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FLAVONOIDS OF *DERRIS ARARIPENSIS*

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Key Word Index—*Derris araripensis*; Leguminosae; dihydrochalcone; flavone; flavonols; flavanone; flavanonols; flavan; mass spectrometry.

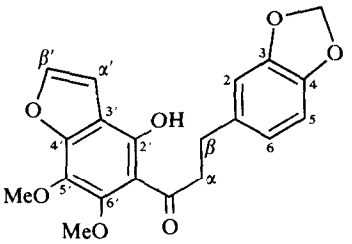
Abstract—Nine flavonoids: a dihydrochalcone, a flavone, four 3-methylflavonols, a flavanone, a 3-methylflavanonol and a flavan were isolated from the roots of *Derris araripensis*. Eight of these compounds are reported for the first time. Structures were established by spectral analysis and chemical degradation.

INTRODUCTION

The flavonoids of several *Derris* (*Lonchocarpus*) species (Leguminosae, Lotoideae) of Northern Brazil have been reported previously [1–6]. The present paper describes the characterisation of a further nine compounds (**1–9**) of this structural class from the roots of *Derris araripensis* Ducke, a large tree known locally as "angelim". Compound **2** has been isolated previously from *D. obtusa* [5] but the remaining eight flavonoids are reported for the first time.

RESULTS AND DISCUSSION

Mass spectral fragmentations may be interpreted by accepted patterns, since the cyclic substituents remain mostly unaffected by electron impact. Only the dimethylchromene nucleus is liable to lose one of the geminal methyl groups as a free radical [7] (flavonols **2** and **3**, Scheme 1). Fragmentation of the flavone skeleton of compounds **4**, **5** and **6** (Scheme 2) as well as of the flavanones **7** and **8**, (Scheme 3) proceeds in a uniform fashion. UV, IR and ^{1}H NMR spectra are in accord with



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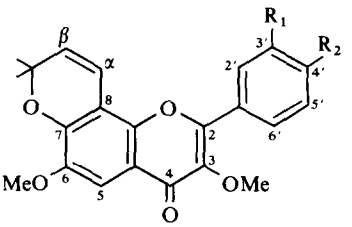
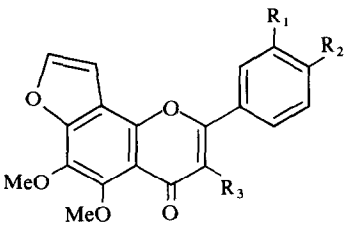
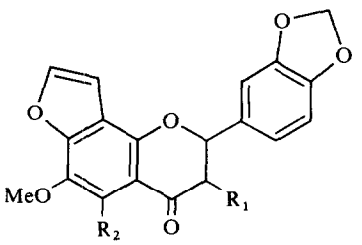


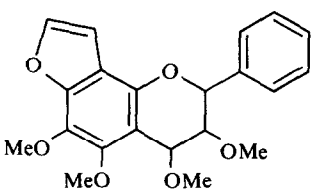
2 $R_1 = R_2 = H$
3 $R_1 + R_2 = O-CH_2-O$



