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# Colouring Matters of Australian Plants. XIX* Haemocorin: Unequivocal Synthesis of the Aglycone and Some Derivatives

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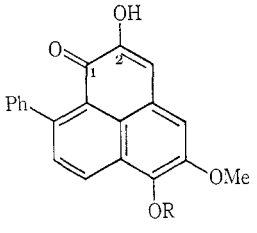
*Abstract*

The structures of haemocorin aglycone, a pigment of *Haemodorum corymbosum* Vahl., and its methyl ethers have been confirmed by unequivocal specific synthesis.

The identification of the pigment haemocorin[1] as a cellobioside of 2,6-dihydroxy-5-methoxy-9-phenylphenalenone (1) or its tautomer stimulated interest in the synthesis of phenalenone derivatives and several model compounds were prepared during the investigation of the natural product.[1,2] Subsequent studies have revealed that arylphenalenone pigments appear to be characteristic of the botanical family Haemodoraceae and several more compounds of this group have been described[3–5] as well as some related compounds.




(1) R = H
(2) R = Me

Some approaches to the synthesis of these natural products, including haemocorin aglycone and its derivatives, have been published.[5–8] Several difficulties arise in the controlled synthesis of the more complex phenalenones and some of these have been reported.[6] In particular, the tautomerism of some hydroxyphenalenones can lead to ambiguity because some reactions inevitably give mixtures of isomers. Thus Laundon and Morrison[6] succeeded only in the synthesis of a mixture of the two isomeric dimethyl ethers of haemocorin aglycone. While this was general confirmation of the original structure analysis[1] it was not a specific controlled synthesis of any one compound and did not provide independent proof of structure. Laundon and Morrison

* Part XVIII, *Aust. J. Chem.*, 1975, **28**, 1053.

[1] Cooke, R. G., Johnson, B. L., and Segal, W., *Aust. J. Chem.*, 1958, **11**, 230.
[2] Cooke, R. G., and Thomson, R. H., *Rev. Pure Appl. Chem.*, 1958, **8**, 85.
[3] Bick, I. R. C., and Blackman, A. J., *Aust. J. Chem.*, 1973, **26**, 1377.
[4] Edwards, J. M., and Weiss, U., *Phytochemistry*, 1974, **13**, 1597.
[5] Cooke, R. G., and Thomas, R. L., *Aust. J. Chem.*, 1975, **28**, 1053.
[6] Laundon, B., and Morrison, G. A., *J. Chem. Soc. C*, 1971, 1694.
[7] Forte, G. J., Zito, J. A., and Edwards, J. M., *Lloydia*, 1976, **39**, 192.
[8] Bazan, A. C., Edwards, J. M., and Weiss, U., *Tetrahedron Lett.*, 1977, **147**.

claimed their approach as a synthesis of haemocorin aglycone on the basis of the report[1] that *some* aglycone was formed by acid hydrolysis of one of its dimethyl ethers despite their failure to repeat this observation. Moreover, the aglycone is one of four possible products from that reaction which cannot be regarded as an efficient or unequivocal synthesis.

The earliest experiments in the synthesis of haemocorin aglycone were based like those of Laundon and Morrison on 2,3,6,7-tetrahydroxynaphthalene derivatives[9] as possible precursors of the two rings carrying the oxygen substituents in the natural pigment. As it was not possible to accomplish an unambiguous synthesis by this approach attention was later turned to the stepwise controlled synthesis of the pigment by means of 2,5,6-trihydroxyphenalenone or its derivatives.[2]

