Tuberosin, a New Pterocarpan from *Pueraria tuberosa* DC.

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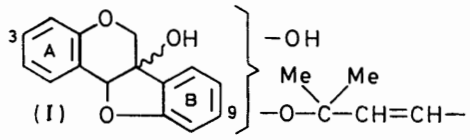
Tuberosin, a new pterocarpan isolated from *Pueraria tuberosa* DC. has been identified as 6a,13a-dihydro-10,10-dimethyl-6*H*,10*H*-furo[3,2-*c*:4,5-*g*']bis[1]benzopyran-3,6a-diol (III). 7-Methoxy-6-(7-methoxychroman-3-yl)-2,2-dimethylchroman (X) has been synthesized and shown to be identical with a degradation product from tuberosin.

Pueraria tuberosa DC. is a large deciduous climber found in hilly regions throughout India. Seshadri *et al.*[1] isolated from the hexane extract of the tubers the isoflavones daidzein, daidzin, puerarin, and 4',6''-di-O-acetylpuerarin. From the benzene extract of the tubers we have isolated, by chromatography, a compound, $C_{20}H_{18}O_5$ (M^+ 338), m.p. 213°, $[\alpha]_D$ +216°, designated tuberosin.[2] Its u.v. spectrum ($\lambda_{max.}$ 223, 280, 286, 301, 317, and 323 nm) is characteristic of pterocarpans,[3] and its i.r. spectrum [$\nu_{max.}$ 3400 and 3200 (OH), 1620 and 1600 cm^{-1} (aromatic)] showed no bands in the carbonyl region. All the five oxygen atoms were therefore present as hydroxy- or ether functions. The n.m.r. spectrum indicated the presence of a 2,2-dimethylchromen ring (six-proton singlet at δ 1·35 and AB quartet, *J* 10 Hz, at 5·55 and 6·35)[4] and two hydroxy-groups (δ 5·9 and 9·5, exchangeable with D_2O) of which one is phenolic. On treatment with 50% acetic acid, tuberosin was readily converted into anhydrotuberosin, $C_{20}H_{16}O_4$, indicating that the second hydroxy-group is tertiary. This product exhibited $\lambda_{max.}$ 240, 332, and 345 nm showing the conversion into a pterocarpen.[5,6] Tuberosin gave monoacetylanhydrotuberosin on reaction with acetic anhydride–pyridine. Hydrogenation of tuberosin afforded a tetrahydro-derivative by reduction of the chromen double bond and hydrogenolysis of one of the ether systems. The tetrahydro-derivative, on treatment with 50% acetic acid, gave the anhydro-compound, $C_{20}H_{20}O_4$, m.p. 120°, which showed a u.v. spectrum similar to those of Δ^3-isoflavenes.[7] Of the five oxygen atoms of tuberosin, two are in hydroxy-groups, one is part of the 2,2-dimethylchromen ring and the remaining two are ether oxygen atoms of the pterocarpan nucleus. On the basis of these data tuberosin can be represented by the partial structure (I), which accounts for the ready dehydration and the opening of the dihydrofuran ring on hydrogenation.

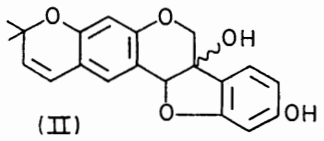
The problem of the placement of the phenolic hydroxy-group and the attachment of the side chain remained to be solved. On biogenetic grounds[8,9] the phenolic hydroxy-group could be located at C-3 or C-9. The side chain must be attached to either ring A or B with the ether oxygen at C-3 or C-9. The n.m.r. spectrum of tuberosin suggested that the side chain could be attached to ring A or B only in a linear disposition. This leads to two alternative structures (II) or (III). Structure (III) was preferred on the basis of the mass spectrum of the tetrahydro-derivative, which showed the fragments (a) and (b) arising by a reverse Diels–Alder reaction. The aromatic protons of tuberosin appearing at δ 7·1 and 6·2 are ascribed to H-7 and H-12.

