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Structure of a Non-Planar Flavonol, 5,7,2′-Trihydroxy-3,6,8,4′,5′-pentamethoxyflavone*

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Abstract. $C_{20}H_{20}O_{10}$, $M_r = 420{\cdot}37$, triclinic, $P\bar{1}$, $a = 8{\cdot}771$ (3), $b = 13{\cdot}508$ (3), $c = 15{\cdot}970$ (4) Å, $\alpha = 86{\cdot}04$ (2), $\beta = 81{\cdot}77$ (2), $\gamma = 84{\cdot}17$ (2)°, $V = 1860{\cdot}0$ (8) Å^3, $Z = 4$ (two molecules per asymmetric unit), D_m(by flotation in $ZnCl_2/H_2O$ solution at 298 K) = 1·491, $D_x = 1{\cdot}503$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}14$ cm^{-1}, $F(000) = 880$, $T = 163$ K. Full-matrix least-squares refinement converged to $R = 0{\cdot}039$ and $wR = 0{\cdot}037$ using 5198 reflections with $I > 3\sigma(I)$. The two molecules in the asymmetric unit differ in the torsion angles involving the methoxy groups and in the dihedral angle between the planes of rings *B* and *C*, 33·31 (7) and 40·83 (7)° in molecules (I) and (II), respectively. This compound belongs to a class of 3,2′-dioxygenated flavonoids whose ultraviolet (UV), mass spectroscopic (MS) and chromatographic properties indicate that in solution these compounds have reduced planarity (and thus reduced conjugation) of the *B*-ring chromophore with the *A*, *C*-ring chromophore.

Introduction. The spectral and chromatographic properties of most flavones and flavonols are closely associated with the three rings (*A*, *B* and *C*) exhibiting a high level of coplanarity such that rings *A* and *B* are in conjugation with the C4 carbonyl group. However, a group of about 75 flavonols exhibit unusual UV and MS spectral properties and paper chromatographic mobilities which suggest that in solution the *B* ring is not coplanar with the *A* and *C* rings. These unusual flavonols are the 3,2′-dioxygenated flavonoids, a group of compounds which have been referred to as the 'distorted flavonols' (Fang & Mabry, 1990). Although the conformation of a compound in the crystalline state is not necessarily the same as in solution, it was nevertheless of interest to determine whether the *B* ring was out of the plane of the other two rings in the crystalline state in at least one of these unusual flavonols. Therefore, 5,7,2′-trihydroxy-3,6,8,4′,5′-pentamethoxyflavone (1) (Fang, Leidig, Mabry & Iinuma, 1985; Fang, Leidig & Mabry, 1986) was crystallized and its crystal structure solved.

Experimental. *Gutierrezia microcephala* (DC.) A. Gray (family Compositae) was collected between Monterrey and Saltillo on the road to Microondas Mariposa. The details of the isolation and purification of all flavonoids from this collection have been previously reported (Fang *et al.*, 1985). Compound (1) was crystallized from benzene.

A colorless crystal of compound (1), 0·21 × 0·24 × 0·28 mm, was mounted and transferred to a Syntex $P2_1$ diffractometer equipped with a graphite monochromator utilizing Mo $K\alpha$ radiation, where it was maintained in an environment of dry N_2 at 163 K using a Syntex LT-1 low-temperature delivery system. Preliminary investigations revealed the crystal system to be triclinic. 45 strong reflections, $21{\cdot}86 \leq 2\theta \leq 28{\cdot}16°$, were used to refine the unit-cell parameters. 9088 reflections (h −11→11, k −17→17, l 0→20) were collected using the ω-scan method, 8526 unique reflections, $R_{\text{int}} = 0{\cdot}022$; 2θ range 4→55°, 1° ω scan at 3–6° min^{-1}, depending upon intensity. Four reflections were remeasured every 96 reflections in order to monitor instrument stability and crystal decay. Absorption corrections were applied based on measured crystal faces (Riley & Davis, 1976); min. and max. transmission 0·934 and 0·981. The structure was solved by direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), which revealed the positions of all non-H atoms. All H atoms were obtained from a difference Fourier map. Refinement was carried out by full-matrix least squares in *SHELX*76 (Sheldrick, 1976) using anisotropic thermal parameters for the non-H atoms and

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* Flavone is 2-phenyl-4*H*-benzopyran-4-one.

