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# DALBERGIA SPECIES—VI

## THE OCCURRENCE OF MELANNEIN[1] IN THE GENUS DALBERGIA

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**Abstract**- Extraction of *Dalbergia baroni* Baker heartwood gave a new 4-phenylcoumarin, melannein (Ia) in addition to the known dalbergin (II), S-4-methoxydalbergione (III) and formononetin (IV). The constitution of melannein is established. Syntheses of O-dimethylmelannein and O-diethylmelannein are described.

AN INVESTIGATION of the heartwood of *Dalbergia baroni*, Baker (Leguminosae-Papilionatae), commonly known as Voamboana or Rosewood of Madagascar, has led to the isolation of S-4-methoxydalbergione[2,3] (III), dalbergin[4] (II), formononnetin[1,5] (IV) and a new phenol $C_{15}H_8O_4(OMe)_2$ (melannein).

S-4-Methoxydalbergione (III) was identified by consideration of its IR spectrum, ORD curve and the formation of a racemate on crystallization with an equimolecular quantity of R-4-methoxydalbergione[3] isolated from *Dalbergia latifolia*. Dalbergin (II) was characterized by spectral data and formation of its O-methylether and monoacetate. The isoflavone, formononetin (IV) was identified by its spectroscopic properties (in particular the UV spectrum, which indicated the presence of the free 7-OH group by a bathochromic shift of 7 mμ on addition of saturated solution of sodium acetate) and confirmed by comparison with an authentic specimen.[6]

The Shinoda colour reaction and the UV spectrum [$\lambda_{max}^{EtOH}$ 234 mμ (log ε 4·38) sh; 256 mμ (log ε 4·17) sh; 308 mμ (log ε 4·0) sh; 344 mμ (log ε 4·09)] of the natural product $C_{15}H_8O_4(OMe)_2$ (Ia) suggested that it was a coumarin and its IR spectrum showed many peaks common to dalbergin and O-methyldalbergin. The phenolic nature of the OH groups in melannein was clearly demonstrated by a 50 mμ bathochromic shift in its UV spectrum on the addition of alkali. The OH groups were characterized by the formation of a diacetate ($\nu_{max}$ 1764 cm$^{-1}$; 7·76 τ and 7·70 τ singlets). Detailed examination of the NMR spectrum ($CDCl_3$) of the O-diacetate showed a multiplet (2·69–3·09 τ) assignable to the aromatic protons; a singlet (6·16 τ) for two OMe's and a signal at 3·82 τ for the proton of the α,β-unsaturated system. Two uncoupled singlets (2·84 τ and 3·09 τ) in the aromatic region were assigned to the *para* hydrogens of ring A.

The behaviour of melannein (Ia) under electron impact closely resembled that of coumarins.[7] The spectrum was interpreted as outlined in Fig. 1.

The ion *m/e* 271 could arise by loss of $C_2H_3O$ from the molecular ion or Me from the *m/e* 286 fragment ion. A metastable peak at M* = 256·8 confirmed that, in part at least, the fragment *m/e* 271 was derived from the ion *m/e* 286 by loss of Me. The lower mass fragment ions were not intense. The molecular ion of melannein O-dimethyl ether (Ib) also lost the stable neutral carbon monoxide molecule to give a benzofuran cation, but no metastable peaks were apparent to support a fragmentation pattern.

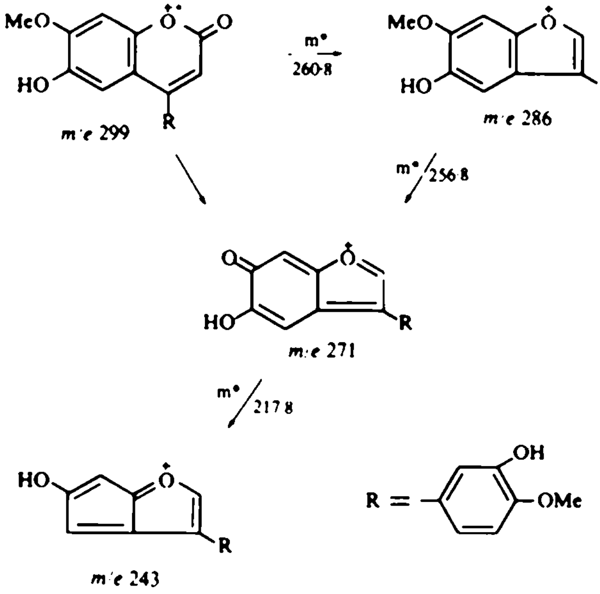


FIG. 1.

