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NOVEL FLAVONOIDS FROM THE STEM OF *POPOWIA CAULIFLORA**

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Key Word Index—*Popowia cauliflora*; Annonaceae; flavones; flavanones; chalcones; structure elucidation; ^{13}C NMR.

Abstract—Six flavonoids, five of them novel, have been isolated from the whole stem of *Popowia cauliflora* and identified as: baicalein trimethyl ether, 5-hydroxy-6,7-dimethoxyflavone, 5,7,8-trimethoxyflavanone, 2′-hydroxy-3′,4′,6′-trimethoxychalcone, 2′,3′,4′,6′-tetramethoxychalcone and 2′,4-dihydroxy-3′,4′,6′-trimethoxychalcone, on the basis of spectral data and simple chemical modifications. The value of ^{13}C NMR in assigning the positions of methoxy substituents is briefly discussed.

INTRODUCTION

Popowia cauliflora is a liane or scrambling bush of the family Annonaceae indigenous to the tropical rain-forest of west Africa from Zaire to S. Nigeria [1, 2]. No previous chemical investigations have been reported on any African species of *Popowia* but several alkaloids have been isolated from an Asiatic species of the genus [3].

As part of a continuing study on the chemistry of west African rain-forest Annonaceae we wish to report the isolation and identification of six simple flavonoids from the whole stem of this species, five of which are reported for the first time from a natural source.

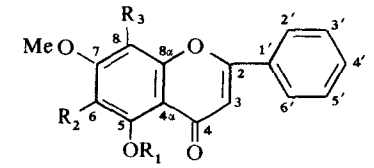
RESULTS AND DISCUSSION

From the petrol extract of the whole stem two compounds were isolated by column chromatography over Si gel. Compound **1**, which had also been obtained as a precipitate on initial concentration of the petrol extract, was present in a total yield of about 1.4%. On analysis it was found to be identical in all respects with literature data for baicalein trimethyl ether [4]. In the absence of authentic reference material its structure was confirmed by alkaline hydrolysis to the corresponding acetophenone (**10a**) and by comparison of lanthanide induced shifts (LIS) in the PMR spectrum with those reported for simple flavones using Eu(fod)$_3$ [5]. The LIS observed for the single A-ring proton (12% of the LIS for the C-5 OMe) indicated its occurrence at C-8 rather than at C-6 where relative LIS are in the order of 45% of the C-5 OMe.

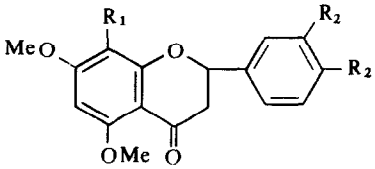
The second compound from the column recrystallised from Me_2CO:petrol as white needles, mp 154°, $C_{18}H_{18}O_5$. It showed an optical rotation of −100.6°. Both the simple UV (286, 327 nm) and the IR were typical of non-phenolic flavanones [6]. The flavanone nucleus was confirmed by the occurrence in the PMR spectrum of an ABX system centred at δ 2.88, 2.93 and 5.46 for the C-2 and C-3 protons. Signals at δ 3.92 (6H) and 3.81 (3H) could be assigned to 3-OMe substituents and the remaining six protons were observed as a 5H multiplet centred at δ 7.41 and a 1H signal at δ 6.13. This spectrum is compatible with that anticipated for a trimethoxy substituted flavanone with all the substituents in the A-ring. The absence of B-ring substitution was confirmed by the presence of ions at *m/e* 210 ($C_{10}H_{10}O_5$, **3a**) and *m/e* 104 (C_8H_8, **3b**) in the MS [7] (see Scheme 1). Alkaline hydrolysis of the flavanone gave an acetophenone different from that obtained from **1** and which gave close agreement with literature data [8] for 2-hydroxy-3,4,6-trimethoxyacetophenone (**10b**). The flavanone was therefore assigned structure **2** and the identity further confirmed by measuring the LIS of the A-ring proton relative to that of the C-5 OMe substituent. The observed shift of 59% was in close agreement with that for the C-6 proton of hesperidin trimethyl ether (**4**) which gave 56% and much greater than that for the C-8 proton which was only 21%.