4 $R_1 = R_2 = H$, $R_3 = OMe$
5 $R_1 + R_2 = O-CH_2-O$, $R_3 = OMe$
6 $R_1 + R_2 = O-CH_2-O$, $R_3 = H$



7 $R_1 = H$, $R_2 = OH$
8 $R_1 = R_2 = OMe$



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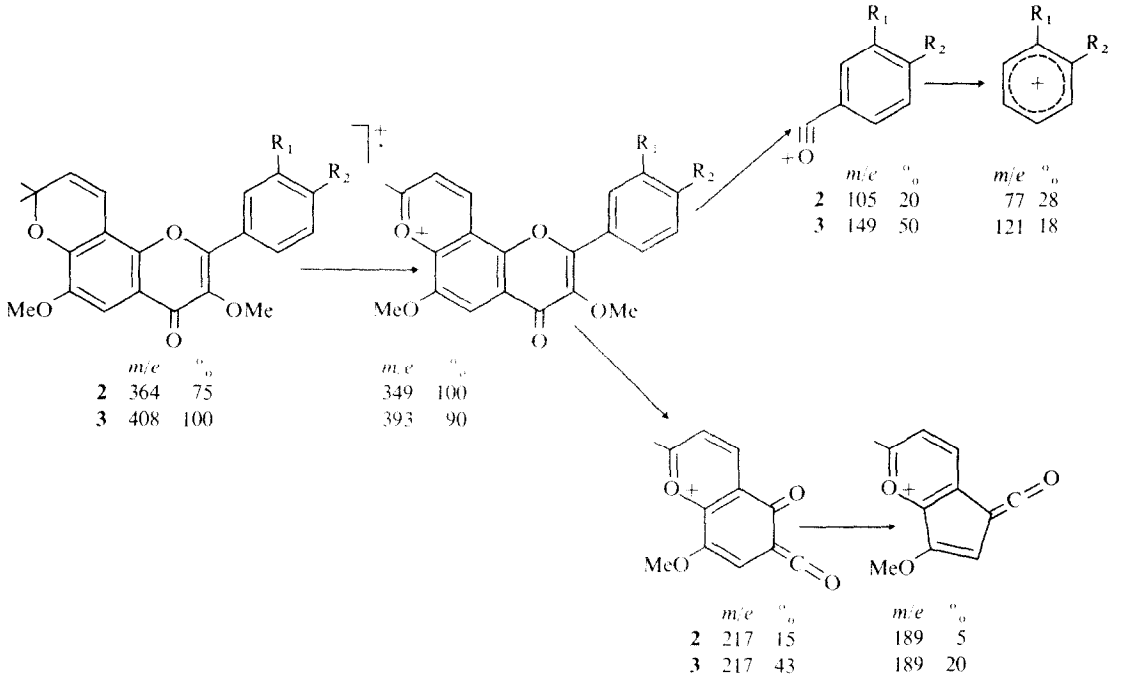
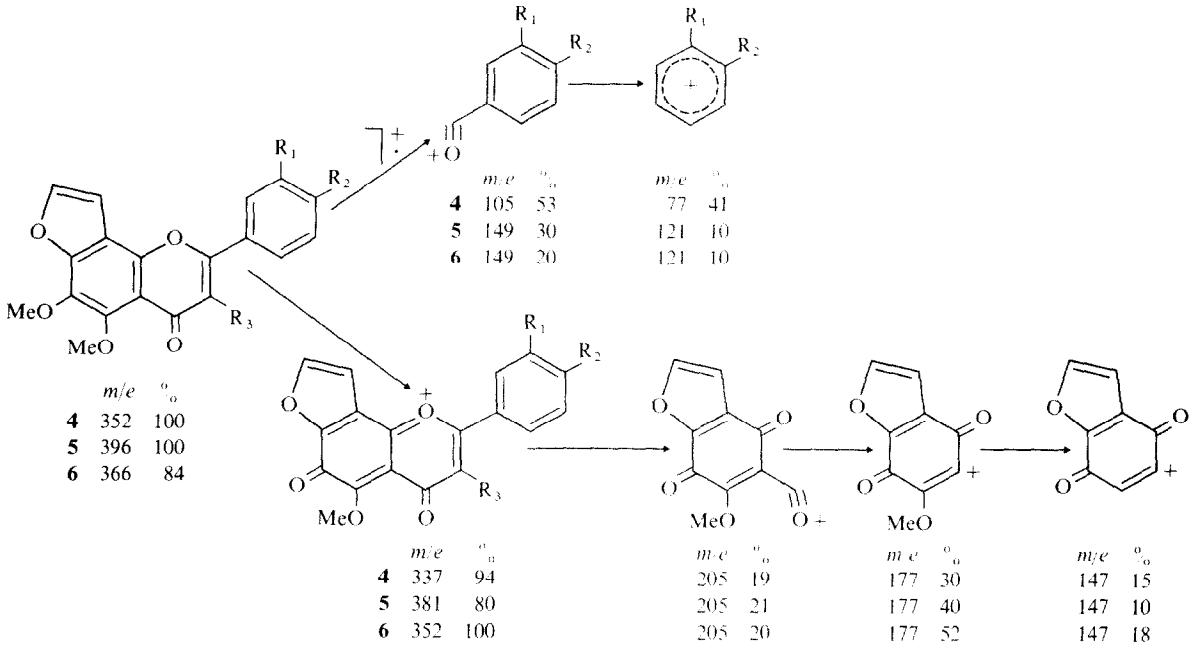


