxycarbonylmethylenetriphenylphosphorane (7·0 g.) in benzene (100 ml.) was heated under reflux for 60 hr. The cooled solution was applied in equal portions to six preparative thin-layer plates (20 × 20 cm. with a wedge-shaped coating of kieselgel G, 2 mm. to 1 mm. taper) and the plates were eluted from the thicker end upwards with ether–benzene (3 : 17). From the band which fluoresced yellow under u.v. light there was obtained, by extraction with ethyl acetate, *ethyl* β-(2,7-*dimethoxy*-1-*naphthyl*)-trans-*acrylate* (2·39 g., 83%) as pale yellow plates, m.p. 57—58°, unchanged on crystallisation from benzene–light petroleum (Found: C, 70·8; H, 5·85. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·35%), $\lambda_{max.}$ 240 and 349 nm. (log ε 4·31 and 3·76), $\nu_{max.}$ (KCl) 1520 and 1708 (unsaturated ester C=O) cm.$^{-1}$, τ 8·64 (3H, t, *J* 7 Hz, CO_2Et), 6·10 (3H, s, ArOMe), 6·08 (3H, s, ArOMe), 5·68 (2H, q, *J* 7 Hz, CO_2-Et), 3·23 (1H, d, *J* 16 Hz, *trans*-β-vinyl H), 2·99 (1H, dd, J_o 9, J_m 2·5 Hz, C-6 H), 2·95 (1H, d, *J* 9 Hz, C-3 H), 2·56 (1H, d, *J* 2·5 Hz, C-8 H), 2·34 (1H, d, *J* 9 Hz, C-5 H), 2·29 (1H, d, *J* 9 Hz, C-4 H), and 1·71 (1H, d, *J* 16 Hz, *trans*-α-vinyl H).

Ethyl β-(2,7-*Dimethoxy*-1-*naphthyl*)*propionate* (**4**; R = Et).—Ethyl β-(2,7-dimethoxy-1-naphthyl)-*trans*-acrylate (2 g.) was hydrogenated in ethyl acetate (100 ml.) over 10% palladium–charcoal (1·7 g.). Uptake of hydrogen ceased after 1 mol. equiv. had been absorbed; *ethyl* β-(2,7-*dimethoxy*-1-*naphthyl*)*propionate* (2 g., 100%) was obtained as a yellow oil, b.p. 188—190°/0·2 mmHg. A small portion of the product was further purified by preparative t.l.c. (0·5 mm. coating of kieselgel G), with ether–benzene (3 : 17) as eluant, then by preparative g.l.c. to give a pale yellow liquid (Found: C, 70·45; H, 7·1. $C_{17}H_{20}O_4$ requires C, 70·8; H, 7·0%), $\nu_{max.}$ (KCl) 1625 and 1728 (saturated ester C=O) cm.$^{-1}$, τ 8·79 (3H, t, *J* 7 Hz, CO_2Et), 7·43 (2H, t, *J* 7 Hz, β-CH_2), 6·60 (2H, t, *J* 7 Hz, α-CH_2), 6·10 (3H, s, ArOMe), 6·09 (3H, s, ArOMe), 5·84 (2H, q, *J* 7 Hz, CO_2Et), 3·00 (1H, dd, J_o 9, J_m 2 Hz, C-6 H), 2·91 (1H, d, *J* 9 Hz, C-3 H), 2·74 (1H, d, *J* 2 Hz, C-8 H), and 2·32 (2H, d, *J* 9 Hz, C-4 and C-5 H).

[21] J. Zink, *Monatsh.*, 1901, **22**, 813; 1902, **23**, 836; S. Wiechowski *ibid.*, 1905, **26**, 749.

β-(2,7-*Dimethoxy*-1-*naphthyl*)*propionic Acid* (4; R = H).—A solution of ethyl β-(2,7-dimethoxy-1-naphthyl)propionate (1·2 g.) and potassium hydroxide (2 g.) in water (8 ml.) and ethanol (52 ml.) was heated under reflux for 2 hr. The cooled solution was diluted with an equal volume of water, and acidified with dilute hydrochloric acid to precipitate β-(2,7-*dimethoxy*-1-*naphthyl*)*propionic acid* (1·1 g., 100%), m.p. 165—169°. One recrystallisation from chloroform gave white needles, m.p. 166—169° (Found: C, 69·2; H, 5·9. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%), $\lambda_{max.}$ 236, 290, 315, and 329 nm. (log ε 4·17, 3·21, 3·00, and 3·05), $\nu_{max.}$ (KCl) 1620 and 1693 (carboxylic C=O) cm.$^{-1}$, τ [$(CD_3)_2$-SO] 7·50 (2H, t, *J* 7·5 Hz, β-CH_2), 6·67 (2H, t, *J* 7·5 Hz, α-CH_2), 6·10 (6H, s, 2 × ArOMe), 5·50—4·40 (1H, diffuse, CO_2H), 2·99 (1H, dd, J_o 9 J_m 2 Hz, C-6 H), 2·80 (1H, d, *J* 9 Hz, C-3 H), 2·67 (1H, d, *J* 2 Hz, C-8 H), and 2·25 (2H, d, *J* 9 Hz, C-4 and C-5 H).

2,3-*Dihydro*-4,9-*dimethoxyphenalen*-1-*one* (5).—(*a*) β-(2,7-Dimethoxy-1-naphthyl)propionic acid (500 mg.) was warmed with oxalyl chloride (15 ml.) for 10 min. After removal of excess of oxalyl chloride under reduced pressure, tin(IV) chloride (2·5 g.) was added to a solution of the residual acid chloride in carbon disulphide (50 ml.) at 0°. The mixture was stirred at 0° for 2 hr., allowed to warm to room temperature, and decomposed with warm water. Organic materials were extracted into chloroform, and the extract was washed successively with dilute hydrochloric acid, dilute sodium hydrogen carbonate, and water, and was then dried. Removal of the solvent *in vacuo* yielded 2,3-*dihydro*-4,9-*dimethoxyphenalen*-1-*one* (300 mg.) as a pale yellow paste. Chromatography on a column of kieselgel G [ethyl acetate–benzene (1 : 1)] gave a crystalline solid (244 mg., 50%), m.p. 122—132°. Several recrystallisations from ethyl acetate–benzene yielded rods, m.p. 135—136° (Found: C, 74·1; H, 5·65. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·85%), $\lambda_{max.}$ 234, 265, and 348 nm. (log ε 4·30, 3·70, and 3·58), $\nu_{max.}$ (KCl) 1616 and 1660 (aryl ketone C=O) cm.$^{-1}$, τ 7·18 (2H, m, β-CH_2), 6·70 (2H, m, α-CH_2), 6·06 (3H, s, ArOMe), 5·99 (3H, s, ArOMe), 2·76 (2H, d, *J* 9 Hz, C-5 and C-8 H), 2·31 (1H, d, *J* 9 Hz, C-6 H), and 2·09 (1H, d, *J* 9 Hz, C-7 H).