An earlier fraction was found, by TLC, to contain a number of compounds. This mixture was separated by column chromatography over Al_2O_3 into three bands, the first of which was still a mixture but the other two appeared chromatographically pure. One of the pure compounds was recrystallised from Me_2CO:petrol as orange plates, mp 136°, $C_{18}H_{18}O_5$. The UV spectrum showed a single band at 340 nm typical of a chalcone [6]. Both the occurrence of a 30 nm bathochromic shift on the addition of $AlCl_3$ and bands at 3400 and 1635 cm^{-1} in the IR confirmed the occurrence of an O—H···C=O system. The PMR spectrum showed signals for 3 × OMe substituents at δ 3.87 (3H) and 3.96 (6H) with a hydrogen bonded OH resonating at δ 13.89. Five of the remaining eight protons occurred as a complex multiplet between δ 7.40 and 7.70 suggesting an unsubstituted B-ring (cf. **2**) the other three being observed as two singlets at δ 6.03 (1H) and 7.88 (2H). This spectrum is compatible with a 2′-hydroxychalcone

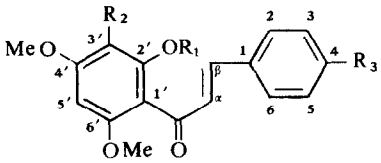
*Part 4 in the series 'Chemical Studies on the Annonaceae'. For Part 3 see Panichpol, K., Waigh, R. D. and Waterman, P. G. (1977) *Phytochemistry* **16**, 621.



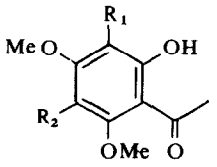
1 R_1 = Me, R_2 = OMe, R_3 = H
7 R_1 = R_3 = H, R_2 = OMe
8 R_1 = R_2 = H, R_3 = OMe



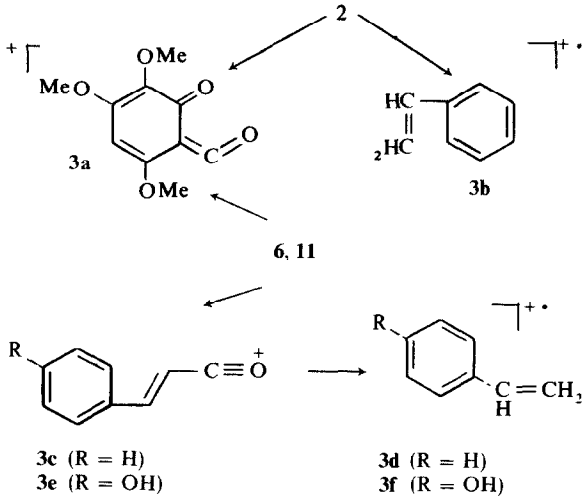
2 R_1 = OMe, R_2 = H
4 R_1 = H, R_2 = OMe



5 R_1 = R_2 = R_3 = H
6 R_1 = R_3 = H, R_2 = OMe
9 R_1 = Me, R_2 = OMe, R_3 = H
11 R_1 = H, R_2 = OMe, R_3 = OH



10a R_1 = H, R_2 = OMe
10b R_1 = OMe, R_2 = H



3c (R = H)
3e (R = OH)

3d (R = H)
3f (R = OH)

Scheme 1. Significant ions in the MS of flavanones and chalcones isolated from *Popowia cauliflora*.

substituted in the A-ring with 3 × OMe. The occurrence of the α and β protons as a singlet is unusual but has previously been observed in the spectrum of **5** [9]. The absence of B-ring substitution is supported by the presence of ions at *m/e* 210 (**3a**), *m/e* 131 (C_9H_7O, **3c**) and *m/e* 103 (C_8H_7, **3d**) in the MS [7]. It remained only to assign the positions of the 3 OMe substituents on the A-ring. This was achieved by the hydrolysis of the chalcone to the corresponding acetophenone which proved to be identical to **10b**, previously obtained from the flavanone **2**. The new chalcone must therefore be **6**. The relationship between **2** and **6** was confirmed by the isomerisation of the former in 50% KOH which gave **6** in high yield. Although **6** does not appear to have been isolated before it has been synthesised [10]. The data recorded here is in agreement with that available for the synthetic material.

