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CHEMICAL EXAMINATION OF ANDROGRAPHIS ECHIOIDES—I

STRUCTURE AND SYNTHESIS OF ECHIOIDININ

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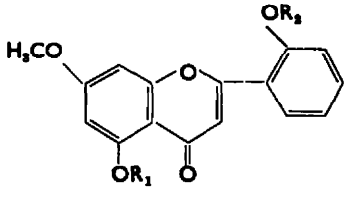
Abstract—The isolation of echioidinin, a new flavone and echioidin its glucoside from *Andrographis echioides* Nees. is reported. On the basis of spectral, degradative and synthetic evidence, echioidinin is shown to be 5,2′-dihydroxy-7-methoxyflavone.

Andrographis echioides Nees. (Acanthacea), an annual herb occurring in South India, is listed in the Indian Materia Medica, being used as a remedy for fevers.[1] Rangaswamy and Rao[2] who first examined the plant, isolated some unidentified amorphous compounds and reported that no crystalline bitter principle analogous to andrographolide could be obtained. A reinvestigation of *Andrographis echioides*‡ has now been undertaken.

From an extraction of the defatted plant material echioidinin, a new flavone and its glucoside echioidin have been isolated. Evidence is here presented to show that echioidinin which is also a constituent of *Andrographis wightiana* is 5,2′-dihydroxy-7-methoxyflavone (I) and the constitution of the echioidin is dealt with in a subsequent paper.



I: $R_1 = R_2 = H$
Ia: $R_1 = H$; $R_2 = CH_3$
Ib: $R_1 = R_2 = CH_3$

The purification of the crude echioidinin was effected by conversion to its acetate followed by hydrolysis with alcoholic hydrochloric acid. Echioidinin crystallizes from alcohol as greenish-yellow needles, m.p. 264–265° (dec) and gives a single spot in thin layer (silica) chromatogram, revealing the homogeneity of the compound. It has the formula $C_{16}H_{12}O_5$ with one methoxyl group (Zeisel). It gives a brown ferric

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‡ The plant material was collected from the suburbs of Madras City during October–November.

[1] K. M. Nadkarni, *Indian Materia Medica* (Popular book depot) Vol. I; p. 101. Bombay (1954).
[2] S. Rangaswamy and V. Subba Rao, *Indian J. Pharm.* **13**, 63 (1951); *Chem. Abstr.* **45**, 10505 (1951).

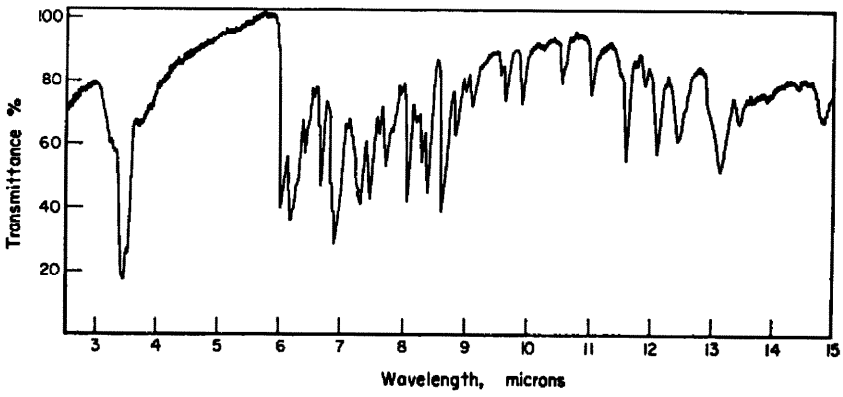


FIG. 1 IR spectrum of echioidinin in nujol mull.

