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SYNTHESIS OF HOMOISOFLAVANONES—II*

CONSTITUENTS OF *EUCOMIS AUTUMNALIS* AND *E. PUNCTATA*

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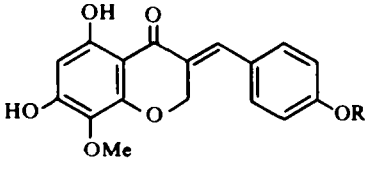
Abstract—The synthesis of punctatin (**1**), (±)-3,9-dihydro-punctatin (**3**), 4'-O-methylpunctatin (**2**), (±)-4'-O-methyl-3,9-dihydropunctatin (**4**), eucomnalin (**9**), (±)-3,9-dihydroeucomnalin (**10**), 4'-demethyleucomin (**11**) and (±)-4'-demethyl-5-O-methyl-3,9-dihydro-eucomin (**12**) are described and a novel alkali-catalysed ring-isomerization is reported.

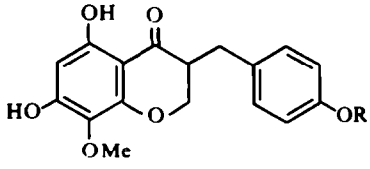
THE ISOLATION of eight new compounds belonging to the recently discovered class of 3-benzyl- and 3-benzylidene-chromanones (homoisoflavanones), represented before only by eucomin and eucomol[1] has been recently reported by Tamm *et al.*.[2,3] 4'-O-Methylpunctatin (**2**), eucomnalin (**9**) and 3, 9-dihydro-eucomnalin (**10**) were isolated from *Eucomis autumnalis* Graeb.[2,**] punctatin (**1**), 3,9-dihydro-punctatin (**3**), 4'-O-methyl-3,9-dihydro-punctatin (**4**), 4'-demethyleucomin (**11**) and 4'-demethyl-5-O-methyl-3,9-dihydro-eucomin (**12**) from *Eucomis punctata* L'Hérit,[3] both plants belonging to the family of Liliaceae.

In a previous paper[4] we described a general method for the preparation of benzylidene-chromanones and the synthesis of eucomin and (±)-eucomol. Now we report the synthesis of all the newly discovered compounds, a new approach to the 3-benzyl-chroman-4-one system and a novel ring-isomerization of chromones.

The general scheme for the syntheses consisted of the ring-closure of an appropriate 2-hydroxy-acetophenone with ethyl formate and Na to give a chromone, conversion of the chromone to a chromanone by hydrogenation, followed by condensation with an aldehyde in boiling Ac_2O to yield the acetate of a 3-benzylidene-chroman-4-one, which if necessary was hydrogenated to the corresponding 3-benzyl-chroman-4-one.



1: R = H; punctatin
2: R = Me; 4'-O-methylpunctatin



3: R = H; dihydropunctatin
4: R = Me; 4'-O-methyldihydropunctatin

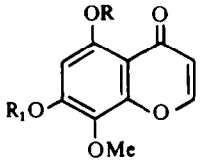
Punctatin (**1**) *and* (±)-3,9-*Dihydropunctatin* (**3**). 7-Benzyloxy-5,8-dimethoxychromone (**5**) prepared from 4-benzyloxy-3,6-dimethoxy-2-hydroxyacetophenone[5] by ring closure with ethyl formate and Na was selectively demethylated to **6** and hydrogenated to give 5,7-dihydroxy-8-methoxychroman-4-one. Condensation of the latter

* Part I. see Ref. 4.

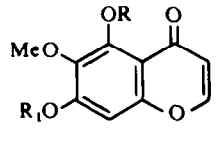
** The name autumnalin, designating **9** was changed later to eucomnalin.[3]

with *p*-hydroxybenzaldehyde gave punctatin triacetate which was deacetylated to punctatin (**1**). Hydrogenation of **1** gave (±)-3,9-dihydro-punctatin (**3**).