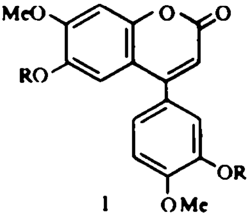
Melannein was methylated to give its O-dimethyl ether (Ib), which on neutral permanganate oxidation gave veratric acid and 2-hydroxy-3',4,4',5-tetramethoxybenzophenone. An authentic sample of the benzophenone was synthesized by Friedel–Crafts acylation of 1,2,4-trimethoxybenzene with veratroyl chloride under conditions which affected demethylation of the *ortho* OMe group. Reaction of the benzophenone (Va) with sodium acetate and acetic anhydride yielded a product identical with natural O-dimethylmelannein.

Isolation of 3-ethoxy-4-methoxybenzoic acid from the potassium permanganate oxidation of O-diethylmelannein (Ic) showed it to have one of two possible structures (Ic or VI). Structure Ic seemed more probable since compounds with a 6-hydroxy-7-methoxy- oxidation pattern had already been isolated from Dalbergia species and a displacement[8] of the $C_5$ proton signal in the NMR spectra was observed in going from the dimethyl ether to the diacetate of melannein.

The synthesis of Ic was effected by condensation of 1-ethoxy-2,4-dimethoxybenzene with 3-ethoxy-4-methoxybenzoyl chloride to yield 2-hydroxy-3',5-diethoxy-4,4'-dimethoxybenzophenone (Vb). Treatment of Vb with sodium acetate and acetic anhydride gave the acetate of Vb which cyclized on fusion with sodium acetate to give the coumarin Ic. A mixed m.p. determination with natural O-diethylmelannein showed no depression and the IR spectra of the two compounds were superposable.

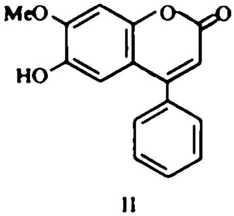
The synthesis of 7-ethoxy-6-methoxy-4-(3-ethoxy-4-methoxyphenyl)coumarin VI was carried out by a procedure similar to the preparation of Ic. A mixed m.p. of VI with O-diethylmelannein gave a depression and the IR spectra, though showing many features in common, were not superposable.

The 4-phenylcoumarin structure is relatively rare among natural products and this is the first reported isolation of a B-ring substituted 4-phenylcoumarin.*

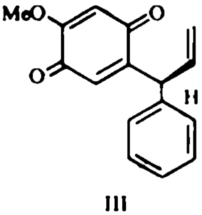


I

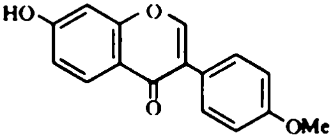
a: R = H
b: R = Me
c: R = Et



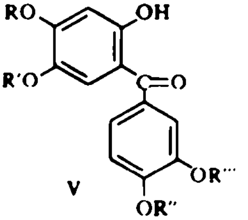
II



III

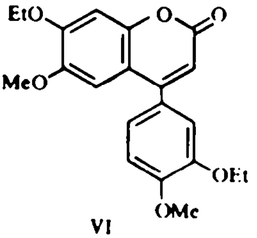


IV



V

a: R = R′ = R″ = R‴ = Me
b: R = R″ = Me, R′ = R‴ = Et
c: R′ = R″ = Me, R = R‴ = Et



VI

Melannein (Ia) has also been isolated from *Dalbergia melanoxylon*,[9] Guill. and Perr. In this heartwood it occurred with the known 2,5-dimethoxybenzoquinone[10] and a new natural product $C_{17}H_{18}O_5$ which has a dihydroxydimethoxy-3-methyl-2-phenyldihydrobenzofuran structure.