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isotropic thermal parameters for the H atoms. $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0{\cdot}5\,kI^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}02I)^2\}^{1/2}$, I(intensity) = $(I_{\rm peak} - I_{\rm background})$(scan rate), and $\sigma(I) = (I_{\rm peak} + I_{\rm background})^{1/2}$(scan rate). k is the correction due to decay and Lp effects, and 0·02 is a factor used to down weight intense reflections and to account for instrument instability. Convergence was attained with R and wR of 0·039 and 0·037, respectively, for 5198 reflections of intensity greater than $3\sigma(I)$. In the last cycle of refinement, 701 variables were refined to a goodness-of-fit of 1·53; the largest shift/e.s.d. did not exceed 0·05; min. and max. peaks in the difference Fourier map were $-0{\cdot}22$ and 0·26 e Å^{-3}, respectively. The linear absorption coefficient was calculated from values from *International Tables for X-ray Crystallography* (1974). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), while those of H atoms were from Stewart, Davidson & Simpson (1965). The least-squares-planes program was supplied by Cordes (1983) while other programs used are cited in reference 11 of Gadol & Davis (1982). Positional parameters of all non-H atoms with their equivalent isotropic thermal parameters are given in Table 1. Bond lengths and angles for the non-H atoms are listed in Table 2.* Fig. 1 shows the *ORTEP* drawing (Johnson, 1976) of molecule (I) with the atom- and ring-labeling schemes; Fig. 2 is a drawing of the two molecules in the asymmetric unit superimposed on each other.

Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for atoms of* 5,7,2′-*trihydroxy*-3,6,8,4′,5′-*pentamethoxyflavone*