(*b*) β-(2,7-Dimethoxynaphthyl)propionic acid (5·45 g.) was stirred and heated on a steam-bath with polyphosphoric acid (50 g.) for 10 min. A further quantity of polyphosphoric acid (50 g.) was added, and heating was continued for another 15 min. The mixture was cooled to room temperature, and ice (300—500 g.) was added with stirring. Organic material was extracted with chloroform, and, after being washed with dilute sodium hydrogen carbonate the extract was evaporated *in vacuo*. The residue was chromatographed on a column of kieselgel G [ethyl acetate–chloroform (1 : 1) to give 2,3-dihydro-4,9-dimethoxyphenalen-1-one (4 g., 79%), identical with material obtained in (*a*).

Reaction of 2,3-*Dihydro*-4,9-*dimethoxyphenalen*-1-*one* (5) *with* p-*Nitrosodimethylaniline*.—A solution of the dihydrophenalenone (92 mg.), *p*-nitrosodimethylaniline (60 mg.), and potassium hydroxide (2N aq.; 2 drops) in ethanol (15 ml.) was left at room temperature overnight. An equal volume of 5N-hydrochloric acid was added and the mixture was heated under reflux for 4 h. The mixture was extracted with chloroform and the extract was washed with water, dried, and evaporated *in vacuo* to give a dark brown solid (70 mg.). Chromatography on a column of kieselgel G (10 g.) [ethyl acetate–chloroform (1 : 1)] afforded 9-*hydroxy*-4-*methoxyphenalenone* (6; R^1 = Me, R^2 = H) (20 mg.) as an orange solid, m.p. 184—196°. Sublimation at 125°/0·1 mmHg gave clusters of orange needles, m.p. 190—199° (Found: C, 74·2; H, 4·55. $C_{14}H_{10}O_3$ requires C, 74·35; H, 4·15%), $\lambda_{max.}$ 206, 235, 260, 275, 285, 379, and 420 nm. (log ε 4·50, 4·38, 4·00, 3·85, 3·70, 4·06, and 4·12), $\nu_{max.}$ 1590 and 1630 (C=O) cm.$^{-1}$, τ 5·91 (3H, s, ArOMe), 3·09 (1H, d, *J* 9 Hz, C-5 H), 3·04 (1H, d, *J* 9 Hz, C-8 H), 2·91 (1H, d, *J* 10 Hz, C-2 H), 2·11 (2H, d, *J* 9 Hz, C-6 and C-7 H), 1·55 (1H, d, *J* 10 Hz, C-3 H), and −6·38 (1H, s, OH).

Oxidation of 2,3-*Dihydro*-4,9-*dimethoxyphenalen*-1-*one* (5) *with Selenium Dioxide*.—A solution of 2,3-dihydro-4,9-dimethoxyphenalen-1-one (50 mg.) and selenium dioxide (25 mg.) in acetic anhydride (10 ml.) was heated under reflux for 30 min., then cooled and poured into water. The aqueous suspension was extracted with chloroform, and the extract was washed successively with sodium hydrogen carbonate solution, dilute hydrochloric acid, and water, then dried and evaporated *in vacuo*. The residue was chromatographed on a preparative t.l.c. plate (20 × 20 cm., 0·5 mm. layer of kieselgel G) [ethyl acetate–chloroform (1 : 1)] to give 2,3-dihydro-4,9-dimethoxyphenalen-1-one (10 mg.) and 9-hydroxy-4-methoxyphenalenone (2 mg.), identified in each case by direct comparison with an authentic sample.

Attempted Oxidation of 2-*Bromo*-2,3-*dihydro*-4,9-*dimethoxyphenalen*-1-*one* (8).—A solution of trimethylanilinium tribromide (233 mg.) in dry tetrahydrofuran (10 ml.) was added, with stirring, to a solution of 2,3-dihydro-4,9-dimethoxyphenalen-1-one (150 mg.) in dry tetrahydrofuran (5 ml.); the mixture was stirred at room temperature for 10 min. The precipitated quaternary ammonium salt was filtered off; the filtrate was evaporated, leaving 2-*bromo*-2,3-*dihydro*-4,9-*dimethoxyphenalen*-1-*one* (190 mg., 95%) as a yellow solid which quickly decomposed, $\nu_{max.}$ 1680 (α-bromo-ketone C=O) cm.$^{-1}$, τ 6·26 (2H, m, β-CH_2), 6·02 (3H, s, ArOMe), 5·94 (3H, s, ArOMe), 5·17 (1H, t, *J* 4·5 Hz, C-2 H), 2·82 (2H, d, *J* 9 Hz, C-5 and C-8 H), 2·25 (1H, d, *J* 9 Hz, C-6 H), and 2·01 (1H, d, *J* 9 Hz, C-7 H).

A solution of the bromo-ketone (8) (190 mg.) and sodium hydrogen carbonate (250 mg.) in dimethyl sulphoxide (5 ml.) was heated at 130° for 1 hr., then cooled and poured into water (50 ml.). The aqueous mixture was extracted with chloroform, and the extract was washed successively with dilute hydrochloric acid and water, then dried and evaporated *in vacuo* to give 9-hydroxy-4-methoxyphenalen-1-one (90 mg., 63%), identical with the material obtained by other routes.

2-*Bromo*-4,9-*dimethoxyphenalenone* (10).—A solution of trimethylanilinium tribromide (315 mg.) in dry tetrahydrofuran (20 ml.) was added, with stirring, to a solution of 2,3-dihydro-4,9-dimethoxyphenalen-1-one (100 mg.) in dry tetrahydrofuran, and the mixture was stirred at room temperature for 10 min. It was then filtered and the filtrate was evaporated *in vacuo*, leaving 2,2-*dibromo*-2,3-*dihydro*-4,9-*dimethoxyphenalen*-1-*one* (9) (170 mg., 100%) as an orange solid which quickly decomposed, $\nu_{max.}$ 1690 (αα-dibromo-ketone C=O) cm.$^{-1}$, τ 6·00 (3H, s, ArOMe), 5·91 (3H, s, ArOMe), 5·67 (2H, s, β-CH_2), 2·81 (2H, d, *J* 9 Hz, C-5 and C-8 H), 2·21 (1H, d, *J* 9 Hz, C-6 H), and 1·99 (1H, d, *J* 9 Hz, C-7 H).

The dibromo-ketone (9) (50 mg.) in dry methanol (5 ml.) was mixed with a solution of sodium (25 mg.) in dry methanol (20 ml.), and the mixture was heated under

reflux for 1 hr., then cooled and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure to afford *2-bromo-4,9-dimethoxyphenalenone* (38 mg., 95%) as an orange solid which, after sublimation at 180—200°/0·5 mmHg and crystallisation from chloroform–ether, formed orange-yellow rosettes, m.p. 255—260° [Found: C, 56·35; H, 3·8; Br, 24·3%; *m/e* 317·9897, 319·9876. $C_{15}H_{11}BrO_3$ requires C, 56·45; H, 3·5; Br, 25·05%; $M(^{79}Br)$ 317·9891, $M(^{81}Br)$ 319·9871], $\lambda_{max.}$ 216, 231, 265, 325, 395, 425, and 451 nm. (log ε 4·41, 4·37, 4·37, 3·54, 4·41, 4·30, and 4·11), $\nu_{max.}$ (KCl) 1630 cm.$^{-1}$, τ 5·98 (3H, s, ArOMe), 5·85 (3H, s, ArOMe), 2·93 (1H, d, *J* 9 Hz, C-5 H), 2·77 (1H, d, *J* 9 Hz, C-8 H), 2·11 (1H, d, *J* 9 Hz, C-6 H), 1·97 (1H, d, *J* 9 Hz, C-7 H), and 1·49 (1H, s, C-3 H).