[1] S. P. Bhatani, S. S. Chibber, and T. R. Seshadri, *Indian J. Chem.*, 1969, **7**, 210.
[2] B. S. Joshi, V. N. Kamat, and T. R. Govindachari, *Indian J. Chem.*, 1972, **10**, 1112.
[3] H. Suginome, *Experientia*, 1962, **18**, 161; I. A. M. Cruickshank and D. R. Perrin, *Life Sciences*, 1963, 680.
[4] J. C. P. Schwarz, A. I. Cohen, W. D. Ollis, E. A. Kaczka, and L. M. Jackman, *Tetrahedron*, 1964, **20**, 1317.
[5] H. Suginome, *J. Org. Chem.*, 1959, **24**, 1655.
[6] D. R. Perrin and W. Bottomley, *J. Amer. Chem. Soc.*, 1962, **82**, 1919.
[7] K. H. Dudley, H. W. Miller, R. C. Corley, and M. E. Wall, *J. Org. Chem.*, 1967, **32**, 2317.
[8] W. D. Ollis, in 'Recent Advances in Phytochemistry,' vol. 1, ed. T. J. Mabry, North Holland Publishing Co., Amsterdam, 1968, p. 350.
[9] K. K. Purushothaman, V. M. Kishore, N. Narayanaswami, and J. D. Connolley, *J. Chem. Soc.* (*C*), 1971, 2420.

The one-proton doublet (J 8·5 Hz) at 7·27 is due to H-1 and the *ortho,meta*-coupled doublets (J 8·5 and 2 Hz)

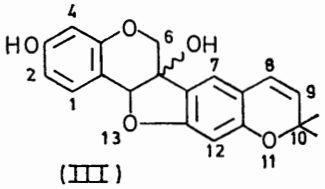


(I)

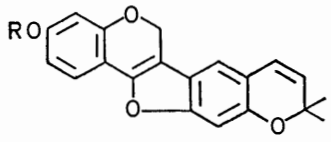


(II)

at 6·5 to H-2. The H-4 signal appears as a *meta*-coupled doublet (J 2 Hz) at 6·25. The sharp singlets at δ 4·0 and 5·25 are due to H-6 and H-13a, respectively.

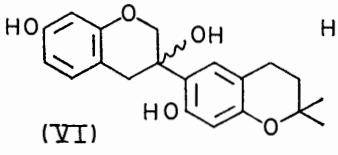


(III)

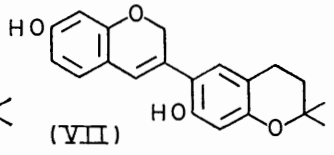


(IV) R = H
(V) R = Ac
(VIII) R = Me

On the basis of structure (III) for tuberosin, anhydrotuberosin and monoacetylanhydrotuberosin can be formulated as (IV) and (V), respectively. The properties of the hydrogenolysis product and its anhydroderivative are consistent with the formulations (VI) and (VII). Anhydrotuberosin (IV) on methylation provided the methyl ether (VIII), m.p. 166°. The pterocarpen (IV) on hydrogenation gave the hydrogenolysis product (IX), which was also obtained by reduction of (VII). The isoflavan (IX) on methylation gave the corresponding methyl ether (X), m.p. 120°. Mass spectra of compounds (IX) and (X) showed the expected retro-Diels–Alder fragments (a) and (c), and (d) and (e), respectively.