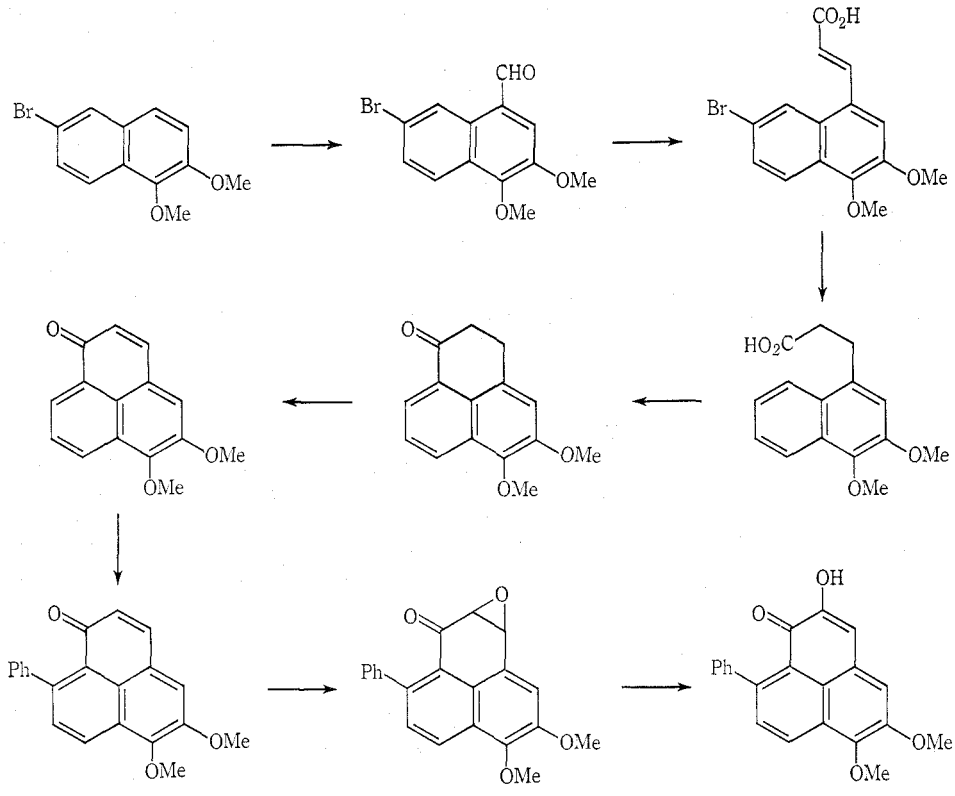
Two prototype reactions seemed ideally suitable for this project. Epoxidation of phenalenone has been used for the preparation of 2-hydroxyphenalenone,[10] and conjugate addition of a Grignard reagent to phenalenone, followed by dehydrogenation, is a specific route to 9-phenylphenalenone.[11] The general applicability of these reactions had to be explored and both had to be improved by modifications.

In the light of observations on the stability of hydrogen peroxide solutions[12] the epoxidation was found to be more efficient when sodium hydroxide and hydrogen peroxide in aqueous dioxan were used.[5] Even better results are obtained with t-butyl hydroperoxide and Triton B—a method for epoxidation of conjugated ketones introduced by Yang and Finnegan.[13] The conjugate addition of aryl Grignard reagents to phenalenones is improved by use of a high potential quinone for dehydrogenation of the intermediates. These modified reactions have been used successfully for the recent synthesis of several arylphenalenones including the natural pigments anigorufone and hydroxyanigorufone.[5,14]

Haemocorin aglycone monomethyl ether A (2) was eventually chosen as the primary objective for specific synthesis because selective hydrolysis of the activated 6-methoxy group is an acceptable unambiguous final step for the preparation of the aglycone, whilst further methylation of the monomethyl ether A gives only dimethyl ether A. In this way the structures of all the ethers would also be confirmed. The starting point chosen for this synthesis was 6-bromo-1,2-naphthoquinone. This compound offers several potential advantages. The bromine atom could be useful for the introduction of the required phenyl group at various stages in the synthesis. It also confers stability and suitable reactivity to the intermediates in the early stages of the synthesis, e.g. reduction to the quinol and methylation to give 6-bromo-1,2-dimethoxynaphthalene. It also served to simplify the n.m.r. spectra of intermediates thus facilitating confirmation of structures. Finally it seemed possible that the bromine atom might help to provide other options for the introduction of the 2-hydroxy group, e.g. by Barton oxidation of a dihydrophenalenone or condensation with nitrosodimethylaniline to give an anilinophenalenone. Both these methods have been used with varying success in earlier syntheses. Some of these alternatives were explored, and

[9] Cooke, R. G., Johnson, B. L., and Owen, W. R., *Aust. J. Chem.*, 1960, **13**, 256, and unpublished data.
[10] Fieser, L. F., and Newton, L. W., *J. Am. Chem. Soc.*, 1942, **64**, 917.
[11] Koelsch, C. F., and Anthes, J. A., *J. Org. Chem.*, 1941, **6**, 558.
[12] Nicoll, W. D., and Smith, A. F., *Ind. Eng. Chem.*, 1955, **47**, 2548.
[13] Yang, N. C., and Finnegan, R. A., *J. Am. Chem. Soc.*, 1958, **80**, 5845.
[14] Cooke, R. G., Dagley, I. J., and Perlmutter, P., unpublished data.

will be described later, but the most satisfactory sequence of operations proved to be that shown in Scheme 1.