## EXPERIMENTAL

NMR spectra were determined on $CDCl_3$ solns unless otherwise stated, using a Varian HR-60A spectrometer; TMS was used as the internal standard. IR spectra were determined on KBr discs on a Grubb Parsons spectromaster. UV spectra were taken in MeOH solns unless otherwise stated, on a Bausch and Lomb spectronic 505 instrument. M.p.'s are uncorrected.

### *Extraction of* Dalbergia baroni, Baker *heartwood*

*Isolation of* S-4*-methoxydalbergione* (III), *dalbergin* (II), *melannein* (Ia) *and formononetin* (IV). Shavings of the heartwood (3 kg) were exhaustively extracted with ligroin and the extract after concentration and standing gave a yellow solid (25·7 g) which on repeated crystallization from ligroin afforded S-4-methoxydalbergione[2,3] as yellow needles, m.p. 118–119°. Crystallization from ligroin with an equimolecular quantity of R-4-methoxydalbergione[3] gave a racemate, m.p. 125–126°.

The heartwood shavings were subjected to further exhaustive extraction with MeOH and evaporation of the solvent yielded a brown oil (250 g). This oil was subsequently extracted with $Et_2O$ followed by EtOAc yielding brown oils on evaporation of the solvents. The $Et_2O$ soluble portion (80 g) was fractionated into acidic, phenolic and neutral fractions. Chromatography of the phenolic fraction on a silica gel column with dimethoxy-4-(4-methoxyphenyl)coumarin. F. Sanchez-Viesca, E. Diaz and G. Chavez, Sobretiro de Ciencia,

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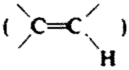
* Exostemin isolated from *Exostemma caribaeum* has been given the tentative structure 8-hydroxy-5,7-dimethoxy-4-(4-methoxyphenyl)coumarin F. Sánchez-Viesca, E. Díaz and G. Chávez, Sobretiro de Ciencia, Mex., XXV, (4) 135 (1967).

benzene–$CHCl_3$ (50/50) as eluant yielded dalbergin, m.p. 212–214°; the derivative O-methyldalbergin[11] had m.p. 142–143°.

The EtOAc soluble portion (40 g) was chromatographed on a silica gel column and elution with $CHCl_3$ gave a brown solid which crystallized from EtOH in a mixture of brown rhombs and colourless needles. The colourless compound was removed by heating with absolute EtOH and decanting the supernatant solution which, on concentration, deposited formononetin (160 mg) as needles, m.p. 252–253°. NMR (DMSO) spectrum $\tau$ 6·1 singlet ($—OC\underline{H}_3$); $\tau$ 5·42 singlet ($—O\underline{H}$); $\tau$ 3·14 to 2·99 doublet (aromatic protons in 6, 8, 3′, 5′ positions); $\tau$ 2·6 to 2·45 doublet (aromatic protons in 2′, 6′ positions); $\tau$ 2·1 to 1·94 doublet (aromatic proton in 5 position); $\tau$ 1·79 singlet ($—O—CH{=}\overset{|}{C}—$). The brown rhombs on repeated recrystallization from abs EtOH gave melannein (200 mg) as yellow rhombs, m.p. 221–223°. (Found: C, 65·1; H, 4·4; OMe, 19·8. $C_{17}H_{14}O_4$ requires: C, 65·0; H, 4·5; OMe, 19·8%); $\nu_{max}$ 3289 cm$^{-1}$ (OH); 1664 cm$^{-1}$ (CO); 1616 cm$^{-1}$, 817 cm$^{-1}$ (double bond); 2950 cm$^{-1}$, 1274 cm$^{-1}$, 1244 cm$^{-1}$, 1174 cm$^{-1}$, 1138 cm$^{-1}$, 1026 cm$^{-1}$ (OMe). NMR spectrum (DMSO) $\tau$ 7·5 to 6·2 multiplet (2X-O$\underline{H}$); $\tau$ 6·15 and 6·12 (2X-OC$\underline{H}_3$); $\tau$ 3·9 singlet (  $>C{=}C<_{H}$ ); $\tau$ 3·1 to 2·82 multiplet (5X aromatic protons).