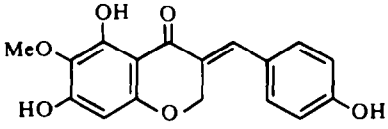
4'-O-Methylpunctatin (**2**) *and* (±)-*4'-O-Methyl-3,9-dihydropunctatin* (**4**). Condensation of 5,7-dihydroxy-8-methoxychroman-4-one with anisaldehyde gave after saponification 4'-O-methyl-punctatin (**2**). hydrogenation of **2** afforded the racemic dihydrocompound **4**, m.p. 121–122·5°. The natural product was found to be amorphous.[3]



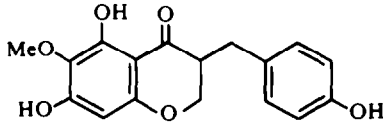
5: R = Me, R_1 = $PhCH_2$
6: R = H, R_1 = $PhCH_2$



7: R = Me, R_1 = $PhCH_2$
8: R = H, R_1 = $PhCH_2$

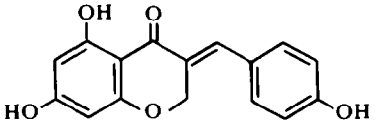


9: eucomnalin

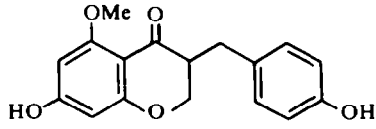


10: dihydro-eucomnalin

Eucomnalin (**9**) *and* (±)-*3,9-dihydroeucomnalin* (**10**). 7-Benzyloxy-5-hydroxy-6-methoxychromone (**8**). the key-intermediate for the synthesis of eucomnalin was readily available in excellent yield by alkali-catalyzed ring-isomerization of the corresponding 5,7,8-substituted chromone **6**. This reaction parallels the similar transformation of isoflavones.[6] Though ring-isomerization of chromones both in acidic[7] and alkaline[8] media have been reported before, all these reactions proceed with the concurrent cleavage of OMe groups. Chromone **8** which was prepared also from 4-benzyloxy-5,6-dimethoxy-2-hydroxyacetophenone[9] via **7**, gave on hydrogenation 5,7-dihydroxy-6-methoxy-chromanone. Condensation of the latter with *p*-hydroxybenzaldehyde followed by saponification gave eucomnalin (**9**). Hydrogenation of **9** gave racemic 3,9-dihydroeucomnalin (**10**).



11: 4'-demethyleucomin



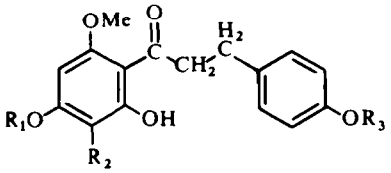
12: 4'-demethyl-5-O-methyl-dihydro-eucomin

4'-Demethyleucomin (**11**), m.p. 221° (lit.[3] 209–213°) was prepared by condensation of 5,7-dihydroxychroman-4-one with *p*-hydroxybenzaldehyde, followed by saponification.

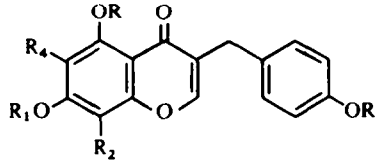
(±)-*4'-Demethyl-5-O-methyl-3,9-dihydro-eucomin* (**12**). 5,7-Dihydroxychromone[10] was monobenzylated to 7-benzyloxy-5-hydroxychromone which after methylation and hydrogenation gave 7-hydroxy-5-methoxychroman-4-one. This was converted in the usual way to racemic 4'-demethyl-5-O-methyl-3,9-dihydro-eucomin (**12**).

A disadvantage of the condensation of chromones with aldehydes in Ac_2O is the

formation of large amounts of aldehyde acylale as by-product. A route to 3-benzylchromones avoiding this difficulty utilized the easily accessible dihydrochalcones **13** and **14**. Ring closure with ethyl formate and Na gave the 3-benzylchromones **15** and **16**. Hydrogenation of **15** led to (±)-di-O-methyl-3.9-dihydro-eucomin. Selective demethylation of **16** yielded the dihydroxychromone **17** which was hydrogenated to (±)-3.9-dihydro-punctatin (**3**). Selective methylation of **17** afforded **18**. which was hydrogenated to yield (±)-3.9-dihydro-4′-O-methylpunctatin (**4**).