For anisotropic atoms, the U value is $U_{\rm eq}$, calculated as $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	U
Molecule (I)				
O1	0·3919 (2)	0·32841 (10)	0·26441 (8)	0·0164 (5)
O2′	0·1511 (2)	0·40288 (12)	0·05372 (11)	0·0290 (6)
O3	0·4463 (2)	0·31942 (11)	0·03588 (9)	0·0224 (5)
O4	0·6313 (2)	0·15218 (11)	0·08382 (9)	0·0238 (5)
O4′	−0·0117 (2)	0·71058 (11)	0·16947 (10)	0·0261 (5)
O5	0·7602 (2)	0·04462 (11)	0·20106 (10)	0·0255 (5)
O5′	0·1844 (2)	0·67402 (11)	0·29349 (10)	0·0276 (5)
O6	0·7827 (2)	0·01691 (11)	0·37456 (9)	0·0241 (5)
O7	0·6042 (2)	0·13830 (11)	0·48441 (9)	0·0227 (5)
O8	0·4155 (2)	0·29764 (10)	0·43198 (9)	0·0181 (5)
C1′	0·2798 (2)	0·44557 (15)	0·17181 (13)	0·0171 (7)
C2	0·3812 (2)	0·35265 (15)	0·18073 (13)	0·0161 (7)
C2′	0·1765 (3)	0·4665 (2)	0·11217 (13)	0·0189 (7)
C3	0·4610 (3)	0·2949 (2)	0·11982 (13)	0·0175 (7)
C3′	0·0867 (3)	0·5579 (2)	0·11201 (14)	0·0203 (7)
C4	0·5595 (3)	0·2071 (2)	0·13989 (13)	0·0180 (7)
C4′	0·0910 (2)	0·6268 (2)	0·17115 (14)	0·0197 (7)
C5	0·6746 (3)	0·1071 (2)	0·25678 (13)	0·0188 (7)
C5′	0·1901 (3)	0·6054 (2)	0·23343 (13)	0·0200 (7)
C6	0·6853 (2)	0·0915 (2)	0·34212 (13)	0·0185 (7)
C6′	0·2832 (3)	0·5171 (2)	0·23168 (13)	0·0181 (7)
C7	0·5974 (2)	0·1550 (2)	0·40063 (13)	0·0175 (7)
C8	0·5023 (2)	0·23639 (15)	0·37389 (13)	0·0164 (6)
C9	0·4926 (2)	0·25085 (14)	0·28787 (13)	0·0153 (6)
C10	0·5760 (2)	0·18782 (14)	0·22835 (13)	0·0154 (6)
C13	0·5857 (3)	0·3484 (2)	−0·0146 (2)	0·0281 (8)
C14′	0·0502 (3)	0·8054 (2)	0·1704 (2)	0·0333 (9)
C15′	0·2906 (4)	0·6524 (2)	0·3541 (2)	0·0356 (9)
C16	0·7387 (4)	−0·0818 (2)	0·3674 (2)	0·0355 (10)
C18	0·4912 (3)	0·3843 (2)	0·4448 (2)	0·0276 (8)
Molecule (II)				
O1	1·1187 (2)	0·21019 (10)	0·23432 (8)	0·0175 (5)
O2′	1·1240 (2)	0·39883 (12)	0·42984 (10)	0·0278 (6)
O3	1·1118 (2)	0·19484 (11)	0·46200 (9)	0·0201 (5)
O4	1·2690 (2)	0·01287 (11)	0·41714 (9)	0·0246 (5)
O4′	0·6988 (2)	0·59101 (11)	0·32653 (10)	0·0268 (5)
O5	1·3847 (2)	−0·11014 (11)	0·29942 (10)	0·0266 (5)
O5′	0·6614 (2)	0·44637 (11)	0·22514 (9)	0·0218 (5)
O6	1·4263 (2)	−0·14354 (11)	0·12501 (10)	0·0269 (5)
O7	1·3183 (2)	−0·00022 (12)	0·01623 (10)	0·0281 (6)
O8	1·1771 (2)	0·17894 (10)	0·06722 (9)	0·0209 (5)
C1′	0·9917 (2)	0·32793 (15)	0·32631 (13)	0·0168 (7)
C2	1·0891 (2)	0·23277 (15)	0·31753 (13)	0·0166 (7)
C2′	1·0114 (3)	0·4029 (2)	0·37927 (13)	0·0189 (7)
C3	1·1405 (2)	0·1687 (2)	0·37881 (13)	0·0171 (7)
C3′	0·9151 (3)	0·4915 (2)	0·38003 (14)	0·0206 (7)
C4	1·2253 (2)	0·0733 (2)	0·36032 (13)	0·0184 (7)
C4′	0·8006 (3)	0·5073 (2)	0·32867 (14)	0·0199 (7)
C5	1·3335 (3)	−0·0390 (2)	0·24353 (13)	0·0196 (7)
C5′	0·7804 (2)	0·4333 (2)	0·27480 (13)	0·0183 (7)
C6	1·3579 (3)	−0·0557 (2)	0·15810 (14)	0·0211 (7)
C6′	0·8747 (3)	0·3465 (2)	0·27437 (13)	0·0178 (7)
C7	1·3008 (3)	0·0161 (2)	0·09948 (13)	0·0199 (7)
C8	1·2224 (3)	0·1061 (2)	0·12567 (13)	0·0186 (7)
C9	1·1988 (2)	0·12152 (15)	0·21120 (13)	0·0166 (7)
C10	1·2531 (2)	0·0518 (2)	0·27153 (13)	0·0177 (7)
C13	0·9690 (3)	0·1639 (2)	0·5056 (2)	0·0368 (10)
C14′	0·7424 (3)	0·6791 (2)	0·3584 (2)	0·0253 (8)
C15′	0·6977 (3)	0·5082 (2)	0·1498 (2)	0·0333 (9)
C16	1·5840 (3)	−0·1727 (2)	0·1402 (2)	0·0324 (9)
C18	1·0212 (3)	0·1756 (2)	0·0505 (2)	0·0387 (10)

