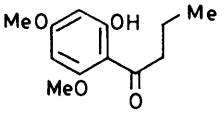
Isolation and Identification of Two Phenolic Ketones and a Chromone from *Dysophylla stellata* Benth.

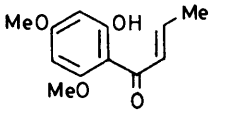
By **Balawant S. Joshi** * and **Kongovi R. Ravindranath**, CIBA-GEIGY Research Centre, Goregaon, Bombay 400 063, India

From the whole plant *Dysophylla stellata* Benth., 2'-hydroxy-4',6'-dimethoxybutyrophenone (1), 1-(2-hydroxy-4,6-dimethoxyphenyl)but-2-en-1-one (2), and 5-hydroxy-6,7-dimethoxy-2-methylchromone (3) (stellatin) have been isolated. Their structures have been assigned on the basis of spectral evidence and synthetic experiments.

Dysophylla stellata Benth. (Labiatae) is a flowering shrub growing in the Western Ghats of India. Chromatography of the hexane extract of the whole plant gave a compound, $C_{12}H_{16}O_4$ (M^+ 224), exhibiting $\lambda_{max.}$ 285 nm (log ε 4.27) and $\nu_{max.}$ 1 620 and 1 600 cm^{-1}. The u.v. maximum suggested a phloroacetophenone chromophore [1] and the 1 620 cm^{-1} i.r. band indicated a hydroxy-group strongly chelated with an adjacent carbonyl group. The n.m.r. spectrum showed doublets at δ 6.08 and 5.92 (1 H each, J 2 Hz, *meta*-coupled ArH), two methoxy signals at 3.85 and 3.8, a chelated hydroxy-resonance at 14.1 (1 H, exchanged with D_2O), and a propyl ketone grouping at 0.95 (3 H, t, J 7 Hz, $CH_2{\cdot}CH_3$), 1.7 (2 H, m, $CH_2{\cdot}CH_2{\cdot}CH_3$), and 2.95 (2 H, t, J 7 Hz, $CO{\cdot}CH_2{\cdot}CH_2$). On the basis of these data, the compound was assigned structure (1). It was identical



(1)



(2)

with the product of a Hoesch reaction of phloroglucinol dimethyl ether with butyronitrile.[2]

The compound eluted next, $C_{12}H_{14}O_4$ (M^+ 222), showed $\lambda_{max.}$ 240 and 312 nm. A bathochromic shift to 327 nm on addition of aluminium chloride, together with an i.r. band at 1 620 cm^{-1}, an n.m.r. signal at δ 14.25 (1 H, exchanged with D_2O), and a blue-green colouration obtained with iron(III) chloride, indicated the presence of a hydroxy-group chelated to a carbonyl. In addition, the n.m.r. spectrum showed signals at δ 7.2 (2 H, m, CH:CH), 6.1 and 5.95 (each 1 H, d, J 2 Hz, *meta* coupled ArH), 3.85 and 3.8 (each 3 H, s, OMe), and 1.95 (3 H, d, J 6 Hz, *Me*CH:). The data suggested that the compound was 1-(2-hydroxy-4,6-dimethoxyphenyl)but-2-en-1-one (2), and this was confirmed by synthesis in low yield from phloroglucinol dimethyl ether and crotonyl chloride. In the preparation of 2-hydroxy-4-methoxy-crotonophenone, the yield is reported to be low and variable.[3] Catalytic reduction of the product (2) afforded the butyrophenone (1).

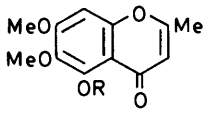
In another attempt to synthesize compound (2), phloroglucinol dimethyl ether was treated with crotononitrile under Hoesch reaction conditions. The resulting compound, $C_{12}H_{14}O_4$, showed $\lambda_{max.}$ 211, 274, and 279 nm and $\nu_{max.}$ 1 755, 1 630, and 1 590 cm^{-1}. 5,8-Dimethoxy-2-methylchromanone prepared by hydrogenation of the corresponding chromone showed $\lambda_{max.}$ 206, 231, 270, and 353 nm and $\nu_{max.}$ 1 680 and 1 598 cm^{-1}. These u.v. data [4] and the n.m.r. spectrum of the compound indicated it to be the ' abnormal ' product, 3,4-dihydro-5,7-dimethoxy-4-methylcoumarin (4).[5]