O-*Diacetylmelannein*. A mixture of melannein (50 mg), anhyd pyridine (2 ml) and $Ac_2O$ (4 ml) was kept at room temp for 36 hr. Dilution of the mixture with ice–water (50 ml) gave O-diacetylmelannein which crystallized from aqueous EtOH (95%) in clusters (50 mg), m.p. 133–136°. (Found: C, 63·1; H, 4·6. $C_{21}H_{18}O_8$ requires: C, 63·3; H, 4·6%); $\nu_{max}$ 1764 cm$^{-1}$ (acetyl CO), 1730 cm$^{-1}$ (lactone CO).

O-*Dimethylmelannein* (Ib). A mixture of melannein (220 mg), $Me_2SO_4$ (0·6 ml), anhyd $K_2CO_3$ (5 g) and dry acetone (50 ml) was refluxed for 48 hr. The K salts were removed and washed with hot acetone. Evaporation of the combined filtrate and washings gave O-dimethylmelannein (215 mg) which crystallized from MeOH as needles, m.p. 220–221°. (Found: C, 66·8; H, 5·3; OMe, 36·4. $C_{19}H_{18}O_6$ requires: C, 66·7; H, 5·3; OMe, 36·2%); $\lambda_{max}$ 211 mμ (log ε 4·43), 236 mμ (log ε 4·17), 336 mμ (log ε 4·00). $\nu_{max}$ 1706 cm$^{-1}$ (CO). NMR spectrum $\tau$ 6·28, 6·12, 6·10 singlets (4X-OC$\underline{H}_3$); $\tau$ 3·82 singlet ($—C(Ar){=}C\underline{H}—CO—$); $\tau$ 3·14 to 2·7 multiplet (5X aromatic protons).

O-*Diethylmelannein* (Ic). Ethylation ($Et_2SO_4$ anhyd $K_2CO_3$–acetone method) afforded O-diethylmelannein (180 mg) which crystallized from MeOH in leaflets, m.p. 146–147°. (Found: C, 68·1; H, 6·1; OMe, 16·6; OEt, 24·3. $C_{21}H_{22}O_6$ requires: C, 68·1; H, 6·0; OMe, 16·8; OEt, 24·3%); $\lambda_{max}$ 236 mμ (log ε 4·39); 250 mμ (log ε 4·19) sh; 314 mμ (log ε 3·98) sh; 339 mμ (log ε 4·14). $\nu_{max}$ 1720 cm$^{-1}$ (CO).

*Oxidation of* O-*dimethylmelannein*. $KMnO_4$ (2 g) was added slowly to a soln of O-dimethylmelannein (400 mg) in acetone (500 ml) at 40°. The soln was stirred at 40° for 12 hr and left overnight at room temp. The acetone was removed, the residue suspended in water (100 ml) and saturated with $SO_2$. The resultant ppt was collected and proved to be unchanged O-dimethylmelannein (180 mg). An ethereal extract of the filtrate was extracted with 5% $NaHCO_3$aq and 10% NaOHaq. Acidification and ether extraction of the $NaHCO_3$ extract yielded veratric acid which crystallized from aqueous EtOH in needles, m.p. 178–179°, m.m.p. with an authentic sample 178–180°. The NaOH extract gave 2-hydroxy-3′,4,4′,5-tetramethoxybenzophenone which crystallized from MeOH in yellow needles, m.p. 144°, mixed m.p. with an authentic sample (see below) 143°.