Scheme 1

The scheme was also modified to specifically synthesize haemocorin aglycone dimethyl ether A by converting 5,6-dimethoxy-2,3-dihydrophenalenone into 2,5,6-trimethoxyphenalenone followed by conjugate addition of phenylmagnesium bromide and dehydrogenation.

In another sequence of reactions the bromine atom was retained in order to prepare some 9-bromophenalenones. Attempts to displace the bromine atom in these compounds or in 6-bromo-1,2-dimethoxynaphthalene by treatment with phenylmagnesium halide and nickel acetylacetonate[15] appeared to offer no advantage so this modification of the synthesis was not pursued further.

As haemocorin aglycone monomethyl ether A can be hydrolysed to give haemocorin aglycone this completes the unequivocal synthesis of the natural pigment.

## Experimental

Microanalyses were done by the Australian Microanalytical Service.

[15] Clough, R. L., Mison, P., and Roberts, J. D., *J. Org. Chem.*, 1976, **41**, 2252.

*6-Bromo-1,2-dimethoxynaphthalene*

6-Bromo-1,2-naphthoquinone[16] was reduced with sulphur dioxide essentially as described by Gates[17] and the crude quinol was methylated with dimethyl sulphate and anhydrous potassium carbonate in acetone. The product was passed over an alumina column in light petroleum and the *6-bromo-1,2-dimethoxynaphthalene* crystallized from the same solvent (b.p. 60–80°) in prisms, m.p. 53–54° (Found: C, 54·1; H, 4·2; Br, 29·7. $C_{12}H_{11}BrO_2$ requires C, 54·0; H, 4·2; Br, 29·9%).

*7-Bromo-3,4-dimethoxy-1-naphthaldehyde*

Phosphoryl chloride (174 ml) and dimethylformamide (174 ml) were mixed in chloroform (30 ml) at 0° and stirred under nitrogen for 10–15 min. A solution of 6-bromo-1,2-dimethoxynaphthalene (25 g) in dimethylformamide/chloroform (40 ml) was added and the mixture was heated in a bath at 110–120° under reflux condenser in a stream of nitrogen and was stirred for about 5 h. Most of the chloroform was evaporated under these conditions. The reaction mixture was then poured onto ice and aqueous sodium acetate. The suspension was extracted several times with toluene and the recovered *product* was sublimed in a vacuum and crystallized from benzene/light petroleum as fine needles, m.p. 99–101°, yield 67% (Found: C, 52·7; H, 3·7; Br, 26·8. $C_{13}H_{11}BrO_3$ requires C, 52·9; H, 3·7; Br, 27·1%).

*Ethyl 3-(7-Bromo-3,4-dimethoxy-1-naphthyl)propenoate*

7-Bromo-3,4-dimethoxynaphthaldehyde (5 g) and ethoxycarbonylmethylenetriphenylphosphorane (6 g) were dissolved in dry benzene (250 ml) and the mixture was boiled under reflux condenser for 6 h. The benzene was removed under reduced pressure and warm methanol was added to the residual oil. The *product* crystallized as pale yellow needles (yield 89%). After further crystallization from aqueous ethanol the m.p. was 96–98° (Found: C, 55·8; H, 4·8; Br, 21·9. $C_{17}H_{17}BrO_4$ requires C, 55·9; H, 4·7; Br, 21·9%).

*3-(7-Bromo-3,4-dimethoxy-1-naphthyl)acrylic Acid*

The above ester (5·5 g) was hydrolysed by boiling with methanol and sodium hydroxide solution (10%). The cooled mixture was acidified with conc. HCl and the bright yellow precipitate was collected and crystallized from chloroform/light petroleum. The *acid* (5·2 g) had m.p. 216–220° (Found: C, 53·4; H, 4·0; Br, 23·8. $C_{15}H_{13}BrO_4$ requires C, 53·4; H, 3·9; Br, 23·7%).