13: $R_1 = R_3 = Me$. $R_2 = H$
14: $R_1 = PhCH_2$. $R_2 = OMe$. $R_3 = H$



15: $R = R_1 = R_3 = Me$. $R_2 = R_4 = H$
16: $R = Me$. $R_1 = PhCH_2$. $R_3 = R_4 = H$. $R_2 = OMe$
17: $R = R_3 = R_4 = H$. $R_1 = PhCH_2$. $R_2 = OMe$
18: $R = R_4 = H$. $R_3 = Me$. $R_1 = PhCH_2$. $R_2 = OMe$
19: $R = R_2 = R_3 = H$. $R_4 = OMe$. $R_1 = PhCH_2$

Treatment with EtOK transformed **17** to a 1:2 equilibrium mixture of the starting material and its 5.6.7-substituted isomer **19** which was separated by fractional crystallization. Hydrogenation of **19** afforded (±)-3.9-dihydro-eucomnalin (**10**).

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage. NMR spectra were determined. if not otherwise stated in $CDCl_3$. on a Perkin-Elmer R12 spectrometer (TMS). IR spectra were taken on a Spectromom 2000 instrument.

Hydrogenations were carried out in the given solvents in the presence of Pd/C catalyst until the calculated amount of hydrogen was absorbed.

Ring-closure of ketones to chromones with ethyl formate and sodium. A solution of the ketone (30 mmol) in ethyl formate (180 ml) was added in small portions to powdered Na (8·5 g. 0·37 mol). Next day the mixture was decomposed with ice-cold 10% HCl. ethyl formate evaporated on the steam-bath and the precipitated oil was heated for 10 min. The crude product. which solidified on cooling was purified by recrystallization.

7-Benziloxy-5.8-dimethoxychromone (5). This was prepared by ring closure of 4-benzyloxy-3.6-dimethoxy-2-hydroxyacetophenone.[5] M.p. 161–163° (from EtOAc). yield 76% NMR (in $CDCl_3$): δ. ppm. 3·87 and 3·90 (s. OMe). 5·26 (s. $PhCH_2$). 6·15 (d. $J = 6$ Hz. C_2—H). 6·47 (C_6—H). 7·42 (s. 5H. C_6H_5). and 17·701 (d. $J = 6$ Hz. C_3—H). (Found: C. 68·8; H. 5·2. $C_{18}H_{16}O_5$ requires: C. 69·2; H. 5·2%).

7-Benzyloxy-5-hydroxy-8-methoxychromone (**6**). A solution of **5** (5·64 g) in dry MeCN (150 ml) was boiled with anhyd. $AlCl_3$ (2·4 g) dissolved in MeCN (36 ml) for 1 hr. Evaporation of solvent and decomposition of the residue with 10% HCl on the steam-bath gave the hydroxy-compound **6**. (3·1 g). m.p. 138–140° (from acetone). (Found: C. 68·4: H. 4·8. $C_{17}H_{14}O_5$ requires: C. 68·5: H. 4·7%).

5.7-Dihydroxy-8-methoxychroman-4-one. Hydrogenation of **6** in EtOAc–MeOH gave the chromanone. m.p. 199–200° (from MeOH). (Found: C. 57·4; H. 5·0. $C_{10}H_{10}O_5$ requires: C. 57·1; H. 4·8%).

5.7-Diacetoxy-8-methoxy-3-(4-acetoxybenzylidene)-chroman-4-one; punctatin-triacetate. To a boiling solution of the preceding chromanone (1·2 g) in Ac_2O (20 ml) *p*-hydroxybenzaldehyde (1·05 g) was added in portions. during 6 hr and refluxing continued for 42 hr. Decomposition of the mixture with water afforded *punctatin-triacetate* as colourless plates (0·84 g). m.p. 151–152°. (from MeOH). NMR ($CDCl_3$): δ. ppm.

2·31 (s. 6H. 4',7-OAc). 2·38 (s. 3H. 5-OAc). 3·82 (s. OMe). 5·44 (d. $J = 2$Hz. C_2—H_2). 4·51 (s. C_6—H). 7·22 and 7·26 (dd. $J = 8$Hz. $C_{2',3',5',6'}$—H). 7·78 (s. broad. —CH=). (Found: C. 62·3; H. 4·4. $C_{23}H_{20}O_9$ requires: C. 62·7; H. 4·6%).

5,7-Dihydroxy-8-methoxy-3-(4-hydroxybenzylidene)-chroman-4-one; punctatin (**1**). Saponification of the preceding triacetate gave **1**. as yellow needles. m.p. 187–189°. (lit.[3] 189–190°). Identified with the natural product by TLC and m.m.p. (Found: C. 64·4; H. 4·8. $C_{17}H_{14}O_6$ requires: C. 65·0; H. 4·5%).