The compound eluted next was stigmasterol. Later fractions yielded stellatin, $C_{12}H_{12}O_5$ (M^+ 236). It gave a violet colouration with iron(III) chloride, i.r. bands at 1 620 and 1 660 cm^{-1}, and u.v. maxima at 231, 252, 258, and 290 nm, characteristic of chromones. Addition of aluminium chloride to an ethanolic solution resulted in a bathochromic shift of the long wavelength band, indicative of a 5-hydroxychromone. The n.m.r. spectrum showed a hydroxy-proton singlet at δ 12.7 (exchanged with D_2O), signals for an aromatic proton at 6.4 (1 H, s) and a vinyl proton at 6.0 (1 H, s), a singlet at 3.91 due to two methoxy-groups, and a singlet at 2.39 due to a methyl group on a double bond. Stellatin did not afford an acetate with acetic anhydride–pyridine,

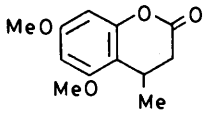
[1] T. W. Campbell and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1951, **73**, 2708.
[2] F. W. Canter, F. H. Curd, and A. Robertson, *J. Chem. Soc.* 1931, 1245.
[3] J. Smith and R. H. Thomson, *J. Chem. Soc.*, 1960, 349.
[4] E. Frasson, G. Rodighiero, and C. Panattoni, *Ricerca Sci.*, 1958, **28**, 517; D. C. Allport and J. D. Bu'Lock, *J. Chem. Soc.*, 1960, 654.
[5] P. E. Spoerri and A. S. Du Bois, *Org. Reactions*, 1949, **5**, 387.

but on heating with acetic anhydride–sodium acetate gave a monoacetate.

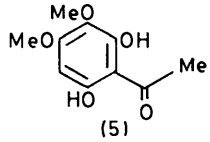
Degradation of stellatin with aqueous potassium hydroxide afforded 2′,6′-dihydroxy-3′,4′-dimethoxyacetophenone (5), m.p. 136—137°. In earlier literature [6] the m.p. of the ketone (5) was reported to be 162—164°;



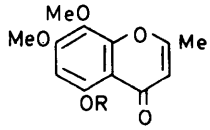
(3) R = H
(8) R = Ac



(4)



(5)



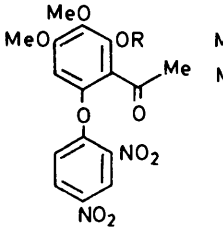
(6) R = H
(7) R = Me
(9) R = Ac

however, this was later corrected,[7] and an authentic sample of (5) prepared according to the procedure of Horton and Stout was identical with our degradation product. Stellatin should therefore be formulated as (3) or (6).

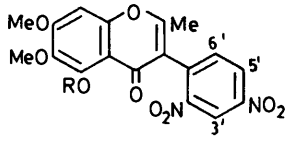
5-Hydroxy-7,8-dimethoxy-2-methylchromone (6) [8] prepared by demethylation of the methyl ether (7) [9] is reported to have m.p. 171°. Since an authentic sample of (6) was not available, it was prepared by a known procedure,[10] and was found to be different from stellatin (m.p., t.l.c., and i.r. spectrum). Stellatin therefore has structure (3). Its monoacetate (8), m.p. 150°, was also different from the acetate (9), m.p. 152—154°, prepared from (6). Structure (3) is also consistent with the mass spectrum; loss of a methyl radical to give an intense $(M - CH_3)^+$ peak and subsequent loss of CO from this is analogous to the fragmentation pattern reported for 6-methoxyflavones.[11]