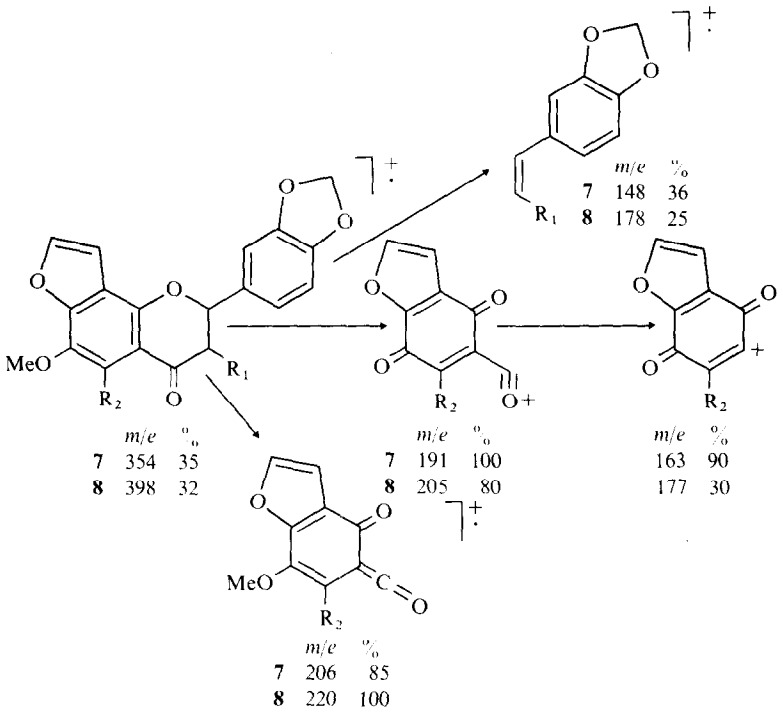
Scheme 1. Principal mass spectral fragmentations of flavonols **2** and **3**.

the proposed structures (for detailed data see Experimental). Compound **9** is remarkable in that it represents the first known completely methoxylated flavan. Its structure was deduced solely from spectral data. (For MS interpretation see Scheme 4; for ^{1}H NMR data, see Experimental.) Any remaining doubt about ^{1}H NMR assignments were dispelled by confirming the presence of the the protons at carbon atoms 2, 3 and 4 by selective proton decoupling. However, chemical degradations were performed to corroborate some of the results. Flavones and flavonols reacted with alkali in solution as expected. Thus, **3**, after two hours, yielded the intermediate **3a**, along with the ketone **3b** and piperonylic acid (**3c**) (Scheme 5).

Flavone **6** gave the corresponding dibenzoylmethane **6a** after 2 hr which after boiling for a further 3 hr was degraded to the β-keto-acid **6b**, the acetophenone **6c** and piperonylic acid **3c** (Scheme 6).



Scheme 2. Principal mass spectral fragmentations of flavones and methylated flavonols **4**, **5** and **6**.

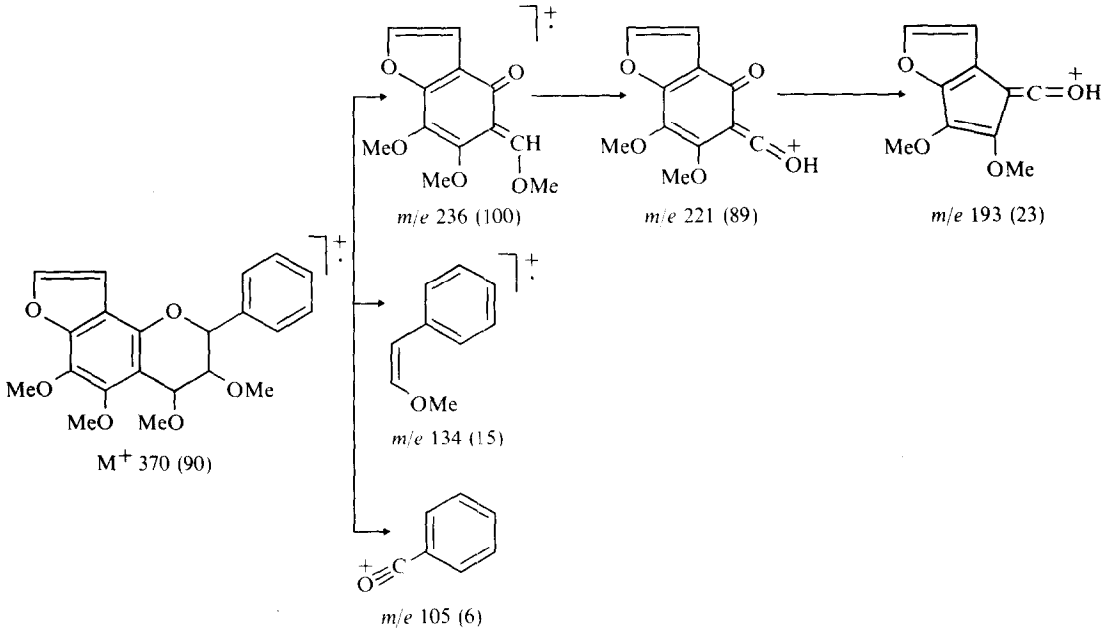


Scheme 3. Principal mass spectral fragmentations of flavanones **7** and **8**.