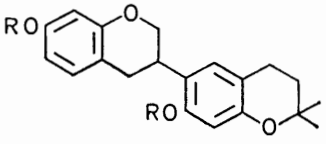


(VI)

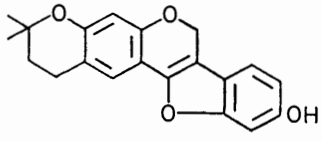


(VII)

In order to obtain unambiguous proof of the structure of tuberosin, we attempted the synthesis of some of the degradation products. Lithium aluminium hydride reduction of isopsoralidine [10] and cyclisation of the resulting alcohol did not give compound (XI) in satisfactory yield. The isoflavone (XII), synthesized by an established sequence of reactions [11] could not be preferentially demethylated to give 7-hydroxy-2′,4′-dimethoxyisoflavone, needed for constructing the 2,2-dimethylpyran system on ring A. However, 7-methoxy-6-(7-methoxychroman-3-yl)-2,2-dimethylchroman (X) was synthesized by the following route. Isoprenylation of 2′,4′-dihydroxyacetophenone with 2-methylbut-3-en-2-ol and boron trifluoride–ether gave a mixture of 3′-isoprenyl and 5′-isoprenyl-2′,4′-dihydroxyacetophenones [12] separated by chromatography. The latter on cyclization gave 6-acetyl-2,2-dimethylchroman-7-ol, which was methylated and submitted to a Willgerodt reaction to give 7-methoxy-2,2-dimethylchroman-6-acetic acid (XIII). The amide (XIV) was converted into the corresponding cyanomethyl derivative (XV).[13] Höesch

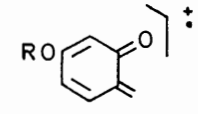


(IX) R = H
(X) R = Me

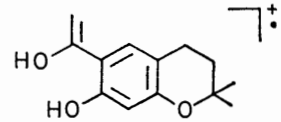


(XI)

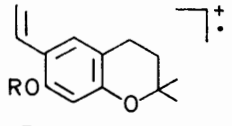
reaction of (XV) with resorcinol furnished the deoxybenzoin (XVI), which was partially methylated to (XVII), m.p. 119°. Reaction of compound (XVII) with ethyl formate and sodium at 0° gave the isoflavone (XVIII), m.p. 187°, which on hydrogenation in ethanol–acetic acid over 10% palladium–charcoal gave the



a; R = H, *m/e* 122
d; R = Me, *m/e* 136

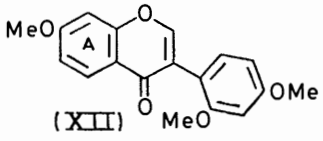


b; *m/e* 220

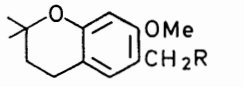


c; R = H, *m/e* 204
e; R = Me, *m/e* 218

chroman (X), m.p. 120°. This was identical (t.l.c., mixed m.p., and i.r. spectra) with the compound ob-



(XII)



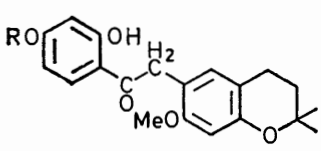
(XIII) R = CO_2H
(XIV) R = $CO{\cdot}NH_2$
(XV) R = CN

tained by hydrogenolysis and subsequent methylation of anhydrotuberosin.

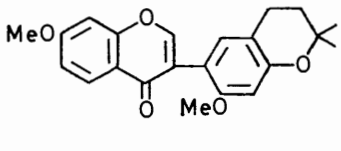
Tuberosin shows a large positive rotation and its o.r.d. curve (Figure) shows a positive Cotton effect. If it is assumed that the replacement of a hydroxy-

[10] H. N. Khastgir, P. C. Duttagupta, and P. Sengupta, *Tetrahedron*, 1961, **14**, 275.
[11] V. K. Kalra, A. S. Kukla, and T. R. Seshadri, *Indian J. Chem.*, 1967, **5**, 287.
[12] A. C. Jain, P. Lal, and T. R. Seshadri, *Tetrahedron*, 1970, **26**, 2631.
[13] J. N. Chatterjea, K. D. Banerji, and N. Prasad, *Chem. Ber.*, 1963, **96**, 2356.

group in a pterocarpan does not change the sign of the o.r.d. curve, then the absolute configuration of tuberosin should be represented as in (XIX).[14-16]