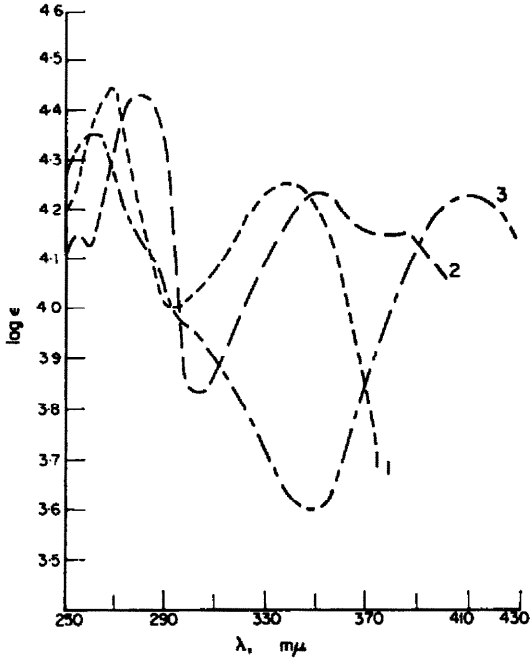


FIG. 2 UV spectrum in absolute ethanol of: I. Echioidinin. II. Echioidinin plus aluminium chloride. III. Echioidinin plus sodium ethoxide.

reaction; the formation of a diacetate and a di-O-methyl ether prove the presence of two hydroxyl groups. Thus the formula may be written as $C_{15}H_7O_2$ (OCH_3) $(OH)_2$, which suggests a flavonoid structure. The characteristic reduction tests for flavonoids with magnesium–hydrochloric acid[3a] and with zinc hydrochloric acid[3b] are positive with echioidinin and its di-O-methyl ether. The IR spectrum of echioidinin (Fig. 1) exhibits sharp bands at 6·05 μ (C=O of γ-pyrone) and at 6·2 μ (methoxylated aromatic ring). The UV spectrum (λ_{max} 268 and 340 mμ) (Fig. 2) is strongly reminiscent of a flavone derivative unsubstituted in the 3-position.[4]

[3a] J. Shinoda, *J. Pharm. Soc. Japan* **48**, 214 (1928); [b] J. C. Pew, *J. Amer. Chem. Soc.* **70**, 3031 (1948).

[4] L. Jurd, *The Chemistry of Flavonoid Compounds* (Edited by T. A. Geissman) p. 107. Pergamon Oxford (1962).

Methylation of echioidinin with diazomethane yields a mono-O-methyl ether (Ia) which gives a brown ferric reaction and a positive Wilson's boric acid test.[5] This evidence indicates that of the two hydroxyl groups present in echioidinin one may be located at the 5-position. This was confirmed by the bathochromic shifts of both the bands in the UV spectrum of echioidinin in the presence of aluminium chloride[6] (Fig. 2). The UV spectrum of echioidinin is not essentially altered by the addition of fused sodium acetate[7] indicating the absence of a free 7-hydroxyl group. The spectrum is also not affected by the presence of sodium acetate–boric acid[8] suggesting that the two hydroxyl groups in echioidinin are not in adjacent positions. Sodium ethoxide[9] produces an unusually large bathochromic shift (75 mμ) of the long wave length band. Although the absence of a free hydroxyl group in the 7-position is indicated by the sodium acetate spectrum, the presence of a maximum at 302 mμ in the spectrum of di-O-acetylechioidinin suggests the presence of a 7-methoxyl group.[4] A positive Gibbs' reaction[10] with mono-O-methylechioidinin (Ia) indicates that the 8-position in echioidinin is free. Echioidinin itself gives a positive Gibbs test.

The NMR spectrum of echioidinin diacetate (Fig. 3) reveals the following chemical shifts and probable assignments.

Chemical shifts (δ values)	Multiplicity (J values)	Relative intensity	Assignment
2·28	Singlet	3	Aromatic acetate
2·47	Singlet	3	Aromatic acetate (5-position acetate)
3·90	Singlet	3	Aromatic methoxyl
6·50	Singlet	1	C_3-proton
6·62	Doublet (J = 2·5 c/s)	1	C_6-proton
6·78	Doublet (J = 2·5 c/s)	1	C_8-proton

Of the two acetate methyl signals, the one at 2·47 δ may be assigned to the 5-acetate group, since a 5-acetate group in a flavone absorbs near 2·48 δ, distinct from other acetate groups which absorb near 2·34 δ.[11] The sharp singlet at 6·50 δ is characteristic of the heterocyclic (C_3) proton. The presence of the two doublets at 6·62 δ and 6·78 δ with typical *meta* splitting (J = 2·5 c/s) suggest that echioidinin is a 5,7-disubstituted flavone. The doublet at 6·62 δ may be assigned to the C_6 proton and the other at 6·78 δ to the C_8 proton.[12,13] The methoxyl group in accordance with biogenetic and UV spectral data is in the 7-position.