2-Bromo-4-methoxy-9-piperidinophenalenone (11).—A solution of 2-bromo-4,9-dimethoxyphenalenone (35 mg.) in piperidine (3 ml.) was heated on a steam-bath for 1 hr., during which time a red colour developed. The solution was cooled and poured into ether, and the ethereal solution was washed with water then extracted with dilute hydrochloric acid. The acid extract was neutralised with dilute sodium carbonate solution, and extracted with ether. The ethereal solution was washed with water, dried and evaporated *in vacuo* to give *2-bromo-4-methoxy-9-piperidinophenalenone* (25 mg., 63%) as a red oil which slowly crystallised. Three recrystallisations from ethyl acetate afforded red prisms, m.p. 165—165·5° (Found: C, 61·35; H, 4·55; Br, 21·5. $C_{19}H_{18}BrNO$ requires C, 61·3; H, 4·85; Br, 21·45%), $\lambda_{max.}$ 265, 413, and 492 nm. (log ε 4·44, 4·30, and 4·12), $\nu_{max.}$ (KCl) 1620 cm.$^{-1}$, τ 8·24 (6H, s, β- and γ-CH_2 on piperidine ring), 6·30—6·70 (4H, diffuse, α-CH_2 on piperidine ring), 6·00 (3H, s, ArOMe), 3·01 (1H, d, *J* 9 Hz, C-5 H), 2·73 (1H, d, *J* 9 Hz, C-8 H), 2·20 (2H, d, *J* 9 Hz, C-6 and C-7 H), and 1·33 (1H, s, C-3 H).

4,9-Dimethoxy-2-hydroxyphenalenone (12; R = H).—A solution of 2,3-dihydro-4,9-dimethoxyphenalen-1-one (100 mg.) in t-butyl alcohol (5 ml.) was added to a solution of potassium (50 mg.) in t-butyl alcohol (4 ml.) and the mixture was shaken in an atmosphere of oxygen. The reaction was carried out in a micro-hydrogenation apparatus, and the uptake of oxygen was observed. After 30 min. 1 mol. equiv. of oxygen (9·3 ml. at N.T.P.) had been absorbed, and the dark-brown solution was poured into water and neutralised with dilute acetic acid. The product was extracted into chloroform and the extract was washed with water, dried, and evaporated under reduced pressure to give a brown oil. Chromatography on a column of kieselgel G (50 g.) (chloroform) gave 9-hydroxy-4-methoxyphenalenone (6; R^1 = Me, R^2 = H) (26 mg., 28%), identified by direct comparison with an authentic specimen, and *2-hydroxy-4,9-dimethoxyphenalenone* (30 mg., 28%) as orange prisms, m.p. 220—225° after one recrystallisation from benzene (Found: C, 70·15; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%), $\lambda_{max.}$ 231infl., 254, 280, 344, 392, and 438 nm. (log ε 4·29, 4·17, 4·27, 3·76, 4·24, and 3·98), $\nu_{max.}$ (KCl) 1640 (aryl ketone C=O) and 3280 (OH) cm.$^{-1}$, τ 5·93 (3H, s, ArOMe), 5·78 (3H, s, ArOMe), 2·83 (1H, d, *J* 9 Hz, C-5 H), 2·73 (1H, d, *J* 9 Hz, C-8 H), 2·35—2·50 (1H, diffuse, OH), 2·35 (1H, s, C-3 H), 2·15 (1H, d, *J* 9 Hz, C-6 H), and 1·89 (1H, d, *J* 9 Hz, C-7 H).

The derived *acetate* (12; R = Ac), prepared by treatment with acetic anhydride–pyridine at room temperature, crystallised from ethyl acetate as yellow rectangular prisms, m.p. 155—158° (Found: C, 68·15; H, 4·75. $C_{17}H_{14}O_5$ requires C, 68·45; H, 4·75%), $\lambda_{max.}$ 233, 265, 391, 420, and 445 nm. (log ε 4·31, 4·22, 4·25, 4·11, and 3·88), $\nu_{max.}$ (KCl) 1630 (aryl ketone C=O), and 1760 (phenolic acetate C=O) cm.$^{-1}$, τ 7·60 (3H, s, ArO·CO·CH_3), 6·11 (3H, s, ArOMe), 5·99 (3H, s, ArOMe), 3·16 (1H, d, *J* 9 Hz, C-5 H), 3·04 (1H, d, *J* 9 Hz, C-8 H), 2·43 (1H, d, *J* 9 Hz, C-6 H), 2·29 (1H, d, *J* 9 Hz, C-7 H), and 2·23 (1H, s, C-3 H).

Attempted Oxidation of 2-Bromo-2,3-dihydro-5,6-dimethoxy-7-phenylphenalenone (13; R = Br).—To a solution of 2,3-dihydro-5,6-dimethoxy-7-phenylphenalen-1-one (50 mg.) in tetrahydrofuran (3 ml.) was added a solution of trimethylanilinium tribromide (60 mg.) in tetrahydrofuran (3 ml.). After 1 hr. at room temperature the mixture was filtered, and the filtrate was evaporated *in vacuo* to yield the α-bromo-ketone (13; R = Br) which, without further purification, was dissolved in dimethyl sulphoxide and left at room temperature overnight. The solution was then heated under reflux for 5 min., cooled, poured into water, and extracted with chloroform. The extract was washed with water, dried, and evaporated under reduced pressure to leave a brown oil (42 mg.), which was separated into its two major components by preparative t.l.c. [20 × 20 cm. plate, 0·5 mm. coating of kieselgel G; chloroform–benzene (1 : 1)]. The band of higher R_F gave, on extraction with chloroform, *2-bromo-5,6-dimethoxy-7-phenylphenalenone* (14; R^1 = Br, R^2 = Me) (10 mg., 20%) as a red oil which, although chromatographically homogeneous, was not obtained in crystalline form (Found: *m/e* 394·0203, 396·0205. $C_{21}H_{15}BrO_3$ requires $M(^{79}Br)$ 394·0205, $M(^{81}Br)$ 396·0190), $\lambda_{max.}$ 275, 372, and 472 nm. (log ε 4·35, 3·98, and 4·04), $\nu_{max.}$ (KCl) 1630 cm.$^{-1}$, τ 6·70 (3H, s, 6-OMe), 6·00 (3H, s, 5-OMe), 2·46—2·63 (7H, m, Ph, C-4 and C-8 H), 1·94 (1H, s, C-3 H), and 1·50 (1H, d, *J* 8 Hz, C-9 H).