The second compound obtained from the Al_2O_3 column recrystallised from $CHCl_3$:petrol as yellow plates, mp 150°, $C_{17}H_{14}O_5$. Both the UV, which showed a bathochromic shift with $AlCl_3$, and IR suggested a 5-hydroxyflavone [6]. The PMR spectrum showed signals at δ 3.94 and 3.98 for 2 × OMe and a sharp singlet at δ 12.77 for the C-5 hydroxyl function. The remaining seven protons occurred in the aromatic region in the form of a 5H multiplet between δ 7.63 and 7.90 and two singlets at δ 6.59 and 6.68 (1H each). As the two protons showed no coupling it was assumed that one occurred at C-3 and the other in the A-ring leading to the conclusion that the compound was a 5-hydroxy flavone substituted in the A-ring with 2 × OMe. The absence of B-ring substitution was again confirmed by the presence of ion **3d** in the MS. From biogenetic considerations it was reasoned that the new flavone must therefore have structure **7** or **8**. The latter has recently been found in *Gnaphalium pellitum* [11] and was recorded to have spectral properties different from those noted here. It therefore seemed likely that the correct structure was the previously unrecorded **7**. This was confirmed by the selective 5-demethylation of **1** in conc HCl [12] which gave a product identical in all respects to the isolated compound. In view of the relative ease of 5-demethylation it was considered possible that **7** might be an artefact derived from **1** during isolation. However TLC of both petrol and $CHCl_3$ extracts indicated it was present in the plant.

From the initial mixture eluted from the Al_2O_3 column a second chalcone was obtained by preparative TLC on Si gel. It recrystallised from $CHCl_3$:Et_2O as yellow plates, mp 72°, $C_{19}H_{20}O_5$. It exhibited a single maximum at 292 nm and carbonyl absorption at 1670 cm^{-1}. Neither UV nor IR suggested a phenolic moiety. The MS was very similar to that of **6**, the presence of ions **3c** and **3d** again indicating an unsubstituted B-ring. The PMR spectrum showed signals for 4 × OMe between δ 3.80 and 3.95, an AB quartet (*J* 16 Hz) centred at δ 7.40 and 7.09 for the α and β protons and six aromatic protons. The latter consisted of a five proton multiplet between δ 7.40 and 7.55 for the B-ring and a singlet at δ 6.40 for the unsubstituted position on the A-ring. The position of the substituents was established by methylation of the previously isolated **6** which gave a product identical in all respects to the isolated tetramethoxychalcone which can therefore be assigned structure **9**. Like **6** this compound has been previously synthesised [10] and the data reported showed close agreement with

that recorded here. An unusual feature of **9** was the exceptionally low wavelength obtained for the UV maximum. It has been noted [13] that chalcones undergo hypsochromic shifts on complete methylation and, also, in the absence of B-ring substitution. It would therefore be anticipated that **9** would show a low wavelength maximum but it remains somewhat surprising to find it below 300 nm.

From the $CHCl_3$ extract of the stem further amounts of the flavones **1** and **7** were obtained by column chromatography over Si gel. After their removal a fifth new flavonoid was eluted from the column and recrystallised from MeOH:Et_2O as orange cubes, mp 215°, $C_{18}H_{18}O_6$. The UV gave a single maximum at 371 nm and underwent bathochromic shifts of 40 and 60 nm with $AlCl_3$ and NaOMe respectively indicating a 2',4-dihydroxychalcone nucleus [6]. The PMR spectrum, run in DMSO-d_6, showed signals at δ 3.72 (3H) and 3.98 (6H) for 3 × OMe, a single A-ring proton at 6.37, four B-ring protons in the form of an AB quartet (J 8 Hz) confirming *para* substitution and a singlet at 7.70 for the equivalent α and β protons. In the MS the previously observed ions **3c** and **3d** were absent being replaced by fragments 16MU higher (**3e** and **3f**). Spectral data thus indicated a 2',4-dihydroxychalcone substituted in the A-ring with 3 × OMe. The position of the substitutuents was established by hydrolysis with 25% KOH to the corresponding acetophenone (**10b**) which proved to be identical in all respects to that previously obtained by the hydrolysis of **2** and **6**. This third novel chalcone must therefore be **11**.