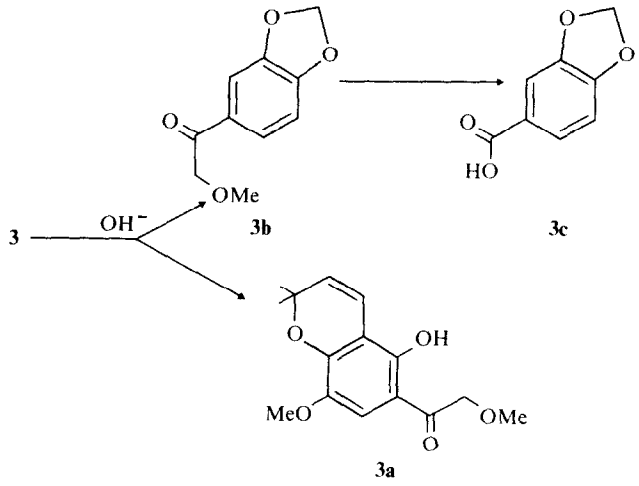
More drastic conditions can produce simultaneous demethylation [8,9]. Thus degradation of the dihydrochalcone **1**, which required alkali fusion, involved cleavage of the methyl ether groups. The 2,3,5-trihydroxybenzfuran-4-carboxylic acid **1a** was the only product isolated in this reaction (Scheme 7).

The methoxyl at C-5 in compound **5** is cleaved easily by treatment with dil. HCl. Such behaviour of a methoxyl group in the β position to the carbonyl occurs in the auronols present in *Derris obtusa* [5], and is due to the fact that it is a methyl ester vinylogue.

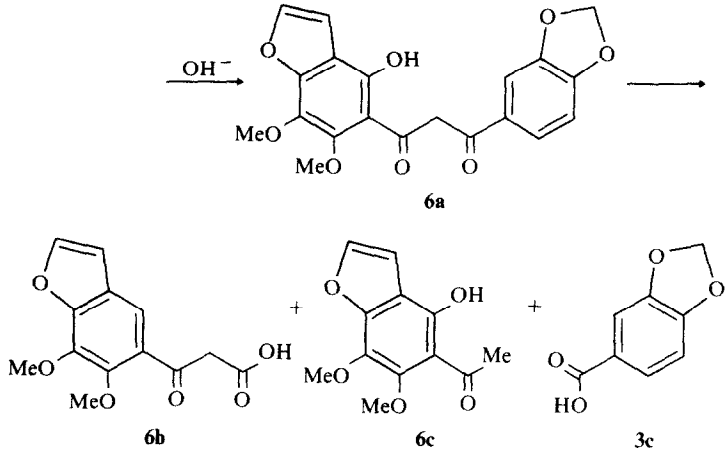
All the substances (**1**–**9**) (a dihydrochalcone and eight compounds with flavan, flavone or flavanone skeleton), are highly methoxylated, have dimethylchromene or furan rings attached to ring A, and have a B ring which is either unsubstituted or has a methylenedioxy substituent. In the wide range of flavonoids found within the genus *Derris*, the present structural types are found also in



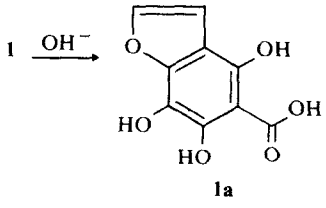
Scheme 4. Principal mass spectral fragmentations of proanthocyanidin **9**.



Scheme 5. Alkaline degradation of flavonol **3**.



Scheme 6. Alkaline degradation of flavone **6**.



Scheme 7. Alkali fusion of dihydrochalcone **1**.

D. obtusa (Benth.) Ducke [5], *D. mollis* (Benth.) Macbr. [6] and *D. spruceana* (Benth.) Ducke (Nascimento, M. C. and Mors, W. B., unpublished results).

EXPERIMENTAL

Mps are uncorr. Spectra were obtained in EtOH (UV), $CDCl_3$ (^{1}H NMR) and KBr pellets (IR). ^{1}H NMR spectra were measured at 100 MHz and MS at 70 eV. Plant material was collected in the state of Ceará, near Fortaleza.