*3-(3,4-Dimethoxy-1-naphthyl)propanoic Acid*

The above unsaturated acid (495 mg) and sodium carbonate (1 g) were dissolved in water (50 ml). Palladium on charcoal (10%, 100 mg) was added and the mixture was shaken with hydrogen at atmospheric pressure until 2 equivalents had been absorbed. The solution was filtered and acidified with conc. HCl. The *product*[18] was collected, dried and crystallized from chloroform/light petroleum as needles (60% yield), m.p. 99·5–100° (Found: C, 68·8; H, 6·1; OMe, 23·2. $C_{15}H_{16}O_4$ requires C, 69·1; H, 6·1; OMe, 23·8%).

*5,6-Dimethoxy-2,3-dihydrophenalenone*

The above acid (100 mg) was suspended in trifluoroacetic anhydride (3 ml) and boron trifluoride diethyl etherate (0·3 ml) was added. The mixture was stirred under dry nitrogen for 130 min and was then poured into crushed ice (50 g). After extraction with benzene, washing with aqueous $NaHCO_3$ and drying ($Na_2SO_4$), the product was purified by chromatography on silica gel ($CHCl_3$/EtOAc 9 : 1). The major yellow band gave the required *5,6-dimethoxy-2,3-dihydrophenalenone*[19] (61% yield) which was crystallized from light petroleum or aqueous acetone as yellow needles, m.p. 92–92·5° (Found: C, 74·8; H, 5·9. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

[16] Fieser, L. F., and Hartwell, J. L., *J. Am. Chem. Soc.*, 1935, **57**, 1479.
[17] Gates, M., *J. Am. Chem. Soc.*, 1950, **72**, 228.
[18] Owen, W. R., Ph.D. Thesis, University of Melbourne, 1961, p. 21.
[19] Williams, B. D., Ph.D. Thesis, University of Melbourne, 1971, p. 132.

*5,6-Dimethoxyphenalenone*

The above dihydrophenalenone (100 mg) was dissolved in dry benzene (25 ml) and dichlorodicyanobenzoquinone (107 mg) was added. The mixture was boiled under nitrogen for 1·5 h. More oxidant was then added and the mixture heated for 0·5 h. The cooled mixture was filtered and evaporated under reduced pressure. The residue was purified by chromatography on a 1-mm layer of silica gel $GF_{254}$ ($CHCl_3$/EtOAc 9 : 1). Extraction of the major orange band and crystallization from benzene/light petroleum gave *5,6-dimethoxyphenalenone* (70%) as fine orange needles, m.p. 131–133° (Found: C, 75·0; H, 5·3. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%).

*5,6-Dimethoxy-9-phenylphenalenone*

A solution of 5,6-dimethoxyphenalenone (80 mg) in dry benzene (5 ml) was added over a period of 20 min to a solution of phenylmagnesium bromide (380 mg) in ether (5 ml). The mixture was stirred for 2¼ h after addition was complete and was then shaken with aqueous ammonium chloride. After separation the aqueous phase was extracted several times with benzene and the combined organic phases were washed with water. The product was boiled in benzene with dichlorodicyanobenzoquinone (70 mg) for 2 h under nitrogen. After standing overnight, the mixture was filtered and the solvent was removed under reduced pressure. The residue was purified by chromatography (silica gel $GF_{254}$, $CHCl_3$/EtOAc 9 : 1) and the major orange band was collected. Crystallization from benzene/light petroleum gave *5,6-dimethoxy-9-phenylphenalenone* (60% yield) as orange needles, m.p. 185–186° (Found: C, 79·7; H, 5·2. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%). N.m.r. ($CDCl_3$) $\delta$ 4·02 (s, 3H), 4·10 (s, 3H), 6·48 (d, 1H, *J* 9·5 Hz), 7·25 (d, 1H, *J* 9·5 Hz), 7·34 (br, 5H), 7·47 (s, 1H), 7·57 (d, 1H), 8·45 (d, 1H, *J* 7·5 Hz). *m/e* 316 (59), 315 (100%).