[6] C. W. Wilson, *J. Amer. Chem. Soc.* **61**, 2303 (1939).
[6] T. Swain, *Chem. & Ind.* 1480 (1954).
[7] L. Jurd and R. M. Horowitz, *J. Org. Chem.* **22**, 1618 (1957).
[8] L. Jurd, *Arch. Biochem. Biophys.* **63**, 376 (1956).
[9] G. H. Mansfield, T. Swain and C. G. Nordstrom, *Nature, Lond.* **172**, 23 (1953).
[10] F. E. King, T. J. King and L. C. Manning, *J. Chem. Soc.* **563**, (1957).
[11] C. A. Henrick and P. R. Jefferies, *Austr. J. Chem.* **17**, 934 (1964).
[12] J. Massicot and J. P. Marthe, *Bull. Soc. Chim. Fr.* 1962 (1962); R. M. Horowitz and B. Gentile, *Chem. & Ind.* 498 (1964).
[13] T. J. Batterham and R. J. Highet, *Austr. J. Chem.* **17**, 428 (1964).

The position of the second hydroxyl group in echioidinin must definitely be in the B-ring, since positions 3, 6 and 8 have been accounted for by the NMR and UV spectra and the Gibbs test. This is supported by the alkaline hydrogen peroxide oxidation of di-O-methylechioidinin which gives a mixture of two acids (TLC). One, m.p. 100–101° was identified as *o*-anisic acid. The second acid analysed for $C_9H_{10}O_5$ with m.p. 154–156°. It gives a violet colour with ferric chloride and its IR spectrum

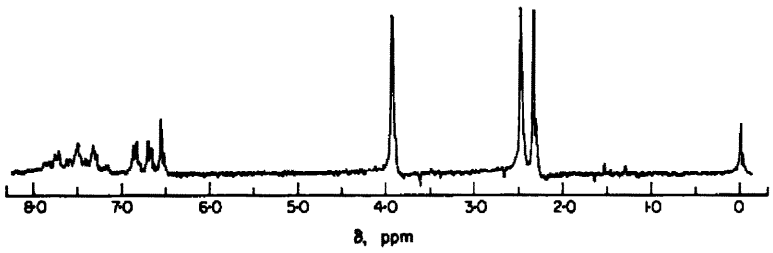
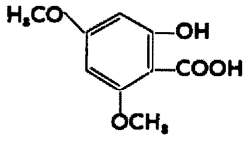


FIG. 3. NMR Spectrum of Echioidinin diacetate in $CDCl_3$.

shows bands at 3·1 μ (bonded OH) and at 6·0 μ (COOH), indicating it to be a salicyclic acid derivative. It was identified as 2-hydroxy-4,6-dimethoxybenzoic acid (II) by comparison with an authentic specimen prepared by oxidizing 2-hydroxy-4,6-dimethoxyacetophenone with pyridine and iodine.[14]

The isolation of *o*-anisic acid and 2-hydroxy-4,6-dimethoxybenzoic acid (II) as degradation products of di-O-methylechioidinin unequivocally establish its structure as 5,7,2′-trimethoxyflavone (Ib). As this compound has been synthesized,[15,16] a

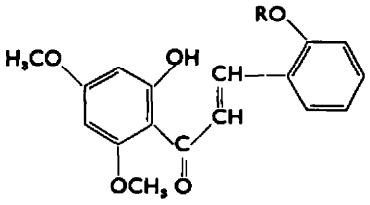


II

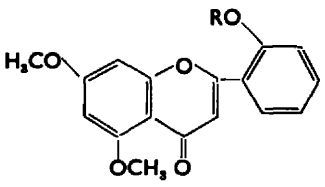
specimen for comparison was prepared[16] and found identical in all respects with Ib. It follows, therefore, that echioidinin itself must have the structure 5,2′-dihydroxy-7-methoxyflavone (I).