The band of lower R_F gave, on extraction with chloroform, 5,6-dimethoxy-7-phenylphenalenone (14; R^1 = H, R^2 = Me) (18 mg., 29%), identical with lachnanthocarpone orange dimethyl ether.[1]

Attempted Acylation of 3,4-Dimethoxy-5-phenyl-1-naphthaldehyde (15; R = Me) *with Methoxyacetyl Chloride*.—A solution of 3,4-dimethoxy-5-phenyl-1-naphthaldehyde (50 mg.), methoxyacetyl chloride (24 mg.), and aluminium chloride (110 mg.) in carbon disulphide (10 ml.) was stirred and heated under reflux for 5 min., then allowed to cool to room temperature and stirred for a further 2 hr. The carbon disulphide was removed under reduced pressure, and the residue was warmed with water (10 ml.), then extracted with benzene. The benzene extract was washed successively with dilute hydrochloric acid and aqueous sodium hydrogen carbonate, dried, and evaporated *in vacuo*. The residual oil was purified by preparative t.l.c. [20 × 20 cm. plate, 0·5 mm. coating of kieselgel G; ether–benzene (1 : 4)] to yield *4-hydroxy-3-methoxy-5-phenyl-1-naphthaldehyde* (15; R = H) which gave very pale yellow crystals, m.p. 165—165·5° (from benzene–light petroleum) (Found: C, 78·5; H, 4·55. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·05%), $\lambda_{max.}$ 222, 254, 338infl., and 372 nm. (log ε 4·22, 4·12, 3·62, and 3·89), $\nu_{max.}$ 1662 and 3300 cm.$^{-1}$, τ 6·02 (3H, s, ArOMe), 3·40 (1H, diffuse, OH), 2·50—2·80 (2H, m, C-6 and C-7 H), 2·64 (5H, s, Ph), 2·22 (1H, s, C-2 H), 0·82 (1H, dd, J_o 9, J_m 2 Hz, C-8 H), and −0·41 (1H, s, ·CHO).

Reaction of 2,3-Dihydro-4,9-dimethoxyphenalen-1-one (5) *with Phenylmagnesium Bromide*.—A solution of 2,3-dihydro-4,9-dimethoxyphenalen-1-one (605 mg.) in ether (50 ml.) was added to a solution of phenylmagnesium bromide [from magnesium (600 mg.)] in ether (20 ml.),

and the mixture was heated under reflux for 30 min. The cooled ethereal solution was shaken with aqueous ammonium chloride, then washed with water, dried, and evaporated under reduced pressure. The residual dark brown oil was heated on a steam-bath for 5 min. with methanol (10 ml.) and dilute hydrochloric acid (2 ml.). The mixture was extracted with benzene, and the benzene solution (50 ml.) was washed with water, dried, and heated under reflux for 3 hr. with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (600 mg.). The mixture was then evaporated to half its volume *in vacuo* and applied to a column of kieselgel G (200 g.), which was eluted with ether–benzene (3 : 7). Two major products were obtained. The product of higher R_F, 6-*methoxy*-9-*phenylphenalenone* (22) (200 mg.), crystallised from benzene–light petroleum as rods, m.p. 186—187° (Found: C, 83·6; H, 4·9. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·95%), $\lambda_{max.}$ 236, 265, 290infl., 360, and 423 nm. (log ε 4·10, 4·29, 4·02, 3·72, and 3·91), $\nu_{max.}$ (KCl) 1633 cm.$^{-1}$, τ 5·99 (3H, s, ArOMe), 3·57 (1H, d, *J* 9·5 Hz, C-2 H), 3·20 (1H, d, *J* 8 Hz, C-5 H), 2·60 (5H, s, Ph), 2·49 (1H, d, *J* 8 Hz, C-8 H), 2·46 (1H, d, *J* 9·5 Hz, C-3 H), 2·40 (1H, d, *J* 8 Hz, C-4 H), and 1·56 (1H, d, *J* 8 Hz, C-7 H). The component of lower R_F, 6-*methoxy*-7-*phenylphenalenone* (23) (225 mg.), crystallised from methanol as golden plates, m.p. 141—142° (Found: C, 84·05; H, 4·95. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·95%), $\lambda_{max.}$ 229infl., 269, 335, 358, and 440 nm. (log ε 4·14, 4·21, 3·63, 3·63, and 4·05), $\nu_{max.}$ (KCl) 1630 cm.$^{-1}$, τ 6·45 (3H, s, ArOMe), 3·40 (1H, d, *J* 9·5 Hz, C-2 H), 3·22 (1H, d, *J* 8 Hz, C-5 H), 2·65 (5H, s, Ph), 2·46 (1H, d, *J* 8 Hz, C-8 H), 2·35 (1H, d, *J* 8 Hz, C-4 H), 2·33 (1H, d, *J* 9·5 Hz, C-3 H), and 1·35 (1H, d, *J* 8 Hz, C-9 H).

2,7-*Dibromo*-3,6-*dimethoxynaphthalene* (24).[14]—This showed τ 6·05 (6H, s, 2 × ArOMe), 2·99 (2H, s, C-4 and C-5 H), and 2·17 (2H, s, C-1 and C-8 H).

Debromination of 2,7-*Dibromo*-3,6-*dimethoxynaphthalene* (24).—A solution of 2,7-dibromo-3,6-dimethoxynaphthalene (5 g.) in dimethyl sulphoxide (50 ml.) was mixed with a solution of sodium methoxide [from sodium (5 g.)] in dimethyl sulphoxide (50 ml.) and the mixture was stirred and heated at 100—110° for 17 hr. Methylene chloride was added, and the solution was washed repeatedly with water, dried, and evaporated under reduced pressure to leave 2,7-dimethoxynaphthalene (1) (2·1 g., 78%) as pale straw-coloured crystals, identical with an authentic specimen.

Treatment of 2,7-*Dibromo*-3,6-*dimethoxynaphthalene* (24) *with Potassium t-Butoxide and Dimethyl Sulphoxide*.—A solution of 2,7-dibromo-3,6-dimethoxynaphthalene (1 g.) and potassium t-butoxide (1 g.) in dimethyl sulphoxide (50 ml.) was stirred at room temperature for 2 hr., then poured into water and extracted with methylene chloride. The extract was washed repeatedly with water, dried, and evaporated *in vacuo* to yield a brown oil (820 mg.). Chromatography on kieselgel G (100 g.) (benzene) afforded a compound (325 mg., 34%) of m.p. 153—157° which was either 7-bromo-3,6-dimethoxy-1-methylthio-2-naphthol (25; R^1 = SMe, R^2 = OH) or 7-bromo-3,6-dimethoxy-2-methylthio-1-naphthol (25; R^1 = OH, R^2 = SMe). Two recrystallisations from benzene gave pale pink rosettes, m.p. 159—160° (Found: C, 47·3; H, 4·0; Br, 24·4; S, 9·95. $C_{13}H_{13}BrO_3S$ requires C, 46·95; H, 4·0; Br, 24·6; S, 9·85%), $\lambda_{max.}$ 254infl., 263, 297infl., 325infl., and 340 nm. (log ε 4·65, 4·74, 3·82, 3·53, and 3·42), $\nu_{max.}$ (KCl) 1530 and 3320 cm.$^{-1}$, τ 7·73 (3H, s, ArSMe), 6·05 (6H, s, 2 × ArOMe), 3·41 (1H, s, ArH), 3·06 (1H, s, ArH), 2·49 (1H, s, OH), and 1·69 (1H, s, ArH).