Extraction. The general procedure has been described previously [5]. Successive percolation of ground root bark of *D. araripensis* with petrol (bp 40–80°) and Et_2O and concn of the combined extracts gave crystals of **2** identified by comparison with an authentic sample [5]. The remaining extract was chromatographed on Si gel; elution started with petrol and the polarity of eluent was increased gradually. Compounds were eluted in the order given below and purified on small columns or by prep. TLC.

Methylenedioxy-(3′,4′)-5-hydroxy-6-methoxy-furano-(7,8,2″,3″)-flavanone (**7**). Eluted with hexane–toluene (1:1). Yellow needles from EtOH, mp 183°, $[\alpha]_D^{25}$ + 7.5° ($CHCl_3$). IR: ν_{max} cm^{-1}: 1650 (>C=O), 1250. UV: λ_{max}^{EtOH} nm (log ε): 370 (3.69), 288 (4.26), 257 (4.76), 250 sh (4.66), 238 (4.56), 232 sh (4.51). ^{1}H NMR ($CDCl_3$, δ): 13.60 (*s*, OH...O=C), 7.50–7.52 (*d*, *J* = 2 Hz, H-β), 7.0 (*q*, *J* = 2 Hz, H-α), 6.78–6.90 (*m*, H-2′, 5′, 6′), 5.99 (*s*, O—CH_2—O), 5.50 (*dd*, *J* = 4, 5 and 11 Hz, H-2), 3.99 (*s*, OMe), 3.10 (*dd*, *J* = 11.0 and 18.9 Hz, H-3), 2.80 (*dd*, *J* = 4.5 and 18.9 Hz, H-3). MS: *m/e* 354 (M^+, rel. int. 35%), 206 (85), 191 (100), 163 (90), 148 (36), 147 (32), 135 (29), 89 (59), 67 (59), 66 (34), 65 (55), 63 (54). Found: 353.9762; $C_{19}H_{14}O_7$ requires 354.0735.

Methylenedioxy-(3′,4′)-5,6-dimethoxyfurano-(7,8, 2″,3″)-flavone (**6**). Eluted with hexane–toluene (1:3). Colourless crystals from EtOH, mp 233°. IR: ν_{max} cm^{-1}: 1655 (>C=O), 1250. UV: λ_{max}^{EtOH} nm (log ε): 332 (4.49), 255 (4.66), 217 (5.32). ^{1}H NMR ($CDCl_3$, δ): 7.68 (*d*, *J* = 2 Hz, H-β), 7.50–7.60 (*q*, *J* = 2.5 Hz, H-6′), 7.42–7.44 (*d*, *J* = 2.5 Hz, H-2′), 7.0–7.10 (*d*, *J* = 2 Hz, H-α), 6.95 (*d*, *J* = 8 Hz, H-5′), 6.62 (*s*, H-3), 6.10 (*s*, O–CH_2–O), 4.30 (*s*, OMe), 4.14 (*s*, OMe). MS: *m/e* 366 (M^+, 84), 352 (100), 322 (38), 205 (20), 177 (52), 149 (20), 147 (18), 121 (10). Found: C, 64.01; H, 4.24. $C_{20}H_{14}O_7$ requires: C, 64.88; H, 4.30.

3,4,5,6-*Tetramethoxyfurano-(7,8,2″,3″)-flavan* (**9**). Eluted with hexane–toluene (1:3). Colourless needles from EtOH, mp 119°, $[\alpha]_D^{25}$ − 10.6°. IR: ν_{max} cm^{-1}: 1250, 1280, 1300, 1306. UV: λ_{max}^{EtOH} nm (log ε): 260 (4.35), 220 (5.27). ^{1}H NMR ($CDCl_3$, δ): 7.52 (*d*, *J* = 2 Hz, H-β), 7.28–7.50 (*m*, H-2′, 3′, 4′, 5′, 6′), 6.84 (*q*, *J* = 2 Hz, H-α), 5.02 (*d*, H-2), 4.78–4.80 (*d*, H-4), 4.08 (*s*, OMe), 4.04 (*s*, OMe), 3.90–4.10 (*dd*, H-3), 3.44 (*s*, OMe), 3.38 (*s*, OMe). MS: *m/e* 370 (M^+, 90), 371 (M^+ + 1, 31), 237 (24), 236 (100), 222 (17), 221 (89), 193 (23), 134 (15), 121 (60), 91 (23), 77 (12). Found: 370.1420; $C_{21}H_{22}O_6$ requires 370.1410.