Finally the structure (I) assigned to echioidinin was fully confirmed by the synthesis of 5,2′-dihydroxy-7-methoxyflavone. Condensation of *o*-benzyloxybenzaldehyde with 2-hydroxy-4,6-dimethoxyacetophenone in the presence of strong alkali gives 2-benzyloxy-2′-hydroxy-4′,6′-dimethoxy-chalcone (III) which also may be obtained by partial benzylation of 2,2′-dihydroxy-4′,6′-dimethoxychalcone[17] (IIIa). Selenium dioxide oxidation of IIIa in amyl alcohol gives 2′-benzyloxy-5,7-dimethoxyflavone (IV)

[14] N. A. Lund, A. Robertson and W. B. Whalley, *J. Chem. Soc.* 2439 (1953).
[15] S. R. Gupta and T. R. Seshadri, *Proc. Indian Acad. Sci.* 37A, 611 (1953).
[16] K. M. Gallagher, A. C. Hughes, M. O'Donnel, E. M. Philbin and T. S. Wheeler, *J. Chem. Soc.* 3770 (1953).
[17] T. H. Simpson and W. B. Whalley, *J. Chem. Soc.* 167 (1955).



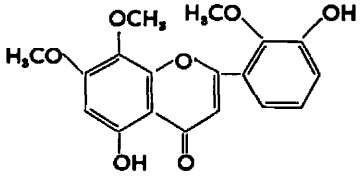
III: R = $CH_2C_6H_5$
IIIa: R = H



IV: R = $CH_2C_6H_5$
IVa: R = H

which may be debenzylated to give 2′-hydroxy-5,7-dimethoxyflavone (IVa) in almost quantitative yield. Selective demethylation of the 5-methoxyl group in IVa gives 5,2′-dihydroxy-7-methoxyflavone which is identical in all respects with natural echioidinin.

The occurrence of 2′-oxygenated flavones in nature is very rare. Excluding the flavonol datiscetin[18], 5,6,2′-trimethoxyflavone*[19] is the only flavone, so far known, bearing a single oxygen in ring B at the 2′-position. Echioidinin is thus the second member of this series. Further, the occurrence of both wightin (V) and echioidinin in the same plant[20] *Andrographis wightiana* is of particular biogenetic interest.



V

EXPERIMENTAL

1. *Extraction of* Andrographis echioides *Nees*

Air dried, powdered plant material (whole plant, 2 kg) was extracted with pet. ether (b.p. 40–60°) thrice (9 l. each time) by cold percolation in an aspirator bottle. The dark green extract after removal of the solvent, yielded only a resinous mass from which no solid material could be isolated. The plant material was then removed from the aspirator, air dried and extracted with acetone thrice (9 l. each time).

(a) *Isolation of echioidin.* The combined acetone extracts were concentrated to a small bulk and the resulting greenish solid material filtered, washed repeatedly with fresh acetone and dried. It was then refluxed with acetone (100 ml) for 10–15 min, filtered hot and the process repeated thrice. The resulting acetone insoluble amorphous material (4·5 g), m.p. 261–267° (dec) was echioidin.

(b) *Isolation of echioidinin.* The total acetone mother liquors obtained above were evaporated and the residue filtered, washed repeatedly with chloroform and dried (4 g). The greenish amorphous material thus obtained was echioidinin, m.p. range of 245–254°.

* In a recent communication by L. Farkas and M. Nogradi, *Chem. Ber.* **98**, 164 (1965), the constitutions of Zapotin (5,6,7,2′-tetramethoxyflavone) and Zapotinin (5-hydroxy-6,7,2′-trimethoxyflavone) (Ref. 19) have been disputed.

[18] J. Kalff and R. Robinson, *J. Chem. Soc.* 1968 (1925).
[19] F. Sondheimer and A. Meisels, *Tetrahedron* **9**, 139 (1960).
[20] Communicated for publication in *Tetrahedron*.

Purification of crude echioidinin through its acetyl derivative

Crude echioidinin (2 g), acetic anhydride (9 ml) and pyridine (9 ml) were heated on a steam-bath for 2 hr. After being cooled, the reaction mixture was poured into ice-water, and the resulting precipitate was collected, washed with water and dried. Repeated crystallization of the crude acetate from ethyl acetate (norite) afforded pure di-O-acetylechioidinin (1·3 g) as colourless prisms, m.p. 174–176°. λ_{max}^{EtOH} 280, 302 mμ; log ε 4·32, 4·28. (Found: C, 65·4; H, 4·4; OCH_3, 3·7. $C_{20}H_{18}O_7$ requires; C, 65·2; H, 4·4; 1 OCH_3, 4·1%.)