The derived *acetate*, obtained by treatment with acetic anhydride and pyridine at room temperature, crystallised from chloroform–light petroleum as cubes, m.p. 159—160° (Found: C, 48·85; H, 4·05; Br, 21·7; S, 8·6. $C_{15}H_{15}BrO_4S$ requires C, 48·55; H, 4·05; Br, 21·55; S, 8·65%), $\lambda_{max.}$ 247infl., 252, 265infl., 300infl., 325, and 342 nm. (log ε 4·76, 4·78, 4·31, 3·85, 3·71, and 3·85), $\nu_{max.}$ (KCl) 1520 and 1756 cm.$^{-1}$, τ 7·65 (3H, s, ArSMe), 7·50 (3H, s, ArO·COMe), 6·05 (3H, s, ArOMe), 6·01 (3H, s, ArOMe), 3·08, 2·99, and 2·08 (each 1H, s, 3 × ArH).

3,6-*Dimethoxynaphthalene*-2,7-*diol* (26; R^1 = R^2 = OH) *and* 3,6-*Dimethoxy*-2-*naphthol* (26; R^1 = H, R^2 = OH).—A solution of butyl-lithium in ether (N; 200 ml.) was added, under nitrogen, to a solution of 2,7-dibromo-3,6-dimethoxynaphthalene (10·26 g.) in dry benzene (150 ml.) and dry ether (400 ml.). The mixture was heated under reflux for 3 hr., then cooled to −70°, and a solution of methyl borate (25 g.) in dry ether (50 ml.) was added slowly, with stirring. Stirring was continued at −70° for 15 min., then the solution was allowed to warm to room temperature and dilute hydrochloric acid (200 ml.) was added. The organic layer was separated, and a solution of hydrogen peroxide (20%; 200 ml.) was added to it slowly, with stirring. The organic layer was again separated, and extracted with dilute sodium hydroxide solution. Acidification of the alkaline aqueous phase gave a grey solid (5·5 g.), which was chromatographed on kieselgel G (200 g.) [ethanol–chloroform (3 : 97)]. From the first few fractions, 3,6-*dimethoxy*-2-*naphthol* (1·3 g., 21%) was obtained as pale pink plates. Three recrystallisations from chloroform–light petroleum gave material m.p. 165—166°, but failed to remove completely the slight colouration (Found: C, 70·55; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·55; H, 5·9%), $\lambda_{max.}$ 254infl., 265, 275, 285infl., 320infl., and 334 nm. (log ε 3·84, 3·77, 3·72, 3·54, 3·57, and 3·78), $\nu_{max.}$ (KCl) 1515, 1535, and 3420 cm.$^{-1}$. Later fractions gave 3,6-*dimethoxynaphthalene*-2,7-*diol* (2·8 g., 43%) as faintly purple plates, m.p. 219—220° after three recrystallisations from chloroform–light petroleum (Found: C, 65·7; H, 5·35. $C_{12}H_{12}O_4$ requires C, 65·45; H, 5·5%), $\lambda_{max.}$ 256infl., 269, 279, 291, 304, 312, 318, 326, and 333 nm. (log ε 3·64, 3·64, 3·63, 3·52, 3·48, 3·62, 3·85, 3·83, and 4·06), $\nu_{max.}$ (KCl) 1520, 3400, 3510, and 3560 cm.$^{-1}$.

2-*Acetoxy*-3,6-*dimethoxynaphthalene* (26; R^1 = H, R^2 = OAc).—Acetylation of 3,6-dimethoxy-2-naphthol with pyridine–acetic anhydride at room temperature gave 2-*acetoxy*-3,6-*dimethoxynaphthalene* as plates, m.p. 141—142° (from chloroform–light petroleum) (Found: C, 68·45; H, 5·75. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·75%), $\lambda_{max.}$ 270, 290infl., 295infl., 304, 311, 317, and 325 nm. (log ε 3·68, 3·50, 3·39, 3·36, 3·50, 3·45, and 3·66), $\nu_{max.}$ (KCl) 1515, 1535, and 1765 cm.$^{-1}$, τ 7·67 (3H, s, ArO·COMe), 6·15 (3H, s, ArOMe), 6·10 (3H, s, ArOMe), 3·00 (1H, dd, J_o 9·5, J_m 2·5 Hz, C-7 H), 2·92 (1H, s, C-4 H), 2·92 (1H, d, *J* 2·5 Hz, C-5 H), 2·61 (1H, s, C-1 H), and 2·40 (1H, d, *J* 9·5 Hz, C-8 H).

2,3,6-*Trimethoxynaphthalene* (26; R^1 = H, R^2 = OMe).—Methylation of 3,6-dimethoxy-2-naphthol with dimethyl sulphate and dilute sodium hydroxide gave 2,3,6-*trimethoxynaphthalene*, which gave plates, m.p. 128—129° (from chloroform–light petroleum) (Found: C, 71·4; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·55; H, 6·45%), $\lambda_{max.}$ 263, 275, 317, and 331 nm. (log ε 3·74, 3·68, 3·60, and 3·71),

$\nu_{max.}$ (KCl) 1510 and 1530 cm.$^{-1}$, τ 6·17, 6·10, and 6·07 (3 × 3H, s, ArOMe), 3·02 (1H, dd, J_o 9·5 Hz, J_m 2·5 Hz, C-7 H), 2·98 (2H, s, C-1 and C-4 H), 2·98 (1H, d, J 2·5 Hz, C-5 H), and 2·48 (1H, d, J 9·5 Hz, C-8 H).

2,7-*Diacetoxy*-3,6-*dimethoxynaphthalene* (26; $R^1 = R^2$ = OAc).—Acetylation of 3,6-dimethoxynaphthalene-2,7-diol with acetic anhydride–pyridine at room temperature gave 2,7-*diacetoxy*-3,6-*dimethoxynaphthalene* as plates, m.p. 212—213° (from chloroform–light petroleum) (Found: C, 63·2; H, 5·2. $C_{16}H_{16}O_6$ requires C, 63·15; H, 5·3%), $\lambda_{max.}$ 269, 271, 290infl., 297infl., 304, 311, 317, and 325 nm. (log ε 3·76, 3·74, 3·56, 3·48, 3·48, 3·66, 3·60, and 3·85), $\nu_{max.}$ 1520, 1540, and 1767 cm.$^{-1}$, τ 7·68 (6H, s, 2 × ArO·CO-Me), 6·10 (6H, s, 2 × ArOMe), 2·89 (2H, s, C-4 and C-5 H), and 2·66 (2H, s, C-1 and C-8 H).