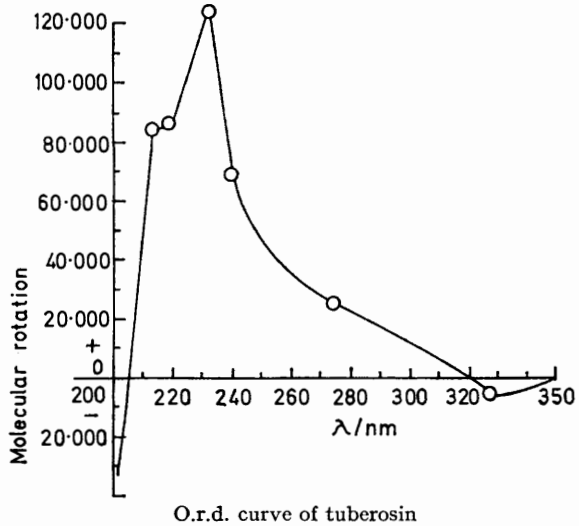


(XVI) R = H
(XVII) R = Me



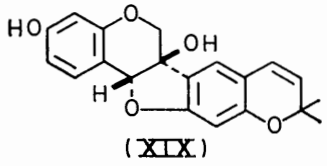
(XVIII)

The only other reported pterocarpan having a hydroxy-group at C-6a is pisatin [6] (XX), $[\alpha]_D$ +280°. Variabilin (XXI) possesses a large positive rotation ($[\alpha]_D$ +211°)

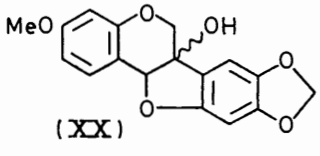


O.r.d. curve of tuberosin

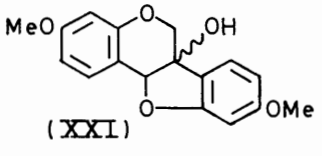
but no details of its chemistry are available.[8] In keeping with other pterocarpans,[8] tuberosin shows *in vitro* antifungal and antitubercular activities of a low order.



(XIX)



(XX)



(XXI)

EXPERIMENTAL

U.v. spectra were taken with a Beckman DK-2A spectrophotometer for solutions in ethanol, and i.r. spectra with a Perkin-Elmer Infracord spectrophotometer. N.m.r. spectra were taken with a Varian A60 or HA100 spectrometers for solutions in $CDCl_3$ with Me_4Si as internal reference.

Isolation of Tuberosin.—The coarsely powdered tubers of *Pueraria tuberosa* DC. (7 kg) were extracted with hot hexane (2 × 13 l) and then with hot benzene (4 × 20 l). The benzene was removed under reduced pressure and the residue was chromatographed on silica gel in chloroform. Elution with chloroform–1% methanol yielded *tuberosin*, which crystallized from chloroform–hexane as needles (350 mg), m.p. 213°, $[\alpha]_D$ +216° (*c* 2% in Me_2CO) (Found: C, 70·4; H, 5·2. $C_{20}H_{18}O_5$ requires C, 70·9; H, 5·3%), $\lambda_{max.}$ 223, 280, 286, 310, 317, and 323 nm (log ε 4·81, 3·80, 3·82, 3·78, 3·74, and 3·72), $\nu_{max.}$ (Nujol) 3400, 3200, 1620, 1600, 1590, 1310, 1290, 1260, 1200, 1160, 1130, 1090, 1030, 950, 930, 890, 830, and 800 cm^{-1}, *m/e* 338 (M^+, 48%), 323 (100), 320 (18), 305 (45), 295 (38), 277 (6), and 185 (18).

3-Acetylanhydrotuberosin (V).—Tuberosin (100 mg), on treatment with pyridine–acetic anhydride gave the *acetate* (V) (from aqueous acetone) (40 mg), m.p. 164° (Found: C, 73·2; H, 5·3. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%), $\lambda_{max.}$ 225, 243, 330, and 345 nm (log ε 4·39, 4·52, 4·24, and 4·28), *m/e* 362 (M^+, 54%), 347 (24), 320 (66), 305 (100), 275 (3), 248 (6), and 235 (6), δ 6·2—7·5 (6H, m), 5·7 (1H, d), 5·5 (2H, s, H-6), 2·25 (3H, s, OAc), and 1·42 (6H, s, CMe_2).