Recently considerable attention has been paid to the ^{13}C NMR of flavonoids [14, 15]. The carbon shifts for all six compounds isolated have been recorded and assignments made by reference to those definitive papers (Table 1). The data obtained are in close agreement with those previously published and permitted unambiguous identification of the three flavonoid nuclei. Of particular note were the characteristic 6-line signals in the off-resonance decoupled spectra of chalcones for the α and β carbons [14, 15a] and the *ca* 5 ppm deshielding of the C=O resonance of flavones on the introduction of a C-5 hydroxyl group (**1**–**7**).

In contrast to the PMR spectra ^{13}C NMR proved of considerable value in assigning the positions of A-ring substituents. The carbon shifts of OMe substituents usually occur between 55.0 and 56.5 ppm but in some cases they are observed further downfield between 59.5 and 63.0 ppm. This deshielding effect is seen only when the OMe is *diortho* substituted by two bulky substituents such as other OMe, or OH, or a ring junction. Dhami and Stothers [16] have suggested that this is due to steric hindrance to resonance between the *O* of the OMe and the aromatic ring, a view that is substantiated by Hofer's observation [17] that an OMe substituent on an aromatic system favours a conformation lying in the plane of the ring to permit maximum overlap between the orbitals of the *O* lone pair and the π-orbitals of the aromatic nucleus. It would follow therefore that where there is an unsubstituted position adjacent to an OMe the Me carbon will be shielded by the conjugated electrons whereas in other cases, when the *O* is not fully conjugated, it will become relatively deshielded. Thus in **1** the occurrence of two resonances for OMe carbons at 61.5 and 62.1 ppm, and one at 56.3 ppm, requires two of the OMe groups to be flanked by either other OMe or ring junctions, and only one to be *ortho* to a proton. Such a situation is only met by the 5,6,7-, or biogenetically unlikely 6,7,8-, substitution pattern. On the other hand in **2** where there are two OMe resonances at 56.1 and one at 61.1 ppm two of the OMe groups are obviously flanked by the A-ring proton necessitating either a 5,7,8-, or biogenetically unlikely 5,6,8-, substitution pattern. The OMe resonances observed for the remaining four flavonoids reported here and for relevant flavonoids reported previously [15, 16] all support this observation

Table 1. Carbon shifts of flavonoids isolated from *P. cauliflora*

Carbons	Flavones		Flavanone	Carbons	Chalcones		
	1	**7**	**2**		**6**	**9**	**11**
2	157.7*	158.8*	79.0		142.6	144.6	143.4
3	108.3	105.4	45.6		127.4	128.8	123.8
4	177.0	182.6	189.2	C=O	193.2	193.5	192.5
4a	112.9	106.2	106.3	1'	106.8	116.6	106.9
5	152.5**	152.9*	156.2*	2'	158.6*	153.3**	157.1*
6	140.4	132.6	89.5	3'	130.8	136.2	130.0
7	161.0*	163.9*	158.7	4'	159.4*	155.0**	157.4*
8	96.3	90.6	131.0	5'	87.1	92.7	88.3
8a	154.5**	153.2*	157.8*	6'	158.5*	151.8**	156.0*
1'	131.5	131.1	138.9	1	135.4	134.8*	125.6
2', 6'	125.9	126.1	125.9	2,6	128.9	128.8	130.5
3',5'	128.9	129.0	128.7	3,5	128.3	128.4	115.9
4'	131.2	131.8	128.4	4	130.1	130.3	160.0
5-OMe	61.5***	—	56.1	2'-OMe	—	61.8***	—
6-OMe	62.1***	60.8	—	3'-OMe	60.7	61.0***	59.9
7-OMe	56.3	56.3	56.1	4'-OMe	56.0	56.2	56.2**
8-OMe	—	—	61.1	6'-OMe	56.0	56.2	55.9**

*Signals with the same superscript within any column may be interchanged. Carbon shifts measured against TMS as internal standard. Spectra run in $CDCl_3$ (**11** in DMSO-d_6).

and suggest that ^{13}C NMR may be of considerable value in assigning substitution patterns to polysubstituted flavonoids.