*2-Hydroxy-5,6-dimethoxy-9-phenylphenalenone*

5,6-Dimethoxy-9-phenylphenalenone (7 mg) was dissolved in dry benzene (5 ml), t-butyl hydroperoxide (14% in t-butyl alcohol, 0·01 ml) and benzyltrimethylammonium hydroxide (Triton B, 40% in methanol, 0·01 ml) were added while the mixture was cooled in ice-water. The stirred reaction mixture was allowed to warm to room temperature over a period of 4 h. After dilution with benzene the solution was washed several times with water, dried ($Na_2SO_4$), filtered and evaporated under reduced pressure. The resulting product was unstable but the p.m.r. spectrum was consistent with the expected epoxide. N.m.r. ($CDCl_3$) $\delta$ 4·03 (s, 6H), 4·09 (d, 1H, *J* 4·5 Hz), 4·50 (d, 1H, *J* 4·5 Hz), 7·39 (s, 5H), 7·53 (d, 1H, *J* 9·0 Hz), 7·62 (s, 1H), 8·37 (d, 1H, *J* 9·0 Hz). The colourless epoxide was easily converted into red 2-hydroxy-5,6-dimethoxy-9-phenylphenalenone by application to silica gel containing 2% oxalic acid, or by dissolving in acidified dichloromethane. The product crystallized from ethanol in red rods (57% yield). After sublimation in a vacuum and chromatography over $MgCO_3$ the compound was identical with haemocorin aglycone monomethyl ether (m.p., $R_F$, i.r.). *m/e* 332, 331 (100%).

*Hydrolysis of Haemocorin Aglycone Monomethyl Ether A*

(i) 2-Hydroxy-5,6-dimethoxy-9-phenylphenalenone (12 mg) in acetic acid (2 ml) and hydrochloric acid (1%, 2 ml) was heated on a steam bath for 6 h. Water was added, the products were extracted with chloroform and separated by t.l.c. on silica gel (toluene/acetone 9 : 1). The upper band (highest $R_F$) contained a small amount of unchanged material, the middle band was identified as haemocorin aglycone by $R_F$ and conversion into the diacetate (m.p. 248–250°) which was identical ($R_F$, m.m.p. i.r.) with material prepared from natural haemocorin aglycone. The third band had the same $R_F$ as lachnanthoside aglycone,[4] which is the expected product of complete demethylation. We thank Dr J. M. Edwards for a sample of lachnanthoside aglycone.

(ii) The monomethyl ether A (25 mg) was suspended in dioxan (15 ml) and dilute hydrochloric acid (3%, 15 ml). The mixture was heated on a steam bath for 7 h and then poured into water (120 ml). The product was extracted twice with ethyl acetate and the washed and dried extract was evaporated under reduced pressure without heating. The residue was twice fractionally sublimed under high vacuum to give black needles (yield 53%). This product, 2,6-dihydroxy-5-methoxy-9-phenylphenalenone, was identical with natural haemocorin aglycone[1] ($R_F$, colour reactions, i.r.). The

diacetate was prepared by reaction with acetic anhydride and a trace of pyridine. It crystallized from acetone as orange needles identical with the product derived from natural haemocorin aglycone[1] ($R_F$, i.r.).

*2,5,6-Trimethoxyphenalenone*

5,6-Dimethoxy-2,3-dihydrophenalenone (0·5 g) and *N,N*-dimethyl-4-nitrosoaniline (0·33 g) were dissolved in ethanol (16 ml) and ethanolic KOH (10%, 1·82 ml) was added. The mixture was stirred for 6·5 h and then poured into water (150 ml) to precipitate the deep violet anil (90% yield). Crystallization from aqueous ethanol gave deep violet needles of *2-(4-dimethylaminoanilino)-5,6-dimethoxyphenalenone*,[18,19] m.p. 169–170° (Found: C, 74·0; H, 6·0; N, 7·3. $C_{23}H_{22}N_2O_3$ requires C, 73·8; H, 5·9; N, 7·5%). This anil (300 mg) was added to hydrochloric acid (10%, 10 ml) and ethanol (3 ml). The mixture was heated at 70° for 2 h then water was added and the product extracted with ether. The recovered solid was methylated with dimethyl sulphate and potassium carbonate in acetone and the *2,5,6-trimethoxyphenalenone* (38 mg) crystallized from benzene/light petroleum as red needles, m.p. 163–166° (Found: C, 71·2; H, 5·3. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%). N.m.r. ($CDCl_3$) $\delta$ 3·89 (s, 3H), 3·99 (s, 3H), 4·04 (s, 3H), 6·75 (s, 1H), 7·34 (s, 1H), 7·66 (dd, 1H, *J* 7·5 and 8·5 Hz), 8·45 (dd, 1H, *J* 1·3 and 8·5 Hz), 8·55 (dd, 1H, *J* 1·3 and 7·5 Hz).