The foregoing acetate (0·65 g) was hydrolysed by refluxing with alcoholic HCl (85% EtOH saturated with HCl; 40 ml) for 2 hr. The greenish-yellow crystals which separated on cooling, were washed with alcohol and dried (0·3 g). Concentration of the mother liquid *in vacuo* gave more flavone (0·1 g). Two crystallizations from a large volume of alcohol, yielded pure *echioidinin* as greenish-yellow needles (0·35 g, m.p. 264–266°, dec.).

Pure echioidinin is sparingly soluble in ether, chloroform, benzene, acetone, ethyl acetate and alcohol, and was freely soluble in warm pyridine, dimethylformamide and dimethyl sulphoxide. It gives an orange-yellow colour with Mg–HCl aq, an orange-red colour with Zn–HCl aq and a brown colour with $FeCl_3$. A yellow colour develops within 2 min with Wilson's boric acid reagent and a greenish-blue colour develops instantaneously with Gibbs reagent; the indophenol chromophore absorbs at 630 mμ. Thin layer (silica) chromatography (benzene:methanol:n-butyl acetate—20:4:1)—single spot. λ_{max}^{EtOH} 267, 340 mμ (log ε 4·5, 4·32); $\lambda_{max}^{EtOH-AlCl_3}$ 255, 280, 350, 380–385 (sh) mμ (log ε 4·15, 4·43, 4·24, 4·05); $\lambda_{max}^{EtOH-NaOEt}$ 265, 410–415 mμ (log ε 4·35, 4·22). (Found: C, 67·9; H, 4·3; OCH_3, 5·2. $C_{16}H_{12}O_5$ requires: C, 67·6; H, 4·2; 1 OCH_3, 5·3%.)

2. *Mono-O-methylechioidinin*

An ethereal solution of diazomethane (from 2 g of nitrosomethylurea) was added to a suspension of echioidinin (0·1 g) in a mixture of abs. MeOH (10 ml) and abs. ether. The suspension clarified instantaneously and became red. After leaving for 12 hr at room temp, the solvents were removed and the residual solid sublimed *in vacuo*. *Mono-O-methylechioidinin* sublimed as a pale yellow solid (150–155°/0·001 mm, bath temp), m.p. 163–164°. The m.p. was raised to 166° by crystallization from benzene–pet. ether (b.p. 40–60°; 54 mg). It gives a brown colour with $FeCl_3$ and bluish-green colour with 2,6-dibromobenzoquinone chlorimide (λ_{max} 650 mμ). (Found: C, 68·4; H, 4·7. $C_{17}H_{14}O_5$ requires: C, 68·5; H, 4·7%.)

3. *Di-O-methylechioidinin*

A mixture of echioidinin (0·4 g), dimethyl sulphate (4 ml) and ignited K_2CO_3 (6 g) in dry acetone (140 ml) was refluxed for 48 hr. Acetone was then distilled off, water added to the residue which was then extracted with chloroform (2 × 100 ml). After washing with cold NaOH aq (4%; 40 ml) and then with water, the chloroform solution was dried (Na_2SO_4) and the solvent distilled off. The residual semi-solid was dissolved in benzene and chromatographed over alumina in the same solvent. The benzene eluate gave only oily material. Elution with chloroform gave *di-O-methylechioidinin* which after crystallization from benzene–pet. ether (b.p. 40–60°) formed pale brown prisms (0·22 g), m.p. 178°. λ_{max}^{EtOH} 265, 330 mμ (log ε 4·36, 4·21). (Found: C, 69·5; H, 5·2; OCH_3, 14·1. $C_{18}H_{16}O_5$ requires: C, 69·2; H, 5·1; 3 OCH_3, 14·4%.)