In another attempted synthesis of the chromone (6), the ether (10) [7] was acetylated to give (11). An attempt to carry out a Baker–Venkataraman rearrangement of (11) with pyridine–potassium hydroxide [12] resulted in an abnormal product, $C_{18}H_{14}N_2O_9$. This gave a blue-green colouration with iron(III) chloride and its n.m.r. spectrum showed a chelated phenolic hydroxy-signal at δ 12.1 which disappeared on acetylation. Both the phenol and its acetate showed intense u.v. absorption at *ca.* 280 nm and an inflection of low intensity in the region 300—320 nm, indicative of an isoflavone.[13] A sharp n.m.r. singlet in the aromatic region at δ 6.9 suggested the presence of an 8- rather than a 6-proton.[14] On the basis of analytical and spectral data, the compound has been provisionally formulated as (12) and its acetate as (13). However, the 5-hydroxy-7,8-dimethoxy-2-methylisoflavone structure is not completely ruled out. An alternative 7,8-dimethoxy-2-methylchromone structure with the dinitrophenyl group at C-6 is ruled out, as the n.m.r. spectrum did not show a vinylic 3-proton signal (δ *ca.* 6.0). The same rearrangement product was obtained when compound (11) was refluxed with acetone and anhydrous potassium carbonate. This is an interesting variation of the Smiles rearrangement,[15] and may provide a useful route to 2-methylisoflavones.

A number of chromones have been isolated previously from lichens and plants belonging to the families Meliaceae, Myrtaceae, Rutaceae, and Umbelliferae,[16,17] but their occurrence in the Labiatae has not been recorded. Although a number of chromanones have been isolated from natural sources, the corresponding open-chain compounds have not been encountered previously, in contrast to the case of the chalcones,



(10) R = H
(11) R = Ac



(12) R = H
(13) R = Ac

which are isomeric with the flavanones.[18] The isolation of the crotonophenone (2) thus appears to be biogenetically significant.

EXPERIMENTAL

U.v. spectra were measured with a Beckman DK-2A spectrophotometer, i.r. spectra with a Perkin-Elmer Infracord instrument, n.m.r. spectra with a Varian A-60 spectrometer (Me_4Si as internal standard), and mass spectra with an Atlas CH-7 instrument.

Extraction of Dysophylla stellata *Benth. and Isolation of the Constituents.*—The dried and powdered whole plant (1.6 kg) was extracted with hexane (8 l × 2), and the solvent was removed under reduced pressure to afford a brown oil (60 g) which on cooling deposited a solid (5.4 g). This was crystallized from benzene–hexane to afford plates of *5-hydroxy-6,7-dimethoxy-2-methylchromone* (*stellatin*) (3),

[6] M. Nierenstein, *J. Chem. Soc.*, 1917, **4**, 111.
[7] W. J. Horton and M. G. Stout, *J. Org. Chem.*, 1962, **27**, 830.
[8] S. Raychaudhuri, T. R. Seshadri, and S. K. Mukerjee, *Indian J. Chem.*, 1972, **10**, 1125.
[9] D. K. Chakravorty, S. K. Mukerjee, V. V. S. Murty, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1952, **35A**, 34.
[10] C. B. Rao, V. K. Murty, T. V. P. Rao, and V. Venkateswarlu, *Rec. Trav. chim.*, 1964, **83**, 1122.
[11] D. G. I. Kingston, *Tetrahedron*, 1971, **27**, 2691.
[12] W. Baker, *J. Chem. Soc.*, 1933, 1381; H. S. Mahal and K. Venkataraman, *ibid.*, 1934, 1767.
[13] L. Jurd in 'The Chemistry of Flavonoid Compounds,' ed. T. A. Geissman, Pergamon, London, 1962, p. 147.
[14] T. J. Mabry, K. R. Markham, and M. B. Thomas, 'The Systematic Identification of Flavonoids,' Springer Verlag, Berlin, 1970, p. 261.
[15] W. J. Evans and S. Smiles, *J. Chem. Soc.*, 1936, 329.
[16] F. M. Dean, 'Naturally Occurring Oxygen Ring Compounds,' Butterworths, London, 1963, p. 251.
[17] T. K. Devon and A. I. Scott, 'Handbook of Naturally Occurring Compounds,' Academic Press, New York, vol. 1, 1975, p. 270.
[18] J. B. Harbourne, T. J. Mabry, and H. Mabry, 'The Flavonoids,' Chapman and Hall, London, 1975, p. 878.

m.p. 124—125°; $\lambda_{max.}$ (EtOH) 231, 252, 258, and 290 nm (log ε 4.32, 4.19, 4.18, and 3.99); $\nu_{max.}$ (Nujol) 1 660, 1 620, 1 590, 1 500, 1 300, 1 210, 1 180, 1 125, and 1 100 cm^{-1}; *m/e* 236 (M^+, 81%), 221 (90), 207 (27), 205 (9), 193 (100), 190 (16), 176 (11), 153 (27), 150 (16), 122 (33), 109 (16), 107 (16), and 93 (18) (Found: C, 61.0; H, 5.4. $C_{12}H_{12}O_5$ requires C, 61.0; H, 5.1%).