*2,5,6-Trimethoxy-9-phenylphenalenone*

2,5,6-Trimethoxyphenalenone (38 mg) was dissolved in dry benzene (5 ml) and the solution was added slowly to an ether solution of phenylmagnesium bromide made from magnesium (41 mg) and bromobenzene (0·16 ml). The mixture was boiled for 6·5 h and then stirred at room temperature for 14 h. Ice-cold aqueous ammonium chloride was added and the organic phase was separated and after drying it was boiled for 2·5 h with 2,3-dichloro-5,6-dicyanobenzoquinone. The cooled reaction mixture was filtered and the recovered product was separated by thin-layer chromatography (silica gel $GF_{254}$, $CHCl_3$/EtOAc 4 : 1). The major red band was removed and the product extracted was further purified by t.l.c. (silica gel $GF_{254}$, toluene/acetone 19 : 1). The product was again recovered and crystallization from ether gave large orange prisms, m.p. 171·5–172°, yield 37%. This product was identical with haemocorin aglycone dimethyl ether A[1] (m.m.p., $R_F$, i.r.).

*3-(7-Bromo-3,4-dimethoxy-1-naphthyl)-2-cyanopropenamide*

Cyanoacetamide (3·8 g) and 7-bromo-3,4-dimethoxy-1-naphthaldehyde (10 g) were dissolved in toluene (500 ml), acetic acid (1 ml) and piperidine (1 ml). The mixture was boiled for 3 h under a water separator and then allowed to stand at room temperature overnight. The orange crystals were collected, washed with light petroleum and dried (yield 84%). The *product* crystallized from aqueous ethanol as yellow needles, m.p. 210–212° (Found: C, 53·2; H, 3·7; Br, 22·0; N, 7·5. $C_{16}H_{13}BrN_2O_3$ requires C, 53·2; H, 3·6; Br, 22·1; N, 7·8%).

*3-(7-Bromo-3,4-dimethoxy-1-naphthyl)-2-cyanopropanamide*

The above cyano amide (5·9 g) was suspended in propan-2-ol (400 ml) and sodium borohydride (1·3 g) was added. The mixture was stirred at room temperature for 24 h and then a second portion of sodium borohydride (1·3 g) was added and the reaction continued for a further period of about 6 h whereupon all the unsaturated cyanoamide had been reduced. The mixture was poured into water and then extracted 3 times with ethyl acetate. The combined extracts were washed with water, dried ($Na_2SO_4$) and evaporated under reduced pressure. The resulting *product* (5 g, 84%) crystallized from acetone/light petroleum as small needles, m.p. 202–203° (Found: C, 52·9; H, 4·1; Br, 22·0; N, 7·6. $C_{16}H_{15}BrN_2O_3$ requires C, 52·9; H, 4·2; Br, 22·0; N, 7·7%).

*3-(7-Bromo-3,4-dimethoxy-1-naphthyl)propanoic Acid*

The above cyano amide (4·9 g) was suspended in aqueous sodium hydroxide (10%, 400 ml) and the mixture was boiled under reflux condenser until ammonia was no longer evolved. The reaction mixture was cooled and acidified to pH 1 with conc. HCl. The precipitate was collected, dissolved in acetone and the solution was filtered. Evaporation gave a white solid (4·3 g, 83%) which crystallized

from acetone/light petroleum in needles which melted with decomposition at 160–170°. This acid was characterized as the dimethyl ester, prepared by heating with methanol and a few drops of sulphuric acid. *Dimethyl (7-bromo-3,4-dimethoxy-1-naphthylmethyl)malonate* crystallized from light petroleum as plates, m.p. 83–85° (Found: C, 52·6; H, 4·7; Br, 19·7. $C_{18}H_{19}BrO_6$ requires C, 52·6; H, 4·7; Br, 19·4%). The substituted malonic acid (4·4 g) above was decarboxylated by heating at 180–200° under high vacuum. The white sublimate (2·7 g, 70%) was crystallized from chloroform/light petroleum to give *3-(7-bromo-3,4-dimethoxy-1-naphthyl)propanoic acid* as needles, m.p. 144–146° (Found: C, 53·2; H, 4·5; Br, 23·7. $C_{15}H_{15}BrO_4$ requires C, 53·1; H, 4·5; Br, 23·5%).