2,3,6,7-*Tetramethoxynaphthalene* (26; $R^1 = R^2$ = OMe).—Methylation of 3,6-dimethoxynaphthalene-2,7-diol with dimethyl sulphate and dilute sodium hydroxide gave 2,3,6,7-*tetramethoxynaphthalene* (93% yield), which crystallised from chloroform–light petroleum as plates which sublimed at, or below 245° (Found: C, 67·45; H, 3·65. $C_{14}H_{16}O_4$ requires C, 67·75; H, 6·5%), $\lambda_{max.}$ 254, 263, 273, 301, 308, 315, 322, and 328 nm. (log ε 3·87, 3·72, 3·70, 3·62, 3·66, 3·87, 3·82, and 4·06), $\nu_{max.}$ (KCl) 1510 and 1610 cm.$^{-1}$, τ 6·05 (12H, s, 4 × ArOMe) and 2·98 (4H, s, 4 × ArH).

2,3,6,7-*Tetramethoxy*-1-*naphthaldehyde* (27).—2,3,6,7-Tetramethoxynaphthalene (3·7 g.) was stirred and heated under reflux for 2 hr., under nitrogen, with a mixture of toluene (23 ml.), dimethylformamide (23 ml.), and phosphoryl chloride (23 ml.; freshly distilled). The cooled mixture was decomposed by carefully adding a solution of sodium acetate. It was then extracted with benzene, and the extract was washed with water, dried, and evaporated *in vacuo* to give a brown solid from which, by chromatography on kieselgel G (200 g.) [ether–benzene (1 : 4)] 2,3,6,7-*tetramethoxy*-1-*naphthaldehyde* (2·3 g., 56%) was obtained. Recrystallisation from benzene–ether gave pale yellow rods, m.p. 155—156° (Found: C, 65·3; H, 5·8. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·85%), $\lambda_{max.}$ 244infl., 275infl., 340infl., and 370 nm. (log ε 4·46, 3·44, 3·82, and 3·91), $\nu_{max.}$ (KCl) 1674, 2840, 2880, 2950, and 3000 cm.$^{-1}$, τ 6·04 (3H, s, ArOMe), 5·99 (9H, s, 3 × ArOMe), 3·01 (1H, s, C-5 H), 2·69 (1H, s, C-4 H), 1·32 (1H s, C-8 H), and −0·78 (1H, s, CHO).

β-(2,3,6,7-*Tetramethoxy*-1-*naphthyl*)-trans-*acrylic Acid* (28; R = H).—A solution of 2,3,6,7-tetramethoxy-1-naphthaldehyde (2·3 g.) and ethoxycarbonylmethylene-triphenylphosphorane (7 g.) in benzene (100 ml.) was heated under reflux for 16 hr., and then evaporated *in vacuo*. The residual gum was dissolved in ethanol (60 ml.), dilute sodium hydroxide solution (2N; 40 ml.) was added, and the mixture was heated under reflux for 1 hr. It was then diluted with an equal volume of water and extracted with ether; the aqueous phase was acidified with dilute hydrochloric acid, and extracted with ether. From the ether extract, β-(2,3,6,7-*tetramethoxy*-1-*naphthyl*)-trans-*acrylic acid* (2·65 g., 100%) was obtained. Recrystallisation from chloroform–light petroleum gave pale yellow crystals, m.p. 174—176° (Found: C, 63·8; H, 5·1%; *m/e* 318·1112. $C_{17}H_{18}O_6$ requires C, 64·15; H, 5·7%; *M*, 318·1104), $\lambda_{max.}$ 237 and 335 nm. (log ε 4·65 and 3·92), $\nu_{max.}$ (KCl) 1685 and 2600—3000 cm.$^{-1}$, τ 6·11 (3H, s, ArOMe), 6·01 (9H, s, 3 × ArOMe), 3·25 (1H, d, J 16 Hz, *trans*-β-vinyl H), 2·95 (1H, s, C-5 H), 2·86 (1H, s, C-4 H), 2·66 (1H, s, C-8 H), 1·67 (1H, d, J 16 Hz, *trans*-α-vinyl H), and 0·84 (1H, diffuse, CO_2H).

β-(2,3,6,7-*Tetramethoxy*-1-*naphthyl*)*propionic Acid* (29).—Hydrogenation of β-(2,3,6,7-tetramethoxy-1-naphthyl)-*trans*-acrylic acid (2·3 g.) in ethyl acetate (100 ml.) at room temperature and pressure over 10% palladised charcoal (3 g.) gave β-(2,3,6,7-*tetramethoxy*-1-*naphthyl*)*propionic acid* (2 g., 87%), which formed needles, m.p. 124—127° (from ether–benzene) (Found: C, 63·6; H, 6·15. $C_{17}H_{20}O_6$ requires C, 63·75; H, 6·3%), $\lambda_{max.}$ 237 and 335 nm. (log ε 4·66 and 3·92), $\nu_{max.}$ (KCl) 1720, 2500—3000, and 3400 cm.$^{-1}$, τ 7·31 (2H, t, J 8 Hz, β-CH_2), 6·60 (2H, t, J 8 Hz, α-CH), 6·10, 6·08, 6·04, and 6·01 (4 × 3H s, ArOMe), 2·99 (1H, s, C-5 H), 2·96 (1H, s, C-4 H), 2·78 (1H, s, C-8 H), and 0·17 (1H, diffuse, CO_2H).

2,3-*Dihydro*-4,5,8,9-*tetramethoxyphenalen*-1-*one* (30).—β-(2,3,6,7-Tetramethoxy-1-naphthyl)propionic acid (2·3 g.) and polyphosphoric acid (10 g.) were stirred and heated on a steam-bath for 1—2 min., during which time the reaction started; it continued without external heating for 5—10 min. More polyphosphoric acid (20 g.) was added, and the mixture was stirred and heated on the steam-bath for a further 10 min. The mixture was decomposed by cooling it in ice and adding ice–water with stirring. It was extracted with benzene, and the extract was washed successively with water and with dilute sodium hydrogen carbonate solution, dried, and evaporated *in vacuo* to yield a golden oil which crystallised slowly. Chromatography on kieselgel G (100 g.) [ether–benzene (1 : 4)] afforded 2,3-*dihydro*-4,5,8,9-*tetramethoxyphenalen*-1-*one* (1·33 g., 62%) which gave white needles, m.p. 130—132° (from ether–benzene–light petroleum) (Found: C, 67·7; H, 6·2. $C_{17}H_{18}O_5$ requires C, 67·55; H, 6·0%), $\lambda_{max.}$ 244infl. and 350 nm. (log ε 4·38 and 3·89), $\nu_{max.}$ (KCl) 1693 cm.$^{-1}$, τ 7·19 (2H, t, J 7·5 Hz, β-CH_2), 6·52 (2H, t, J 7·5 Hz, α-CH_2), 6·13 (3H, s, ArOMe), 6·04 (9H, s, 3 × ArOMe), 3·00 (1H, s, C-6 H), and 2·73 (1H, s, C-7 H).