Methylenedioxy-(3,4)-5′-hydroxy-2′,3′-methoxyfurano-(3′,4′,2″,3″)-dihydrochalcone (**1**). Eluted with C_6H_6. Yellow needles from EtOH, mp 158°. IR: ν_{max} cm^{-1}: 1610 (>C=O). UV: λ_{max}^{EtOH} nm (log ε): 358 (3.47), 288 sh (4.02), 252 (4.47), 218 (4.32). ^{1}H NMR ($CDCl_3$, δ): 13.08 (*s*, OH...C=O), 7.53 (*d*, *J* = 2 Hz, H-β′), 6.92 (*q*, *J* = 2 Hz, H-α′), 6.72–6.78 (*m*, H-2, 5, 6), 5.98 (*s*, O–CH_2–O), 4.14 (*s*, OMe), 4.08 (*s*, OMe), 3.30–3.52 (*qq*, CH_2, C-α), 2.90–3.10 (*qq*, CH_2, C-β). MS: *m/e* 370 (M^+, 64), 356 (65), 339 (23), 325 (22), 221 (100), 194 (55), 190 (30), 121 (98). Found: 370.1078; $C_{20}H_{18}O_7$ requires 370.1047.

3,5,6-*Trimethoxyfurano-(7,8,2″,3″)-flavone* (**4**). Eluted with C_6H_6. Yellow needles from EtOH, mp 173°. IR: ν_{max} cm^{-1}: 1660 (>C=O), 1310, 750. UV: λ_{max}^{EtOH} nm (log ε): 351 (4.01), 315 sh (4.23), 264 (4.84), 220 (4.74). ^{1}H NMR ($CDCl_3$, δ): 8.24 (*m*, H-2′, 6′), 7.64 (*d*, *J* = 2 Hz, H-β), 7.40–7.52 (*m*, H-3′, 4′, 5′), 7.04 (*q*, *J* = 2 Hz, H-α), 4.24 (*s*, OMe), 4.12 (*s*, OMe), 4.02 (*s*, OMe). MS: *m/e* 352 (M^+, 100), 353 (M^+ + 1, 24), 351 (32), 338 (23), 337 (94), 333 (18), 321 (25), 309 (19), 308 (23), 205 (19), 177 (30), 169 (19), 147 (15), 105 (53), 77 (41). Found: C, 67.94; H, 4.63; OMe, 26.26. $C_{20}H_{16}O_6$ requires: C, 68.18; H, 4.58; OMe, 26.42.

Methylenedioxy-(3′,4′)-3,5,6-trimethoxyfurano-(7,8,2″,3″)-flavone (**5**). Eluted with C_6H_6. Colourless crystals from EtOH, mp 212°. IR: ν_{max} cm^{-1}: 1640 (>C=O), 1325. UV: λ_{max}^{EtOH} nm (log ε): 342 (4.32), 257 (4.55), 219 (4.75). ^{1}H NMR ($CDCl_3$, δ): 7.84 (*d*, *J* = 2 Hz, H-2′), 7.60–7.66 (*q*, *J* = 2 Hz, H-6′), 7.62 (*d*, *J* = 2 Hz, H-β), 7.0 (*q*, *J* = 2 Hz, H-α), 6.90–6.98 (*d*, *J* = 8 Hz, H-5′), 6.06 (*s*, O–CH_2–O), 4.22 (*s*, OMe), 4.12 (*s*, OMe), 3.88 (*s*, OMe). MS: *m/e* 396 (M^+, 100), 381 (80), 377 (20), 367 (18), 366 (15), 293 (15), 205 (21), 177 (40), 149 (30), 147 (10), 133 (20), 121 (10). Found: C, 63.46; H, 4.20. $C_{20}H_{16}O_8$ requires: C, 63.64; H, 4.04.

3,5,6-*Trimethoxyfurano-(7,8,2″,3″)-flavanonol* (**8**). Eluted with C_6H_6. Colourless needles from EtOH, mp 138°. IR: ν_{max} cm^{-1}: 1660 (>C=O), 1306, 1280, 1250. UV: λ_{max}^{EtOH} nm (log ε): 355 (3.64), 288 sh (4.20), 249 (4.79), 242 sh (4.74). ^{1}H NMR ($CDCl_3$, δ): 7.46–7.50 (*d*, *J* = 2 Hz, H-2′), 6.76–6.82 (*m*, H-6′, 5′), 6.0 (*s*, O–CH_2–O), 5.24 (*d*, *J* = 8 Hz, H-2), 4.08 (*s*, OMe), 4.02 (*s*, OMe), 3.90–4.0 (*d*, *J* = 8 Hz, H-3), 3.48 (*s*, OMe). MS: *m/e* 398 (M^+, 32), 221 (28), 220 (100), 205 (80), 178 (25), 177 (30), 135 (8), 133 (13). Found: 398.1037; $C_{21}H_{18}O_8$ requires 398.1000.