3-(7-Hydroxy-2,2-dimethylchroman-6-yl)chroman-3,7-diol (VI).—Tuberosin (100 mg) in ethanol (20 ml) was hydrogenated over 10% palladium–charcoal (100 mg) during 18 h to give the *chroman* (VI) (from methylene chloride–hexane) (70 mg), m.p. 211°, $[\alpha]_D$ +30·8° (*c* 2·2 in Me_2CO) (Found: C, 70·2; H, 6·8. $C_{20}H_{22}O_5$ requires C, 70·2; H, 6·5%), $\lambda_{max.}$ 285 nm (log ε 3·83), $\nu_{max.}$ (Nujol) 3440, 3200, 1620, 1600, 1590, 1510, 1310, 1290, 880, 840, and 830 cm^{-1}, *m/e* 342 (M^+, 25%), 324 (100), 269 (100), 220 (75), 205 (65), 165 (75), 147 (33), 134 (20), and 123 (23), δ 6·25—7·05 (5H, m), 4·15 (2H, m, O·CH_2), 2·65 (2H, t, *J* 7 Hz, CH_2), 1·72 (2H, t, *J* 7 Hz, CH_2), and 1·25 (6H, s, CMe_2).

3-(7-Hydroxy-2,2-dimethylchroman-6-yl)-2H-chromen-7-ol (VII).—Tetrahydrotuberosin (90 mg) in 50% aqueous aqueous acetic acid (9 ml) was heated at 80° for 30 min. The clear solution was diluted with water (9 ml) and left at 0° overnight. The precipitate was collected (45 mg) and crystallized from methanol to give the *chromen* (VII), m.p. 120° (Found: C, 70·2; H, 6·6. $C_{20}H_{20}O_4,H_2O$ requires C, 70·2; H, 6·5%), $\lambda_{max.}$ 265, 273, 288, and 327 nm (log ε 4·29, 4·30, 4·19, and 4·48), *m/e* 324 (M^+, 100%), 309 (4), 307 (5), 279 (5), 269 (100), 255 (10), 239 (20), 199 (35), and 147 (50), δ (CD_3·OD) 6·2—7·0 (8H, m), 4·95 (2H, d, *J* 1 Hz, H-2), 2·65 (2H, t, *J* 7 Hz, CH_2), 1·75 (2H, t, *J* 7 Hz, CH_2), and 1·3 (6H, s, CMe_2).

Anhydrotuberosin (IV).—Tuberosin (100 mg) suspended in 50% aqueous acetic acid (10 ml) was warmed for 10 min to produce a clear solution, which was further heated on a water-bath at 70° for 1 h. *Anhydrotuberosin* (IV) separated as clusters of yellow needles (80 mg) (from aqueous acetone), m.p. 186° (Found: C, 75·2; H, 5·2. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%), $\lambda_{max.}$ 240, 332, and 345 nm (log ε 4·47, 4·27, and 4·28), *m/e* 320 (M^+, 50%), 305 (100), 277 (15), 298 (15), 235 (30), 152 (50), and 137 (17), δ 7·25 (1H, d, *J* 9·5 Hz, H-1), 6·9br (2H, s, H-7, H-12), 6·38 (1H, dd, *J* 9·5 and 1·5 Hz, H-2), 6·45 (1H, d, *J* 10 Hz, H-8), 6·4 (1H, d, *J* 1·5 Hz, H-4), 5·6 (1H, d, *J* 10 Hz, H-9), 5·45 (2H, s, H-6), and 1·42 (6H, s, CMe_2).