*2-Hydroxy-3′,4,4′,5-tetramethoxybenzophenone* (Va). To an ice-cold mixture of anhyd $AlCl_3$ (24 g), 1,2,4-trimethoxybenzene (8·4 g) and dry ether (100 ml) was added a suspension of veratroyl chloride (12 g) in dry ether (100 ml). The mixture was kept at room temp for 48 hr and then treated with crushed ice and conc HCl (50 ml). The ether layer was separated and the aqueous layer extracted with $CH_2Cl_2$. Evaporation of the combined organic layers gave a residue, most of which dissolved readily in aqueous 10% NaOHaq. Acidification of the alkaline extract with dil HCl yielded 2-hydroxy-3′,4,4′,5-tetramethoxybenzophenone (7·5 g) which crystallized from MeOH in yellow needles, m.p. 145–146°.[12] (Found: C, 64·2; H, 5·8; OMe, 38·4. Calc. for $C_{17}H_{18}O_6$: C, 64·1; H, 5·7; OMe, 39·0%.)

*Synthetic* O-*dimethylmelannein*. A mixture of 2-hydroxy-3′,4,4′,5-tetramethoxybenzophenone (5 g), fused NaOAc (2 g) and $Ac_2O$ (4 ml) was refluxed for 24 hr. Additional $Ac_2O$ (1 ml) was added after 6 hr and 9 hr. The mixture was treated with ice–water to give a crude orange solid which, on repeated crystallization from MeOH, gave O-dimethylmelannein (1 g) as needles, m.p. 219·5–220·5°, mixed m.p. with natural O-dimethylmelannein 220·5–221°. (Found: C, 66·6; H, 5·3; OMe, 35·8. $C_{19}H_{18}O_6$ requires: C, 66·7; H, 5·3; OMe, 36·2%). The IR spectra of natural and synthetic O-dimethylmelannein were superposable.

*Oxidation of* O-*diethylmelannein*. O-Diethylmelannein (240 mg) was treated with $KMnO_4$ (1 g) using the reaction conditions described for O-dimethylmelannein. The $NaHCO_3$-extract yielded 3-ethoxy-4-methoxybenzoic acid which crystallized from aqueous EtOH in needles, m.p. 159·5–161·5°, mixed m.p. with an authentic sample, prepared by the method of Späth and Bernahuer,[13] showed no depression.

1-*Ethoxy-2,4-dimethoxybenzene*. $POCl_3$ (8 ml) was added slowly to a stirred mixture of resorcinol dimethyl ether (10 g) and dimethylformamide (12 g) maintaining the temp below 60°. The reaction mixture was kept at room temp for 3 hr, ice–water was added and the mixture kept at 0° for 12 hr. 2,4-Dimethoxybenzaldehyde (8·5 g) separated and on crystallization from EtOH gave prisms, m.p. 68–69°. Treatment of 2,4-dimethoxybenzaldehyde with ethereal $H_2O_2$ according to the method of Späth *et al.*[14] gave 2,4-dimethoxyphenol.

A mixture of 2,4-dimethoxyphenol (3 g), EtI (4 g), anhyd $K_2CO_3$ (5 g) and acetone (125 ml) was refluxed for 64 hr. The inorganic salts were removed and washed with hot acetone. Evaporation of the combined filtrate and washings gave a residue which was taken up in ether and washed with 5% NaOHaq and water. Evaporation of the dried ethereal soln and distillation of the residue (147–150°/3·5 mm Hg) afforded 1-ethoxy-2,4-dimethoxybenzene (2·1 g), as a colourless oil.[15]

3-*Ethoxy-4-methoxybenzoyl chloride*. Treatment of 3-ethoxy-4-methoxybenzoic acid[13] with $SOCl_2$ gave, on distillation (117°/0·7 mm Hg), 3-ethoxy-4-methoxybenzoyl chloride, m.p. 102–103°.