4. *Alkaline hydrogen peroxide of echioidinin dimethyl ether*

Di-O-methylechioidinin (0·2 g) in alcohol (5 ml) was refluxed gently with NaOH aq (1 g) in water (5 ml) for 3 hr. After being cooled, water (10 ml) was added to the reaction mixture. Hydrogen peroxide (30%; 5 ml) was added dropwise and the mixture left overnight at room temp. Next day the solution was evaporated to dryness *in vacuo*. The residue was dissolved in water (5 ml) and extracted with ether. The well cooled aqueous layer was acidified and extracted exhaustively with ether (4 × 15 ml). The ether solution was then shaken with $NaHCO_3$ aq (10 g; 3 × 4 ml), the bicarbonate solution acidified (strong cooling) and reextracted with ether (4 × 15 ml). The ether extract was washed with ice water, dried (Na_2SO_4) and ether distilled off. A light brown gummy residue was obtained which was crystallized from absolute ether to give two sharp melting acids "A" and "B".

Acid "A" obtained from the more soluble part, m.p. 100–101° was identified as *o*-anisic acid by

direct comparison (m.p. and mixed m.p. and IR spectra) with an authentic specimen. (Found: C, 63·2; H, 5·2. $C_8H_8O_3$ requires: C, 63·2; H, 5·3%.)

Acid "B" obtained from the less soluble fraction, m.p. 154–156° was identical in all respects (m.p., mixed m.p. and IR spectra) with an authentic specimen of *2-hydroxy-4,6-dimethoxybenzoic acid* prepared by the oxidation of 2-hydroxy-4,6-dimethoxyacetophenone with pyridine and iodine (vide below). (Found: C, 54·6; H, 5·1. $C_9H_{10}O_5$ requires: C, 54·5; H, 5·1%.)

5. Preparation of authentic 2-hydroxy-4,6-dimethoxybenzoic acid

A mixture of 2-hydroxy-4,6-dimethoxyacetophenone (0·8 g), I_2 (1·6 g) and abs. pyridine (8 ml) was heated on a steam-bath for 1 hr, and then kept at 0° for 18 hr. The 1-(2-hydroxy-4,6-dimethoxyphenacyl)-pyridinium iodide, which has separated as a crystalline solid, was filtered, dissolved in the minimum amount of alcohol and heated with KOH aq (2%; 50 ml) on a steam-bath for 1 hr. After cooling, it was acidified with 4 N HCl when *2-hydroxy-4,6-dimethoxybenzoic acid* separated as pale brown needles. It was filtered, dried and crystallized from benzene (norite). It formed short stout colourless needles, m.p. 154–156° alone or when mixed with the degradation acid obtained above. Sarin and Seshadri[21] who prepared this acid have reported m.p. 152–154°.

6. Synthesis of echioidinin (5,2′-dihydroxy-7-methoxyflavone)

(a) *2-Benzyloxy-2′-hydroxy-4,6-dimethoxychalcone.* A mixture of 2-hydroxy-4,6-dimethoxyacetophenone[22] (5 g), *o*-benzyloxybenzaldehyde (9 g) and NaOH (10 g in 10 ml water) in EtOH (20 ml) was refluxed, with stirring, in an atmosphere of N_2 for ½ hr. The resulting deep red solution was acidified to congo-red with 4 N HCl under strong cooling when a semi-solid material separated. It was taken up in chloroform, washed successively with $NaHCO_3$ aq, sat, $NaHSO_3$ aq and then with water. After drying (Na_2SO_4), the chloroform was distilled off and the residual brown semi-solid refluxed with EtOH (80 ml) and on cooling the solution deposited the chalcone as a yellow solid. It was crystallized thrice from alcohol to give *2-benzyloxy-2′-hydroxy-4,6-dimethoxychalcone* as long needles (2·5 g), m.p. 129–130°. It gives a brown colour with alcoholic $FeCl_3$. (Found: C, 73·9; H, 5·8. $C_{24}H_{22}O_5$ requires: C, 73·8; H, 5·6%.)

(b) *2-Benzyloxy-2′-hydroxy-4′,6′-dimethoxychalcone.* The 2,2′-dihydroxychalcone[17] (3 g) was refluxed with benzyl chloride (1·4 g; 1·2 moles) and freshly ignited K_2CO_3 (9 g) in absolute acetone (100 ml) for 6 hr. After being filtered hot, the solvent was distilled off and the yellow semi-solid, obtained on trituration of the residue with water, was steam distilled to remove excess benzyl chloride. On cooling a yellow gritty solid was obtained which after two crystallizations from alcohol formed long yellow needles of 2-benzyloxy-2′-hydroxy-4′,6′-dimethoxychalcone (1·8 g), m.p. 129–130°. (Found: C, 73·9; H, 5·8. $C_{24}H_{22}O_5$ requires: C, 73·8; H, 5·6%.)