CONCLUSION

For its size the Annonaceae is perhaps one of the chemically least known plant families. Most investigations have, until recently, centred upon the alkaloids of which it is undoubtedly a major source [18, 19]. It is now becoming apparent however that the Annonaceae is also adept at producing a wide range of non-alkaloidal compounds such as styrenes [20], pyrones [22] and unusual *C*-formyl, *C*-methyl and *C*-benzyl flavanones and chalcones [23]. A common feature among most of the flavonoids isolated is the absence of B-ring substitution, a trait which may prove to have taxonomic significance.

A further point of note with regard to the flavonoids of *P. cauliflora* concerns the change from C-8 to C-6 substitution in the transition from chalcone/flavanone to flavone. Harborne [27] recognises C-8 hydroxylation as being a characteristic of primitive families and this is obviously the pattern that would be anticipated in the Annonaceae which is usually considered among the most primitive angiosperm families [28]. Harborne [27] further noted that the conversion to C-6 hydroxylation correlated with a reduction in lignin content and it is suggested that in *P. cauliflora* it may reflect the loss of the arboreal habit by this scrambling bush or liane.

EXPERIMENTAL

UV spectra were run in EtOH and IR spectra as KCl discs. PMR spectra were run at 60 MHz in $CDCl_3$ using TMS as internal standard unless otherwise stated. ^{13}C NMR spectra were run at 25.1 MHz in the same solvents using the same internal standard and employing FT. Mp's are uncorrected. Petrol refers to the bp 60–80° fraction unless otherwise stated.

Plant material. Whole stems of *Popowia cauliflora* Chipp. were collected in the Douala-Edea Forest Reserve, Cameroon, in July 1976. A voucher, P. G. Waterman and D. McKey 840, has been deposited at the Herbarium of the Royal Botanic Gardens, Kew.

Isolation of flavonoids. The ground stems (550 g) were extracted separately and successively with petrol (bp 40–60°), $CHCl_3$, and MeOH. Concn of the petrol gave, on standing, **1** (2.82 g). The conc extract was chromaotgraphed over Si gel and gave on elution with petrol:EtOAc 3:2 a mixture of compounds. Further elution with petrol:EtOAc 1:1 gave **1** (305 mg) followed by **2** (405 mg). The initial mixture was rechromatographed over Al_2O_3 (activity II). Elution with petrol containing increasing quantities of EtOAc gave a green oil followed by **6** (90 mg). Further elution with MeOH gave **7** (60 mg). The green oil was subjected to PLC on Si gel (1 mm, solvent C_6H_6:EtOAc) and the fluorescent band eluted with EtOAc to give **9** (600 mg).

The conc $CHCl_3$ extract gave, on column chromatography over Si gel and elution with $CHCl_3$:MeOH 97·3 further quantities of **7** (100 mg) and **1** (4.5 g) followed by **11** (130 mg).

Characterisation of flavonoids. Baicalein trimethyl ether (**1**). Cream plates from petrol, mp 169° (lit. [4] 169°). Found: M^+ 312.0991; $C_{18}H_{16}O_5$ requires: 312.0998. The UV, IR, PMR and MS were in close agreement with previously published data [4]

Hydrolysis of **1** *to 6-hydroxy-2,3,4-trimethoxyacetophenone* (**10a**). **1** (250 mg) was refluxed with 50% KOH in MeOH for 6 hr. The reaction mixture was neutralised and extracted with CH_2Cl_2 to give the acetophenone as an oil (101.5 mg). Found: M^+ 226.0834; $C_{11}H_{14}O_5$ requires: 226.0841. PMR δ 2.67 (3H, *s*, Me), 3.82, 3.92, 4.03 (9H, 3 × *s*, 3 × OMe), 6.30 (1H, *s*, H-Ar), 13.46 (1H, *s*, replaceable by D_2O, OH). UV, IR and MS were in close agreement with published data [4].