Discussion. The title compound consists of a phenyl ring (*A*) fused to the 5,6-positions of a 1,4-pyrone ring (*C*) which in turn is attached to a phenyl ring (*B*) through the 2-position. The UV spectrum of (1) in methanol [band (I) at 352 nm with about half the intensity of band (II) at 262 nm (Fang *et al.*, 1985)] was not typical for non-3,2′-dioxygenated flavones and flavonols. Moreover, the unusual two-dimensional paper chromatographic properties of (1) with an R_f of 0·89 in TBA (*tert*-butyl alcohol:glacial acetic acid:water, 3:1:1) and an R_f of 0·85 in 15% aqueous acetic acid also reflect reduced conjugation of the *B* ring with the C4 carbonyl group (Fang *et al.*, 1985). Compound (1) not only gives most of the same ions in its mass spectrum as other flavonol aglycones (Mabry & Markham, 1975), but in addition gives some characteristic fragments associated with the 3,2′-dioxygenation system: $(M\text{-}17)^+$ at m/z 403 (9%), $(M\text{-}31)^+$ at m/z 389 (21%), $(B_6)^+$ at m/z 208 (68%) and $(B_6\text{-}15)^+$ at m/z 193 (53%). Because of these unusual spectral and chromatographic properties of the 3,2′-dioxygenated flavonoids, which indicate non-planarity in solution, it was of interest to determine for one member of this class whether

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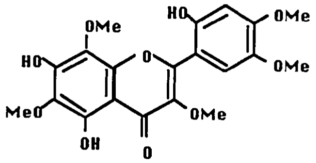
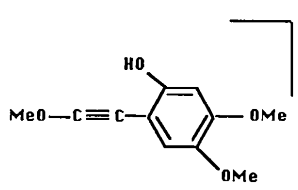
* Lists of structure-factor amplitudes, anisotropic thermal parameters, H-atom positional parameters and bond lengths and angles, hydrogen-bonding distances, and a selected set of torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52025 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

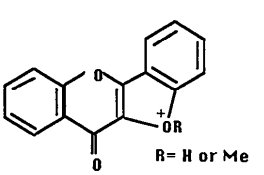
non-planarity was also present in the crystalline state.



(1)



$[B_6]^+$



$[M-17]^+$ or $[M-31]^+$

All bond distances in molecule (I) are equal to their counterparts in molecule (II) with the largest deviation not exceeding 0·018 (4) Å. The two molecules, however, have significant differences in bond angles. The largest differences are in the exocyclic angles at C5′ and C4′ positions. All endocyclic bond angles of the three rings are equivalent to their counterparts in the second molecule. The greatest difference between molecules (I) and (II) appears to be in the orientation of the methoxy groups. The torsion angle C3′—C4′—O4′—C14′ is − 130·7 (2)° in molecule (I) and 20·5 (3)° in molecule (II). Rings *A* and *C* are coplanar in each molecule, whereas the dihedral angles between rings *B* and *C* are 33·31 (7) and 40·83 (7)° in molecules (I) and (II), respectively. This shows that the two molecules differ by a rotation of 7·52° of ring *B* around the C1′–C4′ axis. The non-coplanarity of rings *B* and *C* supports a decrease in the degree of conjugation between the C2—C1′ bond and the π electrons of the pyrone ring. The C2—C1′ distances in the title compound, 1·474 (3) and 1·473 (3) Å, are within 3σ of an average $C(sp^2)$—$C(sp^2)$ bond distance (1·48 Å). They are longer than the C2—C1′ [1·453 (9) Å] reported by Cantrell (1986) for acacetin (5,7-dihydroxy-4′-methoxyflavone) in which rings *B* and *C* are nearly coplanar (reported dihedral angle is 3·1°). This bond distance is also shorter than in other molecules (Cantrell, 1986) where the dihedral angle between rings *B* and *C* increases [1·510 (5) Å, 75·5°; 1·494 (6) Å, 73·3°]. The absence of conjugation between the C2—C1′ bond and the pyrone ring means that there will be more delocalization of the π electrons in the C2—C3—C4—O4 unit. The C2—C3 distances [1·358 (3) and 1·356 (3) Å] are longer than a C—C double bond (average 1·34 Å), and the C3—C4 distances [1·440 (3) and 1·448 (3) Å] are shorter than the average $C(sp^2)$—$C(sp^2)$ distance (1·48 Å). In order to compare further the two molecules of the asymmetric unit, a molecular fitting program [*BMFIT*, reference 11 of Gadol & Davis (1982)] was used. The result revealed that all atoms of rings *A* and *C* as well as atoms C1′ and C4′ of ring *B* are superimposable on their counterparts of the second molecule; C2′, C3′, C5′ and C6′ were at an average distance of 0·14 (1) Å from their counterparts. The difference in the dihedral angles of the planes of rings *B* and *C* can be clearly seen as a result of the rotation of ring *B* along the C1′–C4′ axis, probably to accommodate the packing requirement and to minimize repulsion between the bulky methoxy groups. The three hydroxy groups present in this compound are involved in intermolecular as well as intramolecular hydrogen bonding. The intramolecular H···O distances are 1·75 (3) and 1·78 (3) Å for O4···H5, 1·92 (3) and 2·10 (3) Å for O3···H2′, and 2·21 (2) and 2·27 (3) Å for O6···H7 for molecules (I) and (II), respectively. O4 in both molecules has an intermolecular hydrogen bond with H7 [O4···H7 is 1·96 (3) and 2·01 (2) Å, respectively]. It was proposed by Rossi, Cantrell, Farber, Dyott, Carrell & Glusker (1980) that the hydrogen bonds involving O4 would enhance the electron-withdrawing power of the pyrone ring on the phenyl ring, thus giving C2—C1′ more double-bond character and force coplanarity