(c) *2′-Dimethoxy-5,7-dimethoxyflavone.* A mixture of 2-benzyloxy-2′-hydroxy-4′,6′-dimethoxychalcone (3 g), freshly sublimed SeO_2 (3 g) and n-amyl alcohol (75 ml) was refluxed in an oil-bath (155–169°) for 20 hr. The dark brown solution was then filtered hot and the residue washed with hot alcohol (2 × 10 ml). The alcohol solution was steam distilled and the residual brownish semi-solid separated from water by decantation and dried *in vacuo*. Chromatography of the dried residue over alumina and elution with ethyl acetate–benzene (1:1) followed by repeated crystallization from benzene–pet. ether (b.p. 40–60°) furnished 2′-benzyloxy-5,7-dimethoxyflavone (1·6 g) as colourless prisms, m.p. 134–135°. λ_{max}^{EtOH} 262, 320 mμ (log ε 4·41, 4·22). (Found: C, 74·5; H, 5·4. $C_{24}H_{20}O_5$ requires: C, 74·2; H, 5·2%.)

(d) *2′-Hydroxy-5,7-dimethoxyflavone.* 2′-Benzyloxy-5,7-dimethoxyflavone (0·5 g) was heated on a steam-bath with a mixture of glacial acetic acid (6 ml) and conc. HCl (6 ml for 1 hr). The clear solution obtained, deposited after 30 min the debenzylated product as a crystalline solid. Water (25 ml) was added and the solid filtered off, washed with ether (25 ml) and dried. Crystallization of this crude product from alcohol–acetic acid (1:1) afforded colourless needles of 2′-hydroxy-5,7-dimethoxyflavone (0·25 g), m.p. 282–284° (dec). λ_{max}^{EtOH} 262, 330-335 mμ (log ε 4·46, 4·28). (Found: C, 68·6; H, 4·6. $C_{17}H_{14}O_5$ requires: C, 68·5; H, 4·7%.)

The acetate prepared by the pyridine–acetic anhydride method crystallized from dil. alcohol as colourless cubes, m.p. 128–130° (after drying at 20°/1 mm). (Found: C, 65·3; H, 5·2, 5·1. $C_{19}H_{16}O_6 \cdot \frac{1}{2}H_2O$ requires: C, 65·3; H, 4·9%.)

[21] P. S. Sarin and T. R. Seshadri, *Tetrahedron* **8**, 64 (1960).
[22] Koichi Nakazawa, *Chem. Pharm. Bull.* **10**, 1032 (1962).

(e) *5,2'-Dihydroxy-7-methoxyflavone (echioidinin).* A mixture of 2'-hydroxy-5,7-dimethoxyflavone (0·2 g), anhydrous $AlCl_3$ (0·3 g) and freshly distilled nitrobenzene (5 ml) was heated in a steam-bath for 1 hr. After being cooled, crushed ice and 10 N HCl (9 ml) were added and the whole distilled in steam to remove nitrobenzene. The resulting brown solid product was collected, washed with water and dried. Crystallization from alcohol (norite) afforded yellow needles of *5,2'-dihydroxy-7-methoxyflavone* (0·12 g), m.p. 262–264° (dec), identical in all respects (m.p. and mixed m.p. and IR spectra) with echioidinin. (Found: C, 67·8; H, 4·2. $C_{16}H_{12}O_5$ requires: C, 67·6; H, 4·2%.)

The acetate prepared by the pyridine–acetic anhydride method crystallized as colourless needles from ethyl acetate–pet. ether (b.p. 40–60°), m.p. and mixed m.p. with di-O-acetylechioidinin, 174–176°. Their IR spectra were identical.

Acknowledgement—We are grateful to Professor B. G. L. Swamy for the collection and identification of the plant material. We thank the Council of Scientific & Industrial Research for the award of a senior research fellowship to P.C.P. and to the Government of India and M/s. Amrutanjan Ltd., Madras, for the award of scholarships to P.S.S. during the tenure of this work.