2,3-*Dihydro*-4,5,8,9-*tetramethoxy*-1-*phenylphenalen*-1-*ol* (31).—A solution of 2,3-dihydro-4,5,8,9-tetramethoxyphenalenone (604 mg.) in benzene (20 ml.) and ether (40 ml.) was added to a solution of phenylmagnesium bromide [from magnesium (500 mg.)] in ether (10 ml.), under nitrogen. The mixture was stirred and heated under reflux for 1 hr., cooled, decomposed with ammonium chloride solution, and extracted with ether. The extract was washed with water, dried, and evaporated under reduced pressure to give 2,3-*dihydro*-4,5,8,9-*tetramethoxy*-1-*phenylphenalen*-1-*ol* (760 mg., 99%) as a dark brown oil which crystallised. Two recrystallisations from benzene–light petroleum–methanol afforded plates, m.p. 135—136° (Found: *m/e* 380·1605. $C_{23}H_{24}O_5$ requires *M*, 380·1624), $\lambda_{max.}$ 241, 276, 282, 297, 317, and 331 nm. (log ε 4·85, 3·73, 3·76, 3·65, 3·43, and 3·60), $\nu_{max.}$ (KCl) 3480 cm.$^{-1}$, τ 7·40—7·80 (4H, m, C-2 and C-3 H), 6·67 (3H, s, 9-OMe), 6·19, 6·08, and 6·04 (3 × 3H, s, ArOMe), 4·39 (1H, s, OH), 2·98 and 2·89 (2 × 1H, s, C-6 and C-7H), and 2·75 (5H, s, Ph).

4,5,8,9-*Tetramethoxy*-3-*phenylphenalene* (32).—2,3-Dihydro-4,5,8,9-tetramethoxy-1-phenylphenalen-1-ol (700 mg.) was dehydrated by dissolving it in methanol (10 ml.) and dilute hydrochloric acid (5N; 5 ml.) and heating the solution under reflux for 10 min. The mixture was extracted with ether and the extract was washed with water, dried, and evaporated under reduced pressure to give 4,5,8,9-*tetramethoxy*-3-*phenylphenalene* (665 mg., 100%)

as a dark brown oil which crystallised. Two recrystallisations from chloroform–light petroleum afforded slightly yellow-brown rods, m.p. 151—153° (Found: C, 75·75; H, 6·15%; *m/e* 362·1518. $C_{23}H_{22}O_4$ requires C, 76·2; H, 6·1%; *M*, 362·1518), $\lambda_{max.}$ 240, 315infl., 330, and 342 nm. (log ε 4·65, 3·88, 3·99, and 3·91), $\nu_{max.}$ (KCl) 1602 cm.$^{-1}$, τ 6·93 (3H, s, 4-OMe), 6·15 (9H, s, 3 × ArOMe), 6·10 (2H, d, *J* 4·5 Hz, CH_2), 4·08 (1H, t, *J* 4·5 Hz, C-2 H), 3·14 and 3·09 (2 × 1H, s, C-6 and C-7 H), and 2·72 (5H, s, Ph).

2,5,6-*Trimethoxy*-9-*phenylphenalenone* (*Haemocorin Aglycone Dimethyl Ether A*) (33; $R^1 = R^2 =$ Me), *and* 2,5,6-*Trimethoxy*-7-*phenylphenalenone* (*Haemocorin Aglycone Dimethyl Ether B*) (34; $R^1 = R^2 =$ Me).—A solution of 4,5,8,9-tetramethoxy-3-phenylphenalene (430 mg.) in methanol (10 ml.) containing dilute hydrochloric acid (5N; 3 ml.) was stirred and heated under reflux in a nitrogen atmosphere for 1 hr. The mixture was extracted with chloroform and the extract was washed with water, dried, and evaporated *in vacuo*. The residue was dissolved in benzene (50 ml.), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (100 mg.) was added, and the solution was heated under reflux for 2·5 hr. It was then cooled, evaporated to one-quarter of its volume, and applied to five preparative t.l.c. plates (20 × 20 cm., 1 mm. coating of kieselgel G), which were eluted with phenol–benzene (3 : 17).* Extraction of the orange band of highest R_F value with chloroform gave 2,5,6-trimethoxy-9-phenylphenalenone (haemocorin aglycone dimethyl ether A) (33; $R^1 = R^2 =$ Me) (31 mg., 7·5%), which crystallised from benzene–light petroleum as orange plates, m.p. 171—172°, identical [mixed m.p. and i.r. (KCl), u.v., and mass spectra] with an authentic specimen derived from a natural source, τ 6·14, 5·92, and 5·90 (3 × 3H, s, ArOMe), 3·21, 3·05 (2 × 1H, s, C-3 and C-4 H), 2·58 (5H, s, Ph), 2·44 (1H, d, *J* 8 Hz, C-8 H), and 1·48 (1H, d, *J* 8 Hz, C-7 H).

The orange band of second highest R_F value afforded 2,5,6-trimethoxy-7-phenylphenalenone (haemocorin aglycone dimethyl ether B) (34; $R^1 = R^2 =$ Me) (77 mg., 19%), which crystallised from dry benzene–light petroleum as orange-red rods, m.p. 145—148°, identical [mixed m.p. and i.r. (KCl), u.v., and mass spectra] with an authentic specimen derived from a natural source. Crystallisation of this compound from wet solvents gave material of m.p. 80—82°. N.m.r. spectrum: τ 6·75 (3H, s, 6-OMe), 6·07 and 6·01 (2 × 3H, s, ArOMe), 3·16 (1H, s, C-3 H), 2·61 (5H, s, Ph), 2·55 (1H, s, C-4 H), 2·50 (1H, d, *J* 8 Hz, C-8 H), and 1·38 (1H, d, *J* 8 Hz, C-9 H).

6-*Hydroxy*-2,5-*dimethoxy*-9-*phenylphenalenone* (*Haemocorin Aglycone Monomethyl Ether C*) (33; $R^1 =$ H, $R^2 =$ Me).—Treatment of the phenalene (32), haemocorin aglycone dimethyl ether A (33; $R^1 = R^2 =$ Me), or haemocorin aglycone dimethyl ether B (34; $R^1 = R^2 =$ Me) with a mixture of 5N-hydrochloric acid and methanol (2 : 1) and heating the resulting solutions under reflux for 5 hr. gave in each case a purple phenolic oil. Chromatography of this oil on kieselgel G [ethanol–chloroform (2 : 98)] afforded 6-*hydroxy*-2,5-*dimethoxy*-9-*phenylphenalenone* (33; $R^1 =$ H, $R^2 =$ Me) (15—20% yield) as a purple glass, which, although chromatographically homogeneous, could not be crystallised (Found: C, 76·3; H, 5·15%; *m/e* 332·1047. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·85%; *M*, 332·1048), $\lambda_{max.}$ 247infl., 278, 311infl., 356, 372, and 504 nm. (log ε 4·00, 4·20, 3·87, 3·64, 3·67, and 3·56), $\nu_{max.}$ (KCl) 1628 and 3400 cm.$^{-1}$, τ 6·06 (6H, s, 2 × ArOMe), 3·75 (1H, diffuse, OH), 3·23 (1H, d, *J* 8 Hz, C-8 H), 3·13 (1H, s, C-3 or C-4 H), 2·60 (6H, s, Ph and C-3 or C-4 H), and 1·36 (1H, d, *J* 8 Hz, C-7 H).