(±)-*5,7-Dihydroxy-8-methoxy-3-(4-hydroxybenzyl)-chroman-4-one*: (±)-*dihydro-punctatin* (**3**). Hydrogenation of punctatin or of **17** in EtOAc gave racemic **3**. as colorless needles. m.p. 228–231° (from $CHCl_3$). (lit.[3] for (−)-**3** 204–206°). The synthetic sample was identified with natural **3** by TLC. (Found: C. 64·3; H. 4·9. M (mass spectrometry) 316·0950. $C_{17}H_{16}O_6$ requires: C. 64·6; H. 5·1% M 316·0947).

5,7-Dihydroxy-8-methoxy-3-(4-methoxybenzylidene)-chroman-4-one: *4'-O-methyl-punctatin* (**2**). Condensation of 5,7-dihydroxy-8-methoxychromanone (840 mg) with anisaldehyde (1·25 ml) as described for punctatin acetate gave an oil (lit.[2] amorphous). which was saponified to yield **2** as yellow rods. m.p. 209–210° (from MeOH). (lit.[2] 213·5–214·5°). m.m.p. with the natural product 212–15°. (Found: C. 66·1; H. 5·1. $C_{18}H_{16}O_6$ requires: C. 65·9; H. 4·9%).

(±)-*5,7-Dihydroxy-8-methoxy-3-(4-methoxybenzyl)-chroman-4-one*:(±)-*dihydro-4'-O-methylpunctatin*(**4**). Hydrogenation of **2** or of **18** in EtOAc gave racemic **4** as colorless prisms. m.p. 121–122.5° (from benzene). (lit.[3] amorphous). it was identified with the natural product by TLC. NMR (DMSO-d_6): δ. ppm. 2·75–3·05 (m. 2H. 9—CH_2). 3·05–3·33 (m. 1H. C_3—H). 3·62 (s. 8—OMe). 3·73 (s. 4'—OMe). 4·13–4·37 (m. 2H. 2—CH_2). 5·98 (s. 6—H). 6·88 (d. $J = 8·5$ Hz. $C_{3',5'}$—H) and 7·17 (d. $J = 8·5$ Hz. C_2. $C_{2',6'}$—H). (Found: C. 65·1. H. 5·3. M (mass spectrometry) 330·1102. $C_{18}H_{18}O_6$ requires: C. 65·4; H. 5·5%; M 330·1103).

7-Benzyloxy-5,6-dimethoxychromone (**7**). Prepared from 4-benzyloxy-5,6-dimethoxy-2-hydroxy acetophenone.[9] m.p. 150–152° (from MeOH). yield 68%. (Found: C. 69·2; H. 5·6. $C_{18}H_{16}O_5$ requires: C. 69·2; H. 5·2%). Careful decomposition of the reaction mixture (pH > 4) gave *7-benzyloxy-5,6-dimethoxy-2-hydroxychroman-4-one*. m.p. 138–140° (from MeOH). NMR ($CDCl_3$): δ. ppm. 2·72 (m. 2H. 3—CH_2). 3·80 and 3·90 (s. OMe). 6·50. (broad. OH. exchanged by D_2O). 5·10 (s. $PhCH_2$). 5·70 (t. after D_2O exchange. $J_{A_1} = J_{B_1} = 4$ Hz. C_2H). 6·31 (s. C_8— H) and 7·39 (s. 5H. C_6H_5). (Found: C. 65·1; H. 5·5. $C_{18}H_{18}O_6$ requires: C. 65·4; H. 5·5%).

7-Benzyloxy-5-hydroxy-6-methoxychromone (**8**). Chromone **6** (330 mg) was refluxed in ethanolic EtOK (2%. 33 ml) for 5 min. Acidification with 10% HCl and addition of water precipitated **8** (300 mg). m.p. 171–173° (from acetone). identical with a sample prepared by partial demethylation of **7** with $AlCl_3$ in $PhNO_2$. (Found: C. 68·6; H. 4·7. $C_{17}H_{14}O_5$ requires: C. 68·5; H. 4·7%).