5,7,8-*Trimethoxyflavone* (**2**). White needles from Me_2CO: petrol, mp 154°. Found: M^+ 314.1152; $C_{18}H_{18}O_5$ requires: 314.1154. $[\alpha]_D^{24}$ −100.6° (*c* 1.00, $CHCl_3$). UV λ_{max} 239 *sh*, 284, 325 nm (log ε 4.09, 4.30, 3.83). IR ν_{max} 1700 (CO), 1610, 1510, 1350, 1275, 1120 cm^{-1}. PMR δ 2.88 (1H, *dd*, ABX, J_1 5 Hz, J_2 17 Hz, 3-H), 2.93 (1H, *dd*, ABX, J_2 17 Hz, J_3 10 Hz, 3-H), 3.81 (3H, *s*, OMe), 3.92 (6H, *s*, 2 × OMe), 5.46 (1H, *dd*, ABX, J_1 5 Hz, J_3 10 Hz, 2-H), 6.13 (1H, *s*, 6-H), 7.41 (5H, *m*, 5 × H-Ar). MS *m/e* 314 (100), 211 (10), 210 (99), 195 (52), 181 (13), 167 (36), 153 (11), 152 (11), 104 (11).

Hydrolysis of **2** *to 2-hydroxy-3,4,6-trimethoxyacetophenone* (**10b**). **2** (95 mg) was hydrolysed as previously detailed to give an amorphous cream powder mp 98° (lit. [8] 111°). Found: M^+ 226.0837 $C_{11}H_{14}O_5$ requires: 226.0841. PMR δ 2.65 (3H, *s*, Me), 3.82, 3.92, 3.98 (9H, 3 × *s*, 3 × OMe), 6.04 (1H, *s*, H-Ar), 13.90 (1H, *s*, replaceable by D_2O, OH). UV, IR and MS were in agreement with published data [8].

2′-*Hydroxy-3′,4′,6′-trimethoxychalcone* (**6**). Orange plates from Me_2CO: petrol, mp 136° (lit. [10] 141–142°). Found: M^+ 314.1151; $C_{18}H_{18}O_5$ requires 314.1154. UV λ_{max} 340 nm (log ε 4.17), $\lambda_{max}^{AlCl_3}$ 370 nm. IR ν_{max} 3500 (OH), 1640 (CO), 1560, 1445, 1420, 1330, 1130 cm^{-1}. PMR δ 3.87 (3H, *s*, OMe), 3.96 (6H, *s*, 2 × OMe), 6.03 (1H, *s*, 5′-H), 7.50 (5H, *m*, 5 × H-Ar), 7.88 (2H, *s*, α,β-H), 13.89 (1H, *s*, replaceable by D_2O, 2′-OH). MS *m/e* 314 (100%), 313 (11), 237 (13), 211 (7), 210 (27), 195 (33), 167 (19), 157 (5), 131 (5), 103 (10).

Partial synthesis of **6** *from* **2**. **2** (84 mg) was dissolved in the minimum quantity of 50% KOH in EtOH. After 5 min the reaction mixture was acidified with cold dil. HCl and extracted into $CHCl_3$. Recryst. of the $CHCl_3$ soluble material from $CHCl_3$:petrol gave orange plates, mp 136°, identical in all respects (UV, IR, PMR, MS, TLC, mmp) to **6**.

Hydrolysis of **6** *to* **10b**. **6** (30 mg) when hydrolysed as previously described gave a product identical in all respects (UV, IR, MS, mmp, TLC) to **10b**.