The mother liquor was concentrated to give an oil (30 g) which was dissolved in hexane and chromatographed on silica gel (220 g). Fractions (200 ml) were collected and the separation was monitored by t.l.c. (see Table).

Fraction	Eluant	Weight of fraction (g)	T.l.c. R_F ($CHCl_3$–C_6H_6, 1 : 1)	Compound
1	Hexane	1.2		
2—13	Hexane–benzene (1 : 1)	18.0		
14		0.4	0.65	(1)
15—16		0.3		
17—19	Hexane–benzene (2 : 3)	0.1	0.60	(2)
20—32	Hexane–benzene (1 : 3)	4.1		
33—34	Benzene	0.3	0.55	Stigmasterol
35—38	Benzene–chloroform	2.0	0.50	(3)

Fraction 14 on concentration deposited large plates, recrystallized from hexane to afford 2′-hydroxy-4′,6′-dimethoxybutyrophenone (1) (35 mg), m.p. 72—73°, $\nu_{max.}$ (Nujol) 1 620, 1 600, 1 460, 1 420, 1 380, 1 305, 1 272, 1 210, 1 170, 1 130, and 1 110 cm^{-1}; *m/e* 224 (M^+, 20%), 209 (3), 181 (100), 167 (6), 166 (10), 138 (4), and 123 (3) (Found: C, 64.6; H, 7.7. Calc. for $C_{12}H_{16}O_4$: C, 64.3; H, 7.2%).

Fractions 17—19 on recrystallization from hexane gave 1-(2-*hydroxy*-4,6-*dimethoxyphenyl*)*but*-2-*en*-1-*one* (2) (30 mg), m.p. 102—103°, $\lambda_{max.}$ (EtOH) 240 and 312 nm (log ε 3.9 and 4.24); $\nu_{max.}$ (Nujol) 3 370, 2 940, 1 620, 1 580, 1 460, 1 420, 1 380, 1 350, 1 292, 1 220, 1 170, and 1 110 cm^{-1}; *m/e* 222 (M^+, 4%), 207 (100), 192 (14), 181 (18), 166 (2), 157 (1), 138 (3), 137 (2), 125 (1), 123 (2), 95 (7), and 69 (7) (Found: C, 64.6; H, 6.5. $C_{12}H_{14}O_4$ requires C, 64.8; H, 6.6%).

Fractions 33—34 gave a solid which on crystallization from hexane afforded stigmasterol (105 mg), m.p. 158°, identical with an authentic specimen (mixed m.p., t.l.c., and i.r. spectrum).

Fractions 35—38 on crystallization from benzene–hexane yielded stellatin (3) (120 mg), m.p. 124—125°.

5-*Acetoxy*-6,7-*dimethoxy*-2-*methylchromone* (8).—A mixture of stellatin (300 mg), acetic anhydride (2 ml), and anhydrous sodium acetate (300 mg) was heated under reflux for 2 h, cooled, poured on crushed ice, and extracted with chloroform. Work up of the extract and crystallization from benzene–hexane gave the *acetate* (8) (250 mg), m.p. 150—151°, δ ($CDCl_3$) 6.75 (1 H, s, H-8), 5.9 (1 H, s, H-3), 3.91 and 3.83 (each 3 H, s, OMe), 2.45 (3 H, s, Me), and 2.27 (3 H, s, OAc) (Found: C, 60.8; H, 5.4. $C_{14}H_{14}O_6$ requires C, 60.4; H, 5.1%).