5,7-Dihydroxy-6-methoxychromone. 5,6-Dimethoxy-7-hydroxychromone (1·0 g). m.p. 227–229° (Found: C. 59·1; H. 4·5. $C_{11}H_{10}O_5$ requires: C. 59·4; H. 4·5%). prepared by hydrogenation of **7**. was treated in $PhNO_2$ (120 ml) with anhyd. $AlCl_3$ (0·6 g) for 70 min. at 105°. Steam distillation and crystallization of the residue from water gave long needles (637 mg) of m.p. 211–13°.

Hydrogenation of **8** afforded the same compound. (Found: C. 57·4; H. 4·0. $C_{10}H_8C_5$ requires: C. 57·7; H. 3·9%).

5,7-Dihydroxy-6-methoxychroman-4-one. Hydrogenation of the preceding chromone (624 mg) in acetone (50 ml) gave an oil. which was crystallized from acetone to give colorless crystals of m.p. 77–79°. (Found: C. 56·7; H. 4·8. $C_{10}H_{10}O_5$ requires: C. 57·1; H. 4·8%).

5,7-Diacetoxy-6-methoxy-3-(4-acetoxybenzylidene)-chroman-4-one[3]; *eucomnalin triacetate*. Condensation of the preceding chromanone (840 mg) with *p*-hydroxybenzaldehyde (1·5 g) as described for punctatin triacetate. gave eucomnalin triacetate (650 mg). m.p. 162–163°. (colourless plates from ether). NMR ($CDCl_3$): δ. ppm. 2·42 (s. 6H. 4',6-OAc). 2·55 (s. 3H. 5-OAc). 3·88 (s. OMe). 5·35 (d. $J = 2$ Hz. 2—CH_2). 6·78 (s. C_8—H). 7·34 (dd. $J = 8$Hz. 4H. $C_{2',3',5',6'}$—H). 7·87 (broad s. =CH—). (Found: C. 62·9; H. 4·8. $C_{23}H_{20}O_9$ requires: C. 62·7; H. 4·6%).

5,7-Dihydroxy-6-methoxy-3-(4-hydroxybenzylidene)-chroman-4-one; *eucomnalin* (**9**). Saponification of the preceding triacetate afforded **9** as yellow rods. m.p. 245–246° (from MeOH). (lit.[2] 244·5–247·5°). m.m.p. with natural eucomnalin 246–48°. (Found: C. 65·2; H. 5·0. $C_{17}H_{14}O_6$ requires: C. 65·0; H. 4·5%).

(±)-*5,7-Dihydroxy-6-methoxy-3-(4-hydroxybenzyl)-chroman-4-one*; (±)-*dihydro-eucomnalin* (**10**). Hydrogenation of eucomnalin or of **19** in MeOH gave racemic **10** as rhombic plates) m.p. 205–206° (from MeOH). (lit.[2] for (−)-**10** 207–208°). identified with the natural product by TLC. (Found: C. 64·3; H. 5·0. $C_{17}H_{16}O_6$ requires: C. 64·6; H. 5·1%).

5,7-Diacetoxy-3-(4-acetoxybenzylidene)-chroman-4-one: *4'-demethyl-eucomin triacetate*. Condensation of 5,7-dihydroxychroman-4-one[11] (1·45 g) with *p*-hydroxybenzaldehyde (1·0 g) as described for punctatin

triacetate, yielded the triacetate as colorless cubes, m.p. 133–34° (from MeOH). NMR ($CDCl_3$): δ, ppm. 8·32 and 8·35 (s, 6H, 4',7-OAc), 8·41 (s, 5—OAc), 5·31 (d, J=2Hz, 2—CH_2), 6·50 (d, J=2·5 Hz, C_6—H), 6·77 (d, J=2·5 Hz, C_6—H), 7·29 (s, broad, 4H, $C_{2',3',5',6'}$—H) and 7·80 (s, broad, —CH=). (Found: C, 64·8; H, 4·4. $C_{22}H_{18}O_8$ requires: C, 64·4; H, 4·4%).

5,7-Dihydroxy-3-(4-hydroxybenzylidene)-chroman-4-one; *4'-demethyl-eucomin* (**11**). Saponification of the preceding acetate gave **11** as long yellow needles (from 60% aq. MeOH), m.p. 226–228° (lit.[3] 209–213°), m.m.p. with the natural product 222–225°. (Found: C, 63·7; H, 4·8. $C_{16}H_{12}O_5.H_2O$ requires: C, 63·6; H, 4·7%).