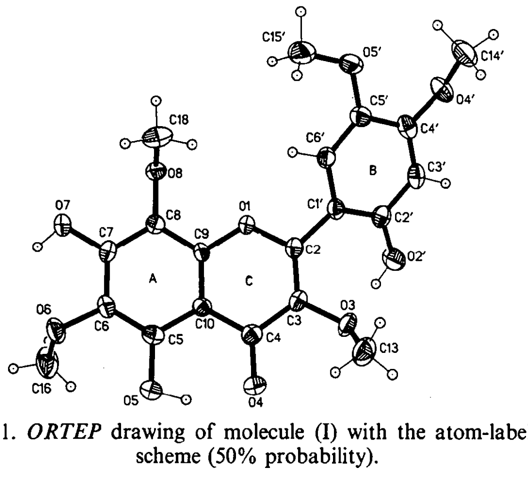


Fig. 1. *ORTEP* drawing of molecule (I) with the atom-labeling scheme (50% probability).

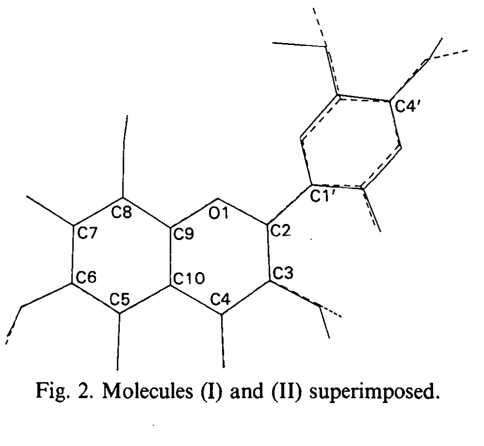


Fig. 2. Molecules (I) and (II) superimposed.

Table 2. *Bond lengths* (Å) *and angles* (°) *for* 5,7,2′-*trihydroxy*-3,6,8,4′,5′-*pentamethoxyflavone*