2′,6′-*Dihydroxy*-3′,4′-*dimethoxyacetophenone* (5).—(*a*) Stellatin (200 mg) was refluxed under nitrogen with 10% potassium hydroxide (8 ml) for 30 min. The mixture was cooled, acidified with concentrated hydrochloric acid, and extracted with chloroform. The gummy solid (125 mg) obtained on removal of the solvent was chromatographed over a short column of silica gel; elution with benzene–chloroform gave a solid which on crystallization from benzene–hexane afforded yellow plates (5) (20 mg), m.p. 137—138°, *m/e* 212 (M^+, 56%), 197 (100), 179 (21), 151 (77), 139 (14), 123 (21), 111 (14), 77 (23), and 69 (42) (Found: C, 56.4; H, 5.9. Calc. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.7%).

(*b*) To a solution of the 2,4-dinitrophenyl ether of antiarol [7] (15 g), in acetic anhydride (130 ml) and glacial acetic acid (50 ml), boron trifluoride–acetic acid (36%; 150 ml) was added, and the mixture was left at 20 °C for 48 h. The solid which separated was collected and crystallized from acetic acid to afford a bright yellow complex (14 g), m.p. 236—238° (decomp.); $\lambda_{max.}$ (EtOH) 212 and 281 nm (log ε 4.45 and 4.31); *m/e* 426 (M^+, 12%), 406 (4), 378 (36), 360 (14), 350 (12), 345 (10), 302 (28), 259 (34), 231 (30), 227 (40), 197 (42), 184 (34), 181 (22), 167 (100), 164 (50), and 153 (30) (Found: C, 45.0; H, 3.5; N, 6.0. Calc. for $C_{16}H_{13}BF_2N_2O_9$: C, 45.1; H, 3.1; N, 6.5%). The solid (600 mg) was heated under reflux with sodium acetate (1 g) and water (5 ml) for 30 min. The mixture was then poured into water and extracted with methylene chloride. Crystallization from methylene chloride–methanol afforded 2-acetyl-3-hydroxy-4,5-dimethoxy-3-hydroxyphenyl 2,4-dinitrophenyl ether (10) (400 mg), m.p. 164—166° (Found: C, 50.8; H, 4.0; N, 7.1. Calc. for $C_{16}H_{14}N_2O_9$: C, 50.8; H, 3.7; N, 7.4%). The ether (10) on treatment with piperidine [7] gave the ketone (5), m.p. 137°, identical with the compound obtained from stellatin.

7-*Acetoxy*-3-*acetyl*-5-*hydroxy*-2-*methylchromone*.—In the preparation of 5,7-diacetoxy-3-acetyl-2-methylchromone [10] by the reaction of phloroacetophenone with acetic anhydride and sodium acetate, the monoacetate was isolated by chromatography of the crude mixture over silica gel. It crystallized from benzene as *plates*, m.p. 135—136°, δ ($CDCl_3$) 11.76 (1 H, s, 5-OH), 6.71 (1 H, d, *J* 2 Hz, H-6), 6.55 (1 H, d, *J* 2 Hz, H-8), 2.61 (3 H, s, COMe), 2.51 (3 H, s, 7-OAc), and 2.37 (3 H, s, Me) (Found: C, 61.1; H, 4.6. $C_{14}H_{12}O_6$ requires C, 60.9; H, 4.4%).

5-*Acetoxy*-7,8-*dimethoxy*-2-*methylchromone* (9).—A solution of 5-hydroxy-7,8-dimethoxy-2-methylchromone (6) (100 mg) in pyridine (1 ml) was treated with acetic anhydride (0.5 ml) and left at room temperature for 48 h. It was then poured into crushed ice and extracted with methylene chloride; the extract was washed with dilute hydrochloric acid and water, dried (Na_2SO_4), and evaporated to leave a gum. Crystallization from methylene chloride–hexane afforded *needles*, m.p. 152—154° (95 mg), δ ($CDCl_3$) 6.66 (1 H, s, H-6), 6.0 (1 H, s, H-3), 3.96 (6 H, s, OMe), 2.43 (3 H, s, OAc), and 2.38 (3 H, s, Me), M^+ 278 (Found: C, 60.7; H, 5.4. $C_{14}H_{14}O_6$ requires C, 60.4; H, 5.1%).