(±)-*5,7-Dihydroxy-3-(4-hydroxybenzyl)-chroman-4-one*. Hydrogenation of **11** in acetone gave the racemic dihydro-compound as clusters of colorless needles, m.p. 162–164° (from benzene). (Found: C, 63·3; H, 5·3. $C_{16}H_{14}O_5$. H_2O requires: C, 63·2; H, 5·3%).

7-Benzyloxy-5-hydroxychromone. 5,7-Dihydroxychromone[10] (1 g) in DMF (10 ml) was stirred at 70° with BzCl (0·64 ml) and anhyd. K_2CO_3 (2 g) for 45 min. Dilution with water and recrystallization of the precipitate gave colorless rods (683 mg), m.p. 142–144° (from 80% aq. MeOH). (Found: C, 71·8; H, 4·5. $C_{16}H_{12}O_4$ requires: C, 71·6; H, 4·5%).

7-Benzyloxy-5-methoxychromone. Methylation of the preceding chromone (585 mg) in dry acetone with dimethyl sulphate (0·25 ml) in the presence of anhyd. K_2CO_3 for 10 hr gave the product as colorless needles (533 mg), m.p. 174–176° (from MeOH). (Found: C, 71·7; H, 4·5. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

7-Hydroxy-5-methoxychroman-4-one. Hydrogenation of the preceding chromone in DMF–MeOH gave the product, m.p. 214–215° (from MeOH). (Found: C, 61·5; H, 5·4. $C_{10}H_{10}O_4$ requires: C, 61·9; H, 5·2%).

7-Acetoxy-5-methoxy-3-(4-acetoxybenzylidene)-chroman-4-one. Condensation of the preceding chromanone (1·36 g) with *p*-hydroxybenzaldehyde (1·32 g) as described for punctatin triacetate gave the diacetate as long needles (460 mg), m.p. 166–168° (from MeOH). NMR ($CDCl_3$): δ, ppm, 8·32 (s, 2xOAc), 7·92 (s, OMe), 5·22 (d, J=2Hz, 2—CH_2), 6·42 (s, 2H, $C_{6,8}$—H), 7·92 (d, J=8 Hz, $C_{3',5'}$—H), 7·35 (d, J=8 Hz, $C_{2',6'}$—H), and 7·83 (broad s, =CH—). (Found: C, 66·4; H, 5·0. $C_{21}H_{18}O_7$ requires: C, 66·0; H, 4·8%).

7-Hydroxy-5-methoxy-3-(4-hydroxybenzylidene)-chroman-4-one. Saponification of the preceding diacetate in ethanolic alkali afforded yellow rhomboid prisms (from MeOH) (190 mg), m.p. 264–266° (decomp.). (Found: C, 67·7; H, 5·6. $C_{17}H_{14}O_5$ requires: C, 68·4; H, 4·7%).

(±)-*7-Hydroxy-5-methoxy-3-(4-hydroxybenzyl)-chroman-4-one*; *4'-demethyl-5-O-methyl-3,9-dihydroeucomin* (**11**). Hydrogenation of the preceding benzylidenechromanone (260 mg) in acetone–EtOAc–MeOH (40–40–20 ml) afforded an oily product solidifying in acetone after 24 h. Crystallization from MeOH yielded white rods of m.p. 178–180° (lit.[3] for (−)-**12** 196–197°), identified with the natural product by TLC. (Found: C, 67·4; H, 5·0; M (by mass spectrometry) 300·0997 $C_{17}H_{16}O_5$ requires: C, 68·0; H, 5·4%, M 300·0998).

5,7-Dimethoxy-3-(4-methoxybenzyl)-chromone (**15**). Ring closure of 2'-hydroxy-4,4',6'-trimethoxy-dihydrochalcone[12] (**13**) with ethyl formate and Na gave white needles (from MeOH), m.p. 115–117°. NMR ($CDCl_3$): δ, ppm. 3·71 (broad s, CH_2), 3·80, 3·87 and 3·94 (s, 3xOMe), 6·39 (s, $C_{6,8}$—H), 6·89 (d, J=8 Hz, $C_{3',5'}$—H), 7·26 (d, J=8 Hz, $C_{2',6'}$—H), and 7·41 (broad s, C_2—H). (Found: C, 66·9; H, 5·8. $C_{19}H_{18}O_5.H_2O$ requires: C, 66·3; H, 5·9%).