1	2	3	1—2	1—2—3	1	2	3	1—2	1—2—3
Molecule (I)					Molecule (II)				
C2	O1	C9	1·368 (2)	120·73 (15)	C2	O1	C9	1·367 (2)	120·6 (2)
C9	O1		1·368 (2)		C9	O1		1·371 (2)	
C2′	O2′		1·367 (3)		C2′	O2′		1·357 (3)	
C3	O3	C13	1·379 (2)	114·2 (2)	C3	O3	C13	1·380 (2)	113·1 (2)
C13	O3		1·438 (3)		C13	O3		1·430 (3)	
C4	O4		1·259 (2)		C4	O4		1·253 (3)	
C4′	O4′	C14′	1·374 (2)	117·0 (2)	C4′	O4′	C14′	1·369 (2)	117·1 (2)
C14′	O4′		1·442 (3)		C14′	O4′		1·433 (3)	
C5	O5		1·360 (3)		C5	O5		1·353 (3)	
C5′	O5′	C15′	1·372 (3)	116·1 (2)	C5′	O5′	C15′	1·389 (3)	112·7 (2)
C15′	O5′		1·433 (4)		C15′	O5′		1·432 (3)	
C6	O6	C16	1·377 (3)	113·7 (2)	C6	O6	C16	1·378 (3)	116·5 (2)
C16	O6		1·441 (3)		C16	O6		1·449 (3)	
C7	O7		1·350 (3)		C7	O7		1·347 (3)	
C8	O8	C18	1·378 (2)	112·8 (2)	C8	O8	C18	1·378 (2)	113·7 (2)
C18	O8		1·444 (3)		C18	O8		1·436 (4)	
C2	C1′	C2′	1·474 (3)	125·9 (2)	C2	C1′	C2′	1·473 (3)	125·2 (2)
C2′	C1′	C6′	1·402 (3)	117·9 (2)	C2′	C1′	C6′	1·402 (3)	117·7 (2)
C6′	C1′	C2	1·411 (3)	116·2 (2)	C6′	C1′	C2	1·402 (3)	117·0 (2)
C3	C2	O1	1·358 (3)	120·4 (2)	C3	C2	O1	1·356 (3)	120·7 (2)
C3	C2	C1′		129·4 (2)	C3	C2	C1′		129·0 (2)
O1	C2	C1′		110·2 (2)	O1	C2	C1′		110·1 (2)
C3′	C2′	O2′	1·395 (3)	115·4 (2)	C3′	C2′	O2′	1·393 (3)	114·9 (2)
C3′	C2′	C1′		119·2 (2)	C3′	C2′	C1′		120·1 (2)
O2′	C2′	C1′		125·4 (2)	O2′	C2′	C1′		125·0 (2)
C4	C3	O3	1·440 (3)	118·4 (2)	C4	C3	O3	1·448 (3)	118·3 (2)
C4	C3	C2		122·1 (2)	C4	C3	C2		122·4 (2)
O3	C3	C2		119·5 (2)	O3	C3	C2		119·2 (2)
C4′	C3′	C2′	1·378 (3)	122·1 (2)	C4′	C3′	C2′	1·377 (3)	120·9 (2)
C10	C4	O4	1·444 (3)	121·7 (2)	C10	C4	O4	1·448 (3)	122·4 (2)
C10	C4	C3		115·9 (2)	C10	C4	C3		115·1 (2)
O4	C4	C3		122·4 (2)	O4	C4	C3		122·4 (2)
C5′	C4′	O4′	1·409 (3)	123·3 (2)	C5′	C4′	O4′	1·403 (3)	115·5 (2)
C5′	C4′	C3′		119·3 (2)	C5′	C4′	C3′		119·6 (2)
O4′	C4′	C3′		117·2 (2)	O4′	C4′	C3′		124·9 (2)
C6	C5	C10	1·380 (3)	119·7 (2)	C6	C5	C10	1·381 (3)	119·5 (2)
C6	C5	O5		119·4 (2)	C6	C5	O5		119·5 (2)
C10	C5	O5	1·413 (3)	120·9 (2)	C10	C5	O5	1·419 (3)	121·0 (2)
C6′	C5′	O5′	1·375 (3)	124·1 (2)	C6′	C5′	O5′	1·364 (3)	120·2 (2)
C6′	C5′	C4′		118·7 (2)	C6′	C5′	C4′		119·3 (2)
O5′	C5′	C4′		117·2 (2)	O5′	C5′	C4′		120·4 (2)
C7	C6	O6	1·404 (3)	116·5 (2)	C7	C6	O6	1·406 (3)	115·6 (2)
C7	C6	C5		120·2 (2)	C7	C6	C5		120·2 (2)
O6	C6	C5		123·2 (2)	O6	C6	C5		124·0 (2)
C1′	C6′	C5′		122·7 (2)	C1′	C6′	C5′		122·4 (2)
C8	C7	O7	1·392 (3)	118·5 (2)	C8	C7	O7	1·394 (3)	117·7 (2)
C8	C7	C6		121·1 (2)	C8	C7	C6		121·1 (2)
O7	C7	C6		120·4 (2)	O7	C7	C6		121·2 (2)
C9	C8	O8	1·388 (3)	121·5 (2)	C9	C8	O8	1·379 (3)	121·3 (2)
C9	C8	C7		117·9 (2)	C9	C8	C7		117·9 (2)
O8	C8	C7		120·5 (2)	O8	C8	C7		120·7 (2)
C10	C9	O1	1·396 (3)	121·3 (2)	C10	C9	O1	1·399 (3)	121·3 (2)
C10	C9	C8		122·3 (2)	C10	C9	C8		122·7 (2)
O1	C9	C8		116·3 (2)	O1	C9	C8		116·0 (2)
C4	C10	C5		122·0 (2)	C4	C10	C5		121·7 (2)
C4	C10	C9		119·2 (2)	C4	C10	C9		119·7 (2)
C5	C10	C9		118·7 (2)	C5	C10	C9		118·5 (2)