3-O-Methylanhydrotuberosin (VIII).—A solution of anhydrotuberosin (80 mg) was refluxed in dry acetone (8 ml) with dimethyl sulphate (0·03 ml) and anhyd. potassium

[14] K. G. R. Pachler and W. G. E. Underwood, *Tetrahedron*, 1967, **23**, 1817.

[15] A. Pelter and P. I. Amenechi, *J. Chem. Soc.* (*C*), 1969, 887.

[16] J. W. Clark-Lewis, I. Dainis, and G. C. Ramsay, *Austral. J. Chem.*, 1965, **18**, 1035.

carbonate (900 mg) for 4 h to give the *methyl ether* (VIII) (from aqueous acetone) (55 mg), m.p. 166° (Found: C, 75·8; H, 5·6. $C_{21}H_{18}O_4$ requires C, 75·5; H, 5·4%), $\lambda_{max.}$ 228, 249, and 325 nm (log ε 4·43, 4·39, and 4·17).

3-(7-*Hydroxy*-2,2-*dimethylchroman*-6-*yl*)*chroman*-7-*ol* (IX).—Anhydrotuberosin (100 mg) dissolved in ethanol (30 ml) was hydrogenated over 10% palladium–charcoal (100 mg) for 4 h. The solution was filtered and evaporated *in vacuo* and the *chroman* (IX) crystallized from aqueous methanol (yield 50 mg); m.p. 203° (Found: C, 73·2; H, 7·0. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%), $\lambda_{max.}$ 285 and 290 nm (log ε 3·89 and 3·89), *m/e* 326 (M^+, 73%), 271 (27), 260 (14), 204 (90), 191 (100), 161 (9), 149 (100), 137 (9), 135 (9), and 123 (27), δ [$(CD_3)_2CO$] 8·1 (2H, m, exchanges with D_2O, OH), 6·2—7·0 (5H, m), 2·65 (2H, t, *J* 7·5 Hz, CH_2), 1·75 (2H, t, *J* 7·5 Hz, CH_2), and 1·25 (6H, s, CMe_2).

7-*Methoxy*-6-(7-*methoxychroman*-3-*yl*)-2,2-*dimethylchroman* (X).—A solution of the chroman (IX) (160 mg) in dry acetone (16 ml) was refluxed with dimethyl sulphate (0·1 ml) and anhyd. potassium carbonate (2 g) for 4 h to give the *methyl ether* (X) (from methanol) (100 mg), m.p. 120° (Found: C, 74·3; H, 7·6. $C_{22}H_{26}O_4$ requires C, 74·5; H, 7·4%), $\lambda_{max.}$ 284 and 290 nm (log ε 3·89 and 3·89), *m/e* 354 (M^+, 55%), 340 (5), 337 (5), 299 (15), 283 (5), 267 (8), 218 (95), 205 (100), 177 (15), and 163 (100), δ 6·3—7·0 (5H, m), 4·35 (1H, q, *J* 5 and 10 Hz, H-2′*eq*), 4·0 (1H, t, *J* 10 Hz, H-2′*ax*), 3·75 (6H, s, OMe), 3·4 (1H, m, H-3′), 2·95 (2H, m, H-4′), 2·7 (2H, t, *J* 7 Hz, H-4), 1·78 (2H, t, *J* 7 Hz, H-3), and 1·35 (6H, s, CMe_2).

6-*Acetyl*-2,2-*dimethylchroman*-7-*ol*.— 2′,4′-Dihydroxy-5′-isopentenylacetophenone (15 g) suspended in formic acid (1200 ml) was heated at 105° for 1 h. The solution was poured on crushed ice, the precipitate was collected, and the *chroman* was crystallized from hexane (yield 13·7 g); m.p. 120° (Found: C, 71·6; H, 7·7. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%), δ 12·3 (1H, s, OH), 7·41 (1H, s, H-5), 6·3 (1H, s, H-8), 2·75 (2H, t, *J* 7 Hz, H-4), 2·5 (3H, s, COMe), 1·8 (2H, t, *J* 7 Hz, H-3), and 1·35 (6H, s, CMe_2).