*9-Bromo-5,6-dimethoxy-2,3-dihydrophenalenone*

To a solution of the above naphthylpropanoic acid (0·2 g) in dichloromethane (3 ml), trifluoroacetic anhydride (1 ml) and boron trifluoride etherate (0·5 ml) were added. The mixture was stirred in a stoppered flask at room temperature for 50 min and then poured over crushed ice (50 g). The product was extracted twice with dichloromethane and the combined extracts were washed with aqueous $NaHCO_3$ and with water, dried ($Na_2SO_4$) and evaporated. The *9-bromo-5,6-dimethoxy-2,3-dihydrophenalenone* crystallized from light petroleum in yellow needles (52%), m.p. 141–143° (Found: C, 56·2; H, 4·0; Br, 24·9. $C_{15}H_{13}BrO_3$ requires C, 56·1; H, 4·1; Br, 24·9%). In another experiment the yield was increased to 71% with excess trifluoroacetic anhydride as solvent, and increasing the reaction time to 90 min.

*9-Bromo-2-(4-dimethylaminoanilino)-5,6-dimethoxyphenalenone*

9-Bromo-5,6-dimethoxy-2,3-dihydrophenalenone (69 mg) was condensed with *p*-nitrosodimethylaniline (32 mg) in dichloromethane (4 ml) and Triton B (40% in methanol, 0·1 ml) for 4 h at room temperature. The mixture was then diluted with dichloromethane, washed well with water, dried ($Na_2SO_4$) and evaporated. The residue was purified by t.l.c. (silica gel $GF_{254}$, chloroform/ethyl acetate 9 : 1) and the *anil* (27 mg, 28%) crystallized from chloroform in deep violet needles, m.p. 215–216° (Found: C, 60·5; H, 4·7; Br, 17·6; N, 6·0. $C_{23}H_{21}BrN_2O_3$ requires C, 60·9; H, 4·7; Br, 17·6; N, 6·2%).

*9-Bromo-5,6-dimethoxyphenalenone*

9-Bromo-5,6-dimethoxy-2,3-dihydrophenalenone (75 mg) was boiled in benzene (50 ml) with dichlorodicyanobenzoquinone (48 mg) under nitrogen for 2·5 h. A further quantity of oxidant (18 mg) was then added and the reaction continued for 1 h. After standing overnight the mixture was filtered and then boiled with oxidant (48 mg) until none of the dihydrophenalenone remained (several hours). The recovered product was purified by t.l.c. (silica gel $GF_{254}$, $CHCl_3$/EtOAc 9 : 1) and the major yellow band was extracted. The *product* (40 mg, 54%) crystallized from benzene/light petroleum as yellow needles, m.p. 205–206° (Found: C, 56·5; H, 3·6; Br, 24·8. $C_{15}H_{11}BrO_3$ requires C, 56·5; H, 3·5; Br, 25·0%).

*Reaction of 9-Bromo-5,6-dimethoxyphenalenone with Phenylmagnesium Iodide*

To a solution of the phenalenone (30 mg) and nickel(II) acetylacetonate (1 mg) in ether/benzene (1 : 1) was added phenylmagnesium iodide (from iodobenzene 0·12 ml) over a period of 1·25 h at −10 to −15°. The reaction was maintained at this temperature for a further period of 2 h and then stirred overnight at room temperature. Aqueous ammonium chloride was added and the recovered product was partly purified by t.l.c. (silica gel $GF_{254}$, $CHCl_3$). N.m.r. analysis indicated a 17% yield of 5,6-dimethoxy-9-phenylphenalenone together with much unchanged bromodimethoxyphenalenone.

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