between rings *B* and *C*. These rings are not coplanar in compound (1) in spite of the hydrogen bonding of O4 and O3. This is in contrast with the 5,6-benzoflavone structure reported by Rossi *et al.* (1980). The seven-membered ring formed by the O3···H2′ bond is not rigid and allows for considerable floppiness, suggesting that the non-coplanarity of the *B* and *C* rings must be due to the steric effect of the substituents on C3 and C2′.

It is well known that the introduction of substituents around the essentially single bond connecting chromophores results in interference and steric inhibition of the coplanarity of the chromophores. Thus, the X-ray results for (1) in the crystalline state support the suggestion that in solution the unusual UV, MS and chromatographic properties of the 3,2′-dioxygenated flavonoids are related to steric hindrance of the C3 and C2′ groups interfering with the rotation of the *B* ring and reducing the conjugation of the chromophores in these compounds.

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Structure of the *NS*-Donor Ligand 4-(Ethylthiomethyl)-5-methylimidazole

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Abstract. $C_7H_{12}N_2S$, $M_r = 156{\cdot}25$, monoclinic, $P2_1/n$, $a = 9{\cdot}684\,(6)$, $b = 11{\cdot}459\,(3)$, $c = 15{\cdot}834\,(4)$ Å, $\beta = 92{\cdot}62\,(3)^\circ$, $V = 1755{\cdot}2$ Å^3, $Z = 8$, $D_x = 1{\cdot}18$ g cm^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, $\mu = 2{\cdot}88$ cm^{-1}, $F(000) = 672{\cdot}92$, $T = 293$ K, final $R = 0{\cdot}060$ for 1914 significant reflections. The asymmetric unit contains two molecules of 4-(ethylthiomethyl)-5-methylimidazole (memi). The molecules are coupled in chains parallel to the *a* axis by hydrogen from the N—H of one molecule to the pyridine-type N atom of the next molecule. The imidazole rings are planar. The least-squares plane through the imidazole ring and the plane through the thioether S and its adjacent C atoms make dihedral angles of 103·9 (2) and 87·1 (3)° in the two independent memi molecules. The corresponding angle in memi ligands coordinated to transition-metal ions is close to 90°, which implies that the conformation of the free ligand is favourable for coordination.

Introduction. As part of a research program to synthesize low-molecular-weight analogues of the active sites of metalloproteins we are designing ligands which contain chromophores similar to those in certain metalloenzymes. Several reports describing the preparation and spectroscopic characterization of transition-metal coordination compounds containing these ligands have been published by our group (see for instance: Ochocki, Driessen, de Graaff & Reedijk, 1988; Bouwman & Driessen, 1988). Most of these reports also include X-ray crystal structures of one or two of the complexes. Hitherto, the crystal structures of the free ligands themselves have not been determined. The conformation of a free ligand is not necessarily identical to the conformation of the complexed ligand (Driessen, Groeneveld & van der Weij, 1970).

The *NS*-donor ligand 4-(ethylthiomethyl)-5-methylimidazole (memi) has been designed to obtain MN_2S_2 chromophores which may serve as models for the active site in plastocyanine (Colman, Freeman, Guss, Murata, Norris, Ramshaw & Venkatappa, 1