2′-*Hydroxy*-4′,6′-*methoxybutyrophenone* (1).—A solution of the unsaturated ketone (2) (200 mg) in ethanol (50 ml) was shaken with palladium–charcoal (10%; 180 mg) in hydrogen. The catalyst was filtered off and the solution concentrated to give the ketone (1) (120 mg), m.p. 72—73°, identical (mixed m.p., t.l.c., and i.r. spectrum) with the natural product (lit.,[2] m.p. 70°).

1-(2-*Hydroxy*-4,6-*dimethoxyphenyl*)*but*-2-*en*-1-*one* (2).—A suspension of aluminium chloride (2.1 g) in carbon disulphide (50 ml) was added to a solution of phloroglucinol dimethyl ether (4.0 g) and crotonyl chloride (2.8 g) in benzene (20 ml) at 5 °C. The mixture was stirred for 4 h and left overnight. The resulting gum was separated from

the supernatant and, after addition of water (25 ml), was extracted with methylene chloride. The organic layer was washed with water, dried (Na_2SO_4), and evaporated to leave a red gum (3.3 g). This was chromatographed on silica gel in benzene; elution with benzene gave a yellow crystalline solid (2.5 mg), m.p. 100—101°, identical (mixed m.p. and t.l.c.) with the natural compound (2).

3,4-*Dihydro*-5,7-*dimethoxy*-4-*methylcoumarin* (4).—Into a mixture of phloroglucinol dimethyl ether (4 g), crotononitrile (2.5 g), anhydrous zinc chloride (1.6 g), and ether (75 ml), dry hydrogen chloride gas was passed for 1.5 h, and the mixture was left overnight. The separated solid was washed with ether and refluxed with water (100 ml) for 1 h. It was then extracted with ether; the extract was washed with 10% sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. Crystallization of the residue from methanol–methylene chloride afforded *plates* (700 mg), m.p. 120—122°; $\lambda_{max.}$ (EtOH) 211, 274, and 279 nm (log ε 4.23, 3.2, and 3.2); *m/e* 222 (M^+, 30%), 207 (100), 208 (15), 192 (4), 193 (3), 180 (3), 179 (3), 165 (12), 163 (8), 157 (6), and 137 (9); δ ($CDCl_3$) 6.28 and 6.2 (each 1 H, d, *J* 2.5 Hz, *meta*-coupled ArH), 3.81 and 3.76 (each 3 H, s, 5- and 7-OMe), 3.4 (1 H, m, CH_2·C*H*Me), 2.7 (2 H, d, *J* 4 Hz, CH·CH_2·CO), and 1.16 (3 H, d, *J* 7.5 Hz, CH*Me*) (Found: C, 65.2; H, 6.6. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.4%).

5,8-*Dimethoxy*-2-*methylchromanone*.—A solution of 5,8-dimethoxy-2-methylchromone (2.5 g) in ethyl acetate (400 ml) was hydrogenated over 10% palladium–charcoal (1.5 g) at atmospheric pressure. The product crystallized from chloroform–hexane to give *needles*, m.p. 110—111°; $\lambda_{max.}$ (EtOH) 206, 231, 270, and 353 nm (log ε 4.21, 3.93, 3.85, and 3.56); *m/e* 222 (M^+, 35%), 207 (8), 193 (5), 180 (50), 165 (30), 151 (25), 137 (100), and 122 (35); δ ($CDCl_3$) 7.05 and 6.42 (each 1 H, d, *J* 9 Hz, H-6 and -7), 4.6 (1 H, m, H-2), 3.85 (6 H, s, OMe), 2.7 (2 H, m, H-3), and 1.55 (3 H, d, *J* 7 Hz, Me) (Found: C, 64.6; H, 6.3. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.4%).