Acetylation of the phenol (33; $R^1 =$ H, $R^2 =$ Me) (60 mg.) with a mixture of acetic anhydride and pyridine at room temperature gave a mixture of two acetates which were separated by preparative t.l.c. (20 × 20 cm. plate, 1 mm. coating of kieselgel G [phenol–benzene (3 : 17)]. The yellow band of higher R_F value afforded 6-*acetoxy*-2,5-*dimethoxy*-9-*phenylphenalenone* (33; $R^1 =$ Ac, $R^2 =$ Me) (50 mg., 74%) which crystallised from benzene–light petroleum as yellow rods, m.p. 211—213° (Found: C, 73·65; H, 4·8%; *m/e*, 374·1159. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·85%; *M*, 374·1154), $\lambda_{max.}$ 250infl., 275, 300infl., 338infl., 356infl., 370, and 445 nm. (log ε 4·23, 4·36, 3·97, 3·73, 3·89, 3·98, and 3·73), $\nu_{max.}$ (KCl) 1644 and 1765 cm.$^{-1}$, τ 7·50 (3H, s, ArO·COMe), 6·15 and 5·99 (2 × 3H, s, ArOMe), 3·24 (1H, s, C-3 H), 2·60 (5H, s, Ph), 2·55 (1H, s, C-4 H), 2·44 (1H, d, *J* 8·5 Hz, C-8 H), and 1·86 (1H, d, *J* 8·5 Hz, C-7 H). The yellow band of next highest R_F value gave 6-*acetoxy*-2,5-*dimethoxy*-7-*phenylphenalenone* (34; $R^1 =$ Me, $R^2 =$ Ac) (10 mg., 15%), which crystallised from benzene–light petroleum as yellow rods, m.p. 218—219° (Found: C, 73·05; H, 4·8%; *m/e* 374·1161. $C_{23}H_{18}O_5$ requires C, 73·8; H, 4·85%; *M*, 374·1154), $\lambda_{max.}$ 248, 276, 355infl., 369, and 450 nm. (log ε 4·12, 4·33, 3·92, 3·97, and 3·69), $\nu_{max.}$ 1632 and 1760 cm.$^{-1}$, τ 8·53 (3H, s, ArO·COMe), 6·03 (6H, s, 2 × ArOMe), 3·19 (1H, d, *J* 8 Hz, C-8 H), 3·12 (1H, s, C-3 H), 2·59 (5H, s, Ph), 2·50 (1H, s, C-4 H), and 1·43 (1H, d, *J* 8 Hz, C-9 H).

Methylation of Haemocorin Aglycone Monomethyl Ether C (33; $R^1 =$ H, $R^2 =$ Me).—Treatment of a solution of the phenol (33; $R^1 =$ H, $R^2 =$ Me) (2 mg.) in ether (2 ml.) with ethereal diazomethane (*ca.* 0·5N; 1 ml.) was shown by t.l.c. of the product [phenol–benzene (3 : 17)] to give a mixture of haemocorin aglycone dimethyl ethers A (33; $R^1 = R^2 =$ Me) and B (34; $R^1 = R^2 =$ Me). The components of the mixture had R_F values, colour, and reactions to conc. sulphuric acid identical (respectively) with those of the authentic dimethyl ethers run alongside on the same plate.

1-*Acetoxyacenaphthylene* (37).—A solution of acenaphthenone (1 g.) and toluene-*p*-sulphonic acid (50 mg.) in isopropenyl acetate (30 ml.) was slowly distilled (1 drop every 2 min.) for 6 hr. The solution was cooled, washed successively with dilute sodium hydrogen carbonate solution and water, dried, and evaporated *in vacuo* to give an orange oil, from which, by chromatography on kieselgel G (50 g.) (benzene), 1-*acetoxyacenaphthylene* (850 mg., 68%) was obtained (Found: C, 80·25; H, 4·9. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%), $\lambda_{max.}$ 229, 266, 277, 314, 320, 334, and 341 nm. (log ε 4·62, 3·57, 3·51, 3·93, 3·99, 3·77, and 3·69), $\nu_{max.}$ (KCl) 1765 cm.$^{-1}$, τ 7·70 (3H, s, OAc), 3·11 (1H, s, C-2 H), and 2·15—2·70 (6H, m, ArH).

Ozonolysis of 1-*Acetoxyacenaphthylene* (37).—A solution of 1-acetoxyacenaphthylene (100 mg.) in methylene chloride (100 ml.) was treated with a stream of ozonised oxygen at −20° until the yellow colour was discharged (0·40 l./min., 2—3 min.). The mixture was stirred with glacial acetic acid (7 ml.) and zinc dust (3 g.), then filtered. The oily product obtained from the filtrate was digested with dilute sodium hydrogen carbonate solution on a steam-bath for 15 min. The solution was acidified with

* We thank Dr. R. Thomas for suggesting this solvent system.

dilute hydrochloric acid and extracted with ethyl acetate. The organic layer was washed with water, dried, and evaporated *in vacuo* to leave a brown solid which gave the lactol (**38**; R = H) (50 mg., 53%) as needles, m.p. 168—171° (from chloroform) (lit.,[19] 168—169°), identical with the product obtained by treating acenaphthenequinone with 30% potassium hydroxide solution.

Methylation of the compound (**38**; R = H) with methanol and hydrochloric acid or diazomethane gave the methyl ether (**38**; R = Me) as white crystals, m.p. 104—105° (lit.,[20] 105°), $\nu_{max.}$ 1720 cm.$^{-1}$, τ 6·30 (3H, s, OMe), 3·55 (1H, s, O·CH·O), and 1·46—2·50 (6H, m, ArH).

Preparation of the β-*Keto-ester* (**39**).—A solution of the methyl ether (**38**; R = Me) (500 mg.) and methyl acetoacetate (372 mg.) in dry methanol (10 ml.) was added to a solution of sodium (75 mg.) in dry methanol (10 ml.) and the mixture was heated under reflux for 15 hr. The solvent was removed under reduced pressure, and the residual oil was chromatographed on a column of kieselgel G (100 g.) [ether–benzene–methanol (50 : 49 : 1)] to give the *condensation product* (**39**) (135 mg., 30%) as white needles, m.p. 143—145° (Found: C, 68·85; H, 4·85. $C_{17}H_{14}O_5$ requires C, 68·45; H, 4·75%), $\lambda_{max.}$ 240, 311, and 327 nm. (log ε 4·24, 3·77, and 3·70), $\nu_{max.}$ 1710 (lactone C=O), and 1725—1740 (ester and ketone C=O) cm.$^{-1}$, τ 7·82 (3H, s, Ac), 6·40 (3H, s, CO_2Me), 6·05 (1H, d, *J* 6 Hz, benzylic H), 3·50 (1H, d, *J* 6 Hz, proton α to ketone and ester groups), and 1·60—2·70 (6H, m, ArH).

We thank Dr. R. Thomas for providing authentic samples of haemocorin aglycone and its methyl ethers. We also thank the S.R.C. for a research studentship (to B. L.).

[0/1630 *Received, September 22nd,* 1970]