6-*Acetyl*-7-*methoxy*-2,2-*dimethylchroman*.—A solution of the chroman-7-ol (26 g) in dry acetone (400 ml) was refluxed with dimethyl sulphate (17 ml) and anhydrous potassium carbonate (80 g) for 24 h. The methyl ether, obtained as an oil, purified by chromatography of a hexane solution on silica gel (yield 24 g), showed a single spot on t.l.c. (silica gel; $CHCl_3$; R_F 0·5); δ 7·5 (1H, s, H-5), 6·25 (1H, s, H-8), 3·85 (3H, s, OMe), 2·7 (2H, t, *J* 7 Hz, CH_2), 2·45 (3H, s, COMe), 1·75 (2H, t, *J* 7 Hz, CH_2), and 1·31 (6H, s, CMe_2).

7-*Methoxy*-2,2-*dimethylchroman*-6-*acetic Acid* (XIII).—The methyl ether from the preceding experiment (9·5 g), morpholine (9·5 ml), and sulphur (3·5 g) were refluxed for 11 h. The product was taken up in chloroform and washed with dil. hydrochloric acid and water; the chloroform was removed by distillation and the morpholide was heated under reflux with 12% sodium hydroxide for 11 h. The product was cooled, filtered, and acidified with dil. hydrochloric acid. The carboxylic acid was purified by dissolving in aq. sodium hydrogen carbonate and precipitation with dil. hydrochloric acid to give the *chroman* (XIII) (from methylene chloride–hexane) (5 g), m.p. 130° (Found: C, 67·0; H, 7·5. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·3%), $\nu_{max.}$ (Nujol) 1700 cm^{-1} (CO_2H), δ 10·25 (1H, s, CO_2H), 6·85 (1H, s, H-5), 6·3 (1H, s, H-8), 3·75 (3H, s, OMe), 3·55 (2H, s, CH_2·CO_2H), 2·7 (2H, t, *J* 7 Hz, CH_2), 1·75 (2H, t, *J* 7 Hz, CH_2), and 1·32 (6H, s, CMe_2).

7-*Methoxy*-2,2-*dimethylchroman*-6-*acetamide* (XIV).—To a solution of the acid (XIII) (5 g) in chloroform (40 ml) was added phosphorous trichloride (2 ml), and the mixture was warmed at 60° for 2 min and left at room temperature for 2 h. The chloroform layer was separated by decantation and the solvent removed under reduced pressure. The acid chloride, obtained as a thick oil, was gradually added with stirring to cold liq. ammonia (25 ml); the *amide* (XIV) crystallized from methylene chloride–hexane (yield 2·8 g); m.p. 126° (Found: C, 67·3; H, 7·7; N, 5·7. $C_{14}H_{19}NO_3$ requires C, 67·4; H, 7·7; N, 5·6%), $\nu_{max.}$ (Nujol) 3420 (NH_2) and 1670 cm^{-1} (amide), δ 6·9 (1H, s, H-5), 6·35 (1H, s, H-8), 5·8br (2H, NH_2), 3·8 (3H, s, OMe), 3·45 (2H, s, $ArCH_2$·CO), 2·7 (2H, t, *J* 7 Hz, CH_2), 1·8 (2H, t, *J* 7 Hz, CH_2), and 1·32 (6H, s, CMe_2).

7-*Methoxy*-2,2-*dimethylchroman*-6-*acetonitrile* (XV).—To a solution of the amide (XIV) (9·2 g) in pyridine (45 ml) was added toluene-*p*-sulphonyl chloride (12 g) in portions with shaking during 15 min. After 20 min the clear solution was poured on crushed ice; the chroman (XV) crystallized from methylene chloride–hexane (yield 7·5 g); m.p. 130° (lit.,[13] 127—128°) (Found: C, 72·7; H, 7·4; N, 6·2. Calc. for $C_{14}H_{17}NO_2$: C, 72·7; H, 7·4; N, 6·1%), $\nu_{max.}$ (Nujol) 2240 cm^{-1} (CN), δ 7·0 (1H, s, H-5), 6·35 (1H, s, H-8), 3·8 (3H, s, OMe), 3·6 (2H, s, CH_2·CN), 2·7 (2H, t, *J* 7 Hz, CH_2), 1·8 (2H, t, *J* 7 Hz, CH_2), and 1·35 (6H, s, CMe_2).