3-*Acetoxy*-2-*acetyl*-4,5-*dimethoxyphenyl* 2,4-*Dinitrophenyl Ether* (11).—A solution of the ether (10) (10 g) in benzene (150 ml) was refluxed with sodium acetate (10 g) and acetic anhydride (45 ml) for 3 h. The mixture was filtered and the solvent removed *in vacuo*; crystallization of the residue from methanol afforded *plates* (10 g), m.p. 90—92°; $\nu_{max.}$ (Nujol) 3 120, 3 080, 1 780, and 1 720 cm^{-1}; *m/e* 420 (M^+, 4%), 378 (100), 363 (4), 319 (2), 317 (2), 302 (11), and 183 (33); δ ($CDCl_3$) 8.86 (1 H, d, *J* 2 Hz, H-3′), 8.38 (1 H, dd, *J* 9 and 2 Hz, H-5′), 7.08 (1 H, d, *J* 9 Hz, H-6′), 6.63 (1 H, s, H-6), 3.9 (6 H, s, OMe), 2.5 (3 H, s, COMe), and 2.36 (3 H, s, OAc) (Found: C, 51.5; H, 4.0; N, 6.6. $C_{18}H_{16}N_2O_{10}$ requires C, 51.4; H, 3.8; N, 6.7%).

5-*Hydroxy*-6,7-*dimethoxy*-2-*methyl*-2′,4′-*dinitroisoflavone* (12) *and its Acetate* (13).—(*a*) A solution of the ether (11) (4 g) in pyridine (18 ml) was treated with powdered potassium hydroxide (600 mg) at 25 °C; the solution turned deep violet. It was kept for 15 min, then acidified with 50% acetic acid and extracted with methylene chloride. The organic layer was washed with 5% sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. Crystallization from methylene chloride–ethanol afforded bright yellow needles (165 mg), m.p. 303—304° (decomp.) (see below).

(*b*) A mixture of the ether (11) (500 mg), anhydrous potassium carbonate (1 g), and acetone (40 ml) was refluxed for 5 h, cooled, and filtered. Removal of the solvent left a residue (2 g) which was dissolved in ethanol (15 ml); the solution was cooled and sulphuric acid (1 ml) was added gradually. A yellow solid separated which on crystallization afforded the *isoflavone* (12) (350 mg), m.p. 303—304° (decomp.); $\lambda_{max.}$ (Me_2N·CHO) 289 and 317infl nm (log ε 4.25 and 3.94); $\nu_{max.}$ (Nujol) 1 670, 1 600, 1 540, 1 300, 1 285, 1 244, 1 218, 1 192, 1 165, 1 155, and 1 130 cm^{-1}; *m/e* 402 (M^+, 100%), 387 (30), 385 (15), 373 (13), 356 (5), 354 (12), 338 (6), 326 (2), 317 (2), 310 (5), 298 (7), 295 (8), and 271 (10), δ [$(CD_3)_2SO$] 12.1 (1 H, s, 5-OH), 9.0 (1 H, d, *J* 2 Hz, H-3′), 8.9 (1 H, dd, *J* 8 and 2 Hz, H-5′), 7.9 (1 H, d, *J* 8 Hz, H-6′), 6.9 (1 H, s, H-6), 4.0 and 3.8 (each 3 H, s, OMe), and 2.43 (3 H, s, Me) (Found: C, 53.8; H, 3.5; N, 7.0. $C_{18}H_{14}N_2O_9$ requires C, 53.7; H, 3.5; N, 7.0%).

The isoflavone (12) (120 mg) on warming with pyridine (8 ml) and acetic anhydride (5 ml) gave the *acetate* (13), which crystallized from chloroform–methanol as plates (90 mg), m.p. 195—196°; $\lambda_{max.}$ (MeOH) 232, 280, and 300infl nm (log ε 4.54, 4.26, and 4.2); *m/e* 444 (M^+, 1%), 402 (100), 387 (22), 373 (12), 369 (5), 356 (6), 354 (11), 326 (1), 310 (1), 295 (2), and 267 (5); δ ($CDCl_3$) 8.9 (1 H, d, *J* 2 Hz, H-3′), 8.53 (1 H, dd, *J* 8 and 2 Hz, H-5′), 7.6 (1 H, d, *J* 8 Hz, H-6′), 6.9 (1 H, s, H-6), 4.03 and 3.9 (each 3 H, s, OMe), 2.37 (3 H, s, OAc or Me), and 2.3 (3 H, s, OAc or Me) (Found: C, 53.8; H, 3.8; N, 6.4. $C_{20}H_{16}N_2O_{10}$ requires C, 54.1; H, 3.6; N, 6.3%).

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