2-*Hydroxy-3′,5-diethoxy-4,4′-dimethoxybenzophenone*. A Friedel–Crafts acylation (method as for Va above) of 1-ethoxy-2,4-dimethoxybenzene (6 g) with 3-ethoxy-4-methoxybenzoyl chloride (8 g) gave a mixture of 3 compounds. A rough separation was effected using a small quantity of warm MeOH giving readily soluble and insoluble fractions. Fractional crystallization from MeOH of the soluble portion gave 2 compounds, (a) 2-hydroxy-3′,5-diethoxy-4,4′-dimethoxybenzophenone (3 g) as yellow needles, m.p. 121–122°. (Found: C, 65·6; H, 6·5; OMe, 17·8; OEt, 25·9. $C_{19}H_{22}O_6$ requires: C, 65·9; H, 6·4; OMe, 17·9; OEt, 26·0%); $\lambda_{max}$ 239, 291, 358 mμ (log ε 4·10, 3·90, 3·92); $\nu_{max}$ 1627 cm$^{-1}$ (chelated CO); NMR spectrum τ 8·62, 8·51 triplets ($J$ = 7 c/s) ($2X\text{-}OCH_2C\underline{H}_3$); τ 6·08, 6·04 singlets ($2X\text{-}OC\underline{H}_3$); τ 6·08, 5·86 quartets ($J$ = 7 c/s) ($2X\text{-}OC\underline{H}_2CH_3$); τ 3·47 singlet and τ 3·09 to 2·55 multiplet (5X aromatic protons); τ −2·43 singlet (—O$\underline{H}$); (b) 3′,5-diethoxy-2,4,4′-trimethoxybenzophenone (450 mg) as white needles, m.p. 101–102°. (Found: C, 66·3; H, 7·0; OMe, 25·8; OEt, 25·0. $C_{20}H_{24}O_6$ requires: C, 66·7; H, 6·7; OMe, 25·8; OEt, 25·0%); $\lambda_{max}$ 236 mμ (log ε 4·40), 283 mμ (log ε 4·10), 317 mμ (log ε 4·08); $\nu_{max}$ 1642 cm$^{-1}$ (CO).

The third compound on crystallization from large volumes of MeOH proved to be 2-(3-ethoxy-4-methoxybenzoyl)-3′,5-diethoxy-4,4′-dimethoxybenzophenone (1 g) obtained as needles, m.p. 148·5–149°. (Found: C, 66·1; H, 6·3; OMe, 18·1; OEt, 26·2. $C_{29}H_{32}O_9$ requires: C, 66·4; H, 6·2; OMe, 17·8; OEt, 26·0%); $\nu_{max}$ 1724 cm$^{-1}$ (benzoate CO), 1658 cm$^{-1}$ (aryl CO).

*Synthetic* O-*diethylmelannein*. A mixture of 2-hydroxy-3′,5-diethoxy-4,4′-dimethoxybenzophenone (2·5 g), fused NaOAc (1 g) and $Ac_2O$ (4 ml) was refluxed for 24 hr. Addition of ice water to the cooled reaction mixture gave a solid, which crystallized from aqueous MeOH as needles, m.p. 90–92°. The solid was a mixture of 2-acetoxy-3′,5-diethoxy-4,4′-dimethoxybenzophenone and O-diethylmelannein. The mixture (400 mg) was fused with NaOAc (400 mg) for 3½ hr at 200°. Treatment of the reaction mixture with ice–water gave a solid, which crystallized from MeOH in leaflets of O-diethylmelannein (230 mg), m.p. 145–146°, mixed m.p. with natural O-diethylmelannein showed no depression. (Found: C, 68·4; H, 6·2; OMe, 16·6; OEt, 24·1. $C_{21}H_{22}O_6$ requires: C, 68·1; H, 6·0; OMe, 16·8; OEt, 24·3%). The IR spectra of synthetic and natural O-diethylmelannein were superposable.

2-*Ethoxy-1,4-dimethoxybenzene*. To a stirred soln of 3-ethoxy-4-hydroxybenzaldehyde (11·0 g) in 1N NaOHaq (90 ml), in atmosphere of $N_2$, a soln of $H_2O_2$ (66 ml, 6%) was added dropwise over 0·5 hr maintaining the temp at 40–50°. Sodium dithionite (0·1 g) was added to the cooled reaction mixture which was then acidified (10% $H_2SO_4$) to pH 3–4. NaCl (20 g) was added to the acid soln, 2-ethoxy-1,4-dihydroxybenzene (8·0 g) separated and on crystallization from 95% EtOH gave prisms, m.p. 112°.[16]