6-(2,4-*Dihydroxybenzoylmethyl*)-7-*methoxy*-2,2-*dimethylchroman* (XVI).—To a mixture of the nitrile (XV) (15·3 g) and resorcinol (30·6 g) in dry ether (350 ml) was added freshly fused zinc chloride (15·3 g) and anhyd. aluminium chloride (350 mg). The mixture was kept at 0° and saturated with dry hydrogen chloride gas for 6 h, and then left at 0° for 48 h. The ether was decanted; the imine hydrochloride precipitate was washed with dry ether and hydrolysed by heating with water (750 ml) on a boiling water-bath for 4 h. The solid obtained was washed with aq. sodium hydrogen carbonate and extracted with 5% sodium carbonate. Acidification of the extract with dil. hydrochloric acid gave the *deoxybenzoin* (XVI), which was purified by chromatography in chloroform over silica gel (3·4 g) (t.l.c.; silica gel; $CHCl_3$–5% MeOH; R_F 0·7).

6-(2-*Hydroxy*-4-*methoxybenzoylmethyl*)-7-*methoxy*-2,2-*dimethylchroman* (XVII).—A solution of the deoxybenzoin (2 g) in dry acetone (40 ml) was refluxed with dimethyl sulphate (0·64 ml) and anhyd. potassium carbonate (9·68 g) for 6 h to give the *methyl ether* (XVII) (from methylene chloride–methanol) (380 mg), m.p. 119° (Found: C, 70·5; H, 7·1. $C_{21}H_{24}O_5$ requires C, 70·8; H, 6·8%), δ 12·8 (1H, s, OH), 7·85 (1H, d, *J* 10 Hz, H-6), 6·2—6·9 (4H, m), 4·1 (2H, s, CO·CH_2), 3·7 (3H, s, OMe), 3·8 (3H, s, OMe), 2·65 (2H, t, *J* 7 Hz, CH_2), 1·75 (2H, t, *J* 7 Hz, CH_2), and 1·3 (6H, s, CMe_2).

7-*Methoxy*-3-(7-*methoxy*-2,2-*dimethylchroman*-6-*yl*)*chromen*-4-*one* (XVIII).—A solution of compound (XVII) (100 mg) in ethyl formate (2 ml) was added dropwise with stirring to granular sodium (100 mg) at 0°. The mixture was stirred for 6 h and then left at 0° for 24 h. 5% Hydrochloric acid (20 ml) was added and the excess of ethyl formate was removed under vacuum. The resulting gum was chromatographed over silica gel; the *isoflavone* (XVIII) crystallized from methanol (yield 45 mg); m.p. 187° (Found: C, 72·1; H, 6·4. $C_{22}H_{22}O_5$ requires C, 72·1; H, 6·1%), $\lambda_{max.}$ 240, 248, and 294 nm (log ε 4·34, 4·35, and 4·21), $\nu_{max.}$ (Nujol)

1630, 1600, 1560, 1320, 1270, 1250, 1200, 1150, 1125, 1100, 1050, 1005, 945, 905, 900, 865, 850, and 830 cm^{-1}.

7-Methoxy-6-(7-methoxychroman-3-yl)-2,2-dimethylchroman (X).—A solution of the isoflavone (XVIII) (10 mg) in ethanol (5 ml) and acetic acid (0·5 ml) was hydrogenated over 10% palladium–charcoal (10 mg) for 4 h. The solution was filtered and the resulting solid crystallized from ethanol as plates (X) (3·5 mg), m.p. 120°, identical (mixed m.p. and i.r. spectra) with the degradation product obtained from anhydrotuberosin.

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