Methylenedioxy-(3,4)-3,6-dimethoxy-6″,6″-dimethylchromeno-(7,8,2″,3″)-flavone (**3**). Eluted with $CHCl_3$. Colourless needles from EtOH, mp 207°. IR: ν_{max} cm^{-1}: 1645 (>C=O), 1405 (*gem*-diMe), 1275, 1255. UV: λ_{max}^{EtOH} nm (log ε): 352 (4.52), 285 (4.12), 245 (4.89), 220 (5.05). ^{1}H NMR ($CDCl_3$, δ): 7.96 (*m*, H-2′, 6), 7.52 (*s*, H-5), 6.90 (*d*, H-5′), 6.86 (*d*, *J* = 10 Hz, H-α), 5.74 (*d*, *J* = 10 Hz, H-β), 4.0 (*s*, OMe), 3.94 (*s*, OMe), 1.60 (*s*, *gem*-diMe). MS: *m/e* 408 (M^+, 100), 407 (85), 393 (90), 217 (43), 197 (39), 189 (20), 182 (36), 174 (32), 149 (50), 121 (18). Found: C, 68.18; H, 5.25; OMe, 14.14. $C_{23}H_{20}O_7$ requires C, 67.65; H, 4.90; OMe, 15.20.

3,6-*Dimethoxy-6″,6″-dimethylchromeno-(7,8,2″,2″)-flavone* (**2**). Eluted with $CHCl_3$. Colourless needles from EtOH, mp 203–205°. Identical with previously isolated compound [5] by mp, mmp, TLC, IR and MS.

Alkaline degradation of **3**. 380 mg **3** were heated in 40% KOH in 25 ml H_2O–EtOH (2:3), under reflux and N_2. Progress of the reaction was monitored by means of TLC. After 2 hr, with three spots discernible, heating was discontinued, the soln cooled, acidified with HCl and extracted with $CHCl_3$. The product was worked up on a Si gel column. *2-Hydroxy-6″,6″-dimethylchromeno-(4,3)-5-methoxy-(1′-methoxy)-acetophenone* (**3a**). Yellow needles from EtOH, mp 114°. ^{1}H NMR ($CDCl_3$, δ): 1.52 (6H, *s*, *gem*-diMe), 3.50 (3H, *s*), 3.83 (3H, *s*), 4.60 (2H, *s*, CH_2O), 5.62 (1H, *d*, *J* = 10 Hz, C-β), 6.75 (1H, *d*, *J* = 10 Hz, C-α), 7.04 (1H, *s*, C-5), 12.49 (1H, *s*, OH...O=C). MS: *m/e* 278 (M^+, 82), 279 (M^+ + 1, 15), 264 (14), 263 (75), 246 (9), 234 (29), 233 (100), 232 (10), 231 (62), 217 (10), 215 (8), 205 (15), 203 (16), 190 (15), 189 (14), 179 (14), 144 (8), 175 (12), 149 (33), 145 (8), 135 (12), 129 (10), 125 (9), 121 (10), 115 (9), 111 (16), 105 (11). Found: 278.1154; $C_{15}H_{18}O_5$ requires 278.1149. *1′-Methoxy-3,4-methylenedioxybenzophenone* (**3b**). Pale yellow oil. ^{1}H NMR ($CDCl_3$, δ): 3.50 (3H, *s*), 4.62 (2H, *s*, CH_2O), 6.04 (2H, *s*, O–CH_2–O), 6.85 (1H, *d*, *J* = 2.5 Hz, C-5′), 7.42) (1H, *d*, *J* = 2.5 Hz, C-2′), 7.70 (1H, *q*, *J* = 2.5 and 8.5 Hz, C-6′). MS: *m/e* 194 (M^+, 15), 149 (100), 121 (15), 75 (12), 73 (10). *Piperonylic acid* (**3c**) was identified by comparison (TLC, mp, mmp, IR) with an authentic specimen.