(±)-*5,7-Dimethoxy-3-(4-methoxybenzyl)-chroman-4-one*; *di-O-methyl-3,9-dihydro-eucomin*. Hydrogenation of **15** in EtOAc gave clusters of white needles (from petroleum ether), m.p. 82–84°. Methylation of (±)-3,9-dihydro-4'-demethyl-eucomin or hydrogenation of eucomin dimethyl ether afforded the same product. (Found: C, 69·8; H, 6·3. $C_{19}H_{20}O_5$ requires: C, 69·5; H, 6·1%).

2',4-Dihydroxy-3',6'-dimethoxy-4'-benzyloxychalcone. 2-Hydroxy-3,6-dimethoxy-4-benzyloxyacetophenone[5] (0·6 g) and 4-hydroxy-benzaldehyde (0·3 g) were boiled in EtOH (8 ml) in the presence of piperidine (0·5 ml) for 8 hr. The mixture was poured into aq. HCl and the oily product crystallized from EtOH to give yellow needles, m.p. 182–185°. (Found: C, 70·9; H, 5·6. $C_{24}H_{22}O_6$ requires: C, 70·9; H, 5·5%).

2',4,4'-Trihydroxy-3',6'-dimethoxy-dihydrochalcone. The preceding chalcone (2·4 g) was hydrogenated in EtOAc–acetone 1:1 (100 ml) to give an oil which crystallized from MeOH to afford the dihydrochalcone of m.p. 159–161°. (Found: C, 63·9; H, 6·0. $C_{17}H_{18}O_6$ requires: C, 64·1; H, 5·7%).

2',4-Dihydroxy-3',6'-dimethoxy-4'-benzyloxy-dihydrochalcone. (**14**). 2',4,4'-Trihydroxy-3',6'-dimethoxy-dihydrochalcone was benzylated with BzCl (0·85 ml, 1·2 mol equiv.) in boiling acetone in the presence of anhyd. K_2CO_3 (2 g) and NaI (0·5 g) for 100 min. After diluting the mixture with water the crude product was crystallized from MeOH to give colorless crystals of m.p. 148–150°. (Found: C, 69·9; H, 5·4. $C_{24}H_{24}O_6$ requires: C, 70·6; H, 5·9%).

5,8-Dimethoxy-7-benzyloxy-3-(4-hydroxybenzyl)-chromone (**16**). Ring closure of **14** (1070 mg) with ethyl

formate and Na gave 990 mg **16**, m.p. 189–190° (from MeOH). (Found: C, 71·7; H, 5·4. $C_{25}H_{22}O_6$ requires: C, 71·8; H, 5·3%).

5-Hydroxy-7-benzyloxy-8-methoxy-3-(4-hydroxybenzyl)-chromone (**17**). A solution of **16** (110 mg) in MeCN (5 ml) and $AlCl_3$ (37 mg in 1 ml MeCN) was boiled for 75 min. MeCN was evaporated, the mixture decomposed with ice and dilute HCl on a steam bath and the crude product (90 mg) crystallized from MeOH to give **17**, m.p. 206–208°. (Found: C, 70·7; H, 5·4. $C_{24}H_{20}O_6$ requires: C, 71·3; H, 5·0%).

5-Hydroxy-7-benzyloxy-8-methoxy-3-(4-methoxybenzyl)-chromone (**18**). Methylation of **17** (280 mg) in boiling dry acetone (15 ml) with methyl sulphate (0·08 ml) in the presence of anhyd. K_2CO_3 for 3 hr afforded **18**, m.p. 126–128° (from MeOH) (160 mg). (Found: C, 71·2; H) 5·4. $C_{25}H_{22}O_6$ requires: C, 71·8; H, 5·3%).

5-Hydroxy-6-methoxy-7-benzyloxy-3-(4-hydroxybenzyl)-chromone (**19**). Benzylchromone **17** (1·25 g) was refluxed in ethanolic EtOK (3%, 125 ml) for 25 min. Acidification with 10% HCl and addition of water precipitated a mixture of **17** and **19** (in 1:2 ratio), which gave on repeated fractional crystallization, **19** as white needles, m.p. 174–176° (from MeOH). (Found: C, 70·8; H, 5·3. $C_{24}H_{20}O_6$ requires: C, 71·3; H, 5·0%).

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