Sodium dithionite (0·13 g) and $Me_2SO_4$ (7 ml) were added to a soln of 2-ethoxy-1,4-dihydroxybenzene (3·2 g) in abs EtOH (5 ml) in an atmosphere of $N_2$. NaOHaq (2·6 g NaOH; 7·0 ml $H_2O$) was added dropwise to the soln over 0·5 hr. The reaction mixture was heated for 1·5 hr and water (50 ml) added. 2-Ethoxy-1,4-dimethoxybenzene (3 g) separated and on crystallization from aqueous EtOH gave needles, m.p. 42–43°.[15]

2-*Hydroxy-3′,4-diethoxy-4′,5-dimethoxybenzophenone* (Vc). A Friedel–Crafts acylation (method as for Va above) of 2-ethoxy-1,4-dimethoxybenzene (2·275 g), and 3-ethoxy-4-methoxybenzoyl chloride (3·2 g) gave a solid. Fractional crystallization of this solid from MeOH gave 2-hydroxy-3′,4-diethoxy-4′,5-dimethoxybenzophenone (1 g) as yellow needles, m.p. 132–133°. (Found: C, 66·2; H, 6·6; OMe, 18·0; OEt, 26·1. $C_{19}H_{22}O_6$ requires: C, 65·9; H, 6·4; OMe, 17·9; OEt, 26·0%); $\lambda_{max}$ 242, 291, 360 mμ (log ε 4·10, 3·92, 3·95).

$\nu_{max}$ 1639 $cm^{-1}$ (CO); NMR spectrum τ 8·55, 8·52 triplets (*J* = 7 c/s) (2X-$OCH_2C\underline{H}_3$); τ 6·24, 6·05 singlets (2X-$OC\underline{H}_3$); τ 5·89, 5·86 quartets (*J* = 7 c/s) (2X-$OC\underline{H}_2CH_3$); τ 3·45 singlet and τ 3·13 to 2·5 multiplet (5X aromatic protons); τ −2·58 singlet (–O$\underline{H}$).

The mother liquors yielded 3′,4-diethoxy-2,5,4′-trimethoxybenzophenone (320 mg) as plates, m.p. 112–113°. (Found: C, 66·4; H, 7·0; OMe, 25·7; OEt, 24·9. $C_{20}H_{24}O_6$ requires: C, 66·7; H, 6·7; OMe, 25·8; OEt, 25·0%); $\lambda_{max}$ 237 mμ (log ε 4·35), 283 mμ (log ε 4·07), 317 mμ (log ε 4·02). $\nu_{max}$ 1656 $cm^{-1}$ (CO).

*7-Ethoxy-6-methoxy-4-(3-ethoxy-4-methoxyphenyl)coumarin.* 2-Hydroxy-3′,4-diethoxy-4′,5-dimethoxybenzophenone (1 g), NaOAc (5 g) and $Ac_2O$ (4 ml) were refluxed for 24 hr. Treatment with ice-water of the reaction mixture gave a solid (500 mg), m.p. 160–162°, which was a mixture of 2-acetoxy-3′,4-diethoxy-4′,5-dimethoxybenzophenone and 7-ethoxy-6-methoxy-4-(3-ethoxy-4-methoxyphenyl)coumarin. The mixture (500 mg) was fused with NaOAc (500 mg) for 4 hr at 210°. Addition of ice–water to the reaction mixture gave a solid which was purified by elution with benzene–$CHCl_3$ (70:30) from a silica gel column, followed by repeated crystallization from MeOH to give 7-ethoxy-6-methoxy-4-(3-ethoxy-4-methoxyphenyl)coumarin (15 mg) as needles, m.p. 141·5–142·5°. (Found: C, 68·1; H, 5·8; OMe, 16·5; OEt, 24·0. $C_{21}H_{22}O_6$ requires: C, 68·1; H, 6·0; OMe, 16·8; OEt, 24·3%). A mixed m.p. with natural O-diethylmelannein showed a depression.

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