Alkaline degradation of **6**. 500 mg **6** were heated in 40% KOH in 25 ml H_2O–EtOH (2:3), under reflux and N_2. Progress of the reaction was monitored by means of TLC (one spot appeared after 2 hr; three additional spots after 7 hr). The product after 2 hr was extracted from the cooled acidified soln with Et_2O and purified on a Si gel column. [*2-Hydroxy-(4,3-furano)-5,6-dimethoxybenzoyl]-piperonyl-methane* (**6a**). Yellow crystals from Et_2O, mp 161–163°. IR: ν_{max} cm^{-1}: 1690 (>C=O). ^{1}H NMR ($CDCl_3$, δ): 3.88 (3H, *s*), 4.04 (3H, *s*), 4.58 (2H, *s*), 6.06 (1H, *s*, O–CH_2–O), 6.84 (1H, *d*, *J* = 8.5 Hz, C-5′), 6.92 (1H, *q*, *J* = 2 Hz, C-α), 7.36–7.50 (2H, *m*, C-2′, 6′), 7.60 (1H, *d*, *J* = 2 Hz, C-β), 12.98 (1H, *s*, OH...O=C). MS: *m/e* 384 (M^+, 35), 353 (33), 221 (9), 220 (62), 205 (54), 194 (37), 191 (12), 179 (10), 177 (31), 163 (13), 150 (10), 149 (100), 121 (26), 119 (8), 105 (10), 91 (10), 79 (15), 65 (33), 63 (16), 51 (8). Found: 384.0806; $C_{20}H_{16}O_8$ requires 384.0840. The products after 7 hr degradation, **6b**, **6c** and piperonylic acid (**3c**), were purified in the same way. *2-Hydroxy-(4,3-furano)-5,6-dimethoxybenzoyl-acetic acid* (**6b**). Yellow crystals from Et_2O, mp 120–122°. MS: *m/e* 280 (17), 266 (34), 248 (8), 235 (43), 234 (24), 222 (15), 221 (100), 220 (10), 219 (9), 207 (30), 206 (37), 205 (10), 192 (11), 191 (47), 163 (15), 55 (20). Found: 280.0974; $C_{13}H_{12}O_7$ requires 280.0579. *2-Hydroxy-(4,3-furano)-5,6-dimethoxyacetophenone* (**6c**). Yellow wax. MS: *m/e* 236 (100), 228 (86), 207 (8), 206 (45), 204 (26), 193 (11), 191 (27), 189 (10), 175 (20), 163 (20), 151 (8), 150 (9), 149 (13), 119 (16), 95 (10), 91 (21), 77 (10). Found: 236.0706; $C_{12}H_{12}O_5$ requires 236.0681. *Piperonylic acid* (**3c**) was identified by comparison (TLC, mp, mmp, IR) with an authentic specimen.

Alkaline degradation of **1**. 10 mg **1** were mixed with powdered NaOH in a porcelain crucible and heated by direct flame during 4 hr. After cooling, the residue was dissolved in water, acidified and extracted ×3 with Et_2O giving 2,5,6-trihydroxy-(3,4-furano)-benzoic acid. Amorphous. MS: *m/e* 210 (M^+, 17), 209 (M^+ − 1, 100), 208 (61), 180 (40), 152 (30), 138 (10).

Partial demethylation of **5**. *Methylene dioxy*-(3′,4′)-5-*hydroxy*-3,6-*dimethoxyfurano*-(7,8,2″,3″)-*flavone* (**5a**). 100 mg of **6** were heated under reflux in 30 ml aq. EtOH (2:1) plus 2 ml conc HCl. Monitoring by means of TLC showed the appearance of a new spot; maximum vield was obtained after 5 hr. On cooling, **6a** crystallized directly from the reaction mixture. Yellow needles, mp 230°. ^{1}H NMR ($CDCl_3$, δ): 3.86 (3H, *s*), 4.12 (3H, *s*), 6.04 (1H, *s*), 7.0 (1H, *q*, J = 2 Hz, C-α), 7.22 (1H, *d*, J = 8.5 Hz, C-5′), 7.58 (1H, *d*, J = 2.5 Hz, C-2′), 7.76 (1H, *q*, J = 2.5 Hz, C-6′), 7.85 (1H, *d*, J = 2 Hz, C-β), 12.96 (1H, *s*, OH...O=C). MS: *m/e* 382 (M^+, 87), 383 (M^+ + 1, 19), 368 (21), 367 (100), 352 (21), 337 (17), 191 (21), 163 (21), 162 (10), 149 (13), 147 (8). Found: 382.0603; $C_{20}H_{14}O_8$ requires 382.0684.

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