5-*Hydroxy-6,7-dimethoxyflavone* (**7**). Yellow plates from $CHCl_3$:petrol, mp 150°. Found: M^+ 298.0837; $C_{17}H_{14}O_5$ requires. 298.0841. UV λ_{max} 249, 272, 313 nm (log ε 4.21, 4.43, 4.17), $\lambda_{max}^{AlCl_3}$ 283, 335 nm. IR ν_{max} 3500 (OH), 1675 (CO), 1625, 1600, 1460, 1360, 1200, 1130 cm^{-1}. PMR δ 3.94 (3H, *s*, OMe), 3.98 (3H, *s*, OMe), 6.59, 6.68 (2H, 2 × *s*, H-3 and H-8), 7.63 (3H, *m*, 3′,4′,5′-H), 7.90 (2H, *m*, 2′,6′-H), 12.77 (1H, *s*, replaceable by D_2O, 5-OH). MS *m/e* 298 (100%), 297 (13), 284 (9), 283 (69), 269 (13), 255 (11), 196 (3), 181 (17), 153 (35), 105 (7), 103 (9).

Partial synthesis of **7** *from* **1**. **1** (100 mg) was refluxed with HOAc (5 ml) and conc HCl (5 ml) for 2 hr. The reaction mixture was extracted with $CHCl_3$ and the $CHCl_3$ soluble residue recryst. from $CHCl_3$:petrol to give yellow plates, mp 150°, identical in all respects (UV, IR, PMR, MS, TLC, mmp) to **7**.

2′,3′,4′,6′-*Tetramethoxychalcone* (**9**). Pale yellow plates from $CHCl_3 \cdot Et_2O$, mp 72°, (lit. [10] (76–78°). Found. M^+ 328.1315; $C_{19}H_{20}O_5$ requires: 328.1311. UV λ_{max} 292 nm (log ε 4.39). IR ν_{max} 1670 (CO), 1615, 1500, 1460, 1410, 1385, 1310, 1115, 1030 cm^{-1}. PMR δ 3.80, 3.87, 3.89, 3.95 (12 H, 4 × *s*, 4 × OMe), 6.40 (1 H, *s*, 5′-H), 7.09, 7.40 (2H, AB*q*, *J* 16 Hz, α,β-H), 7.40–7.55 (5H, *m*, 5 × H-Ar). MS *m/e* 328 (100%), 313 (22), 300 (31), 225 (19), 210 (11), 195 (12), 167 (19), 131 (22), 103 (44).

Partial synthesis of **9** *from* **6**. A soln of **6** (60 mg) in dry Me_2CO was refluxed with Me_2SO_4 (1 ml) and dry K_2CO_3 for 24 hr, cooled and filtered. The filtrate was conc to an oil, dissolved in $CHCl_3$ and washed with H_2O. The resulting amorphous material was identical in all respects (mmp, UV, IR, TLC) to **9**.

2′,4-*Dihydroxy-3′,4′,6′-trimethoxychalcone* (**11**). Orange cubes from MeOH:Et_2O, mp 215°. Found: M^+ 330.1098, $C_{18}H_{18}O_6$ requires: 330.1103. UV λ_{max} 239 *sh*, 371 nm (log ε 4.05, 4.50), $\lambda_{max}^{AlCl_3}$ 411 nm, λ_{max}^{NaOMe} 431 nm. IR ν_{max} 3340 (OH), 1660 (CO), 1630, 1570, 1440, 1340, 1260, 1130 cm^{-1} PMR (DMSO-d_6, DSS, δ) 3.72 (3H, *s*, OMe), 3.98 (6H, *s*, 2 × OMe), 6.37 (1H, *s*, 5′-H), 6.95 (2H, AB*q*, *J* 8 Hz, 3,5-H), 7.65 (2H, AB*q*, *J* 8 Hz, 2,6-H), 7.70 (2H, *s*, α,β-H). MS *m/e* 330 (85%), 329 (6), 315 (2),

237 (3), 211 (21), 210 (100), 195 (66), 181 (20), 167 (43), 153 (19), 152 (14), 147 (7), 119 (8), 107 (4).

Hydrolysis of **11** *to* **10b**. **11** (25 mg) was hydrolysed as previously described to give a product identical in all respects (UV, IR, MS, mmp, TLC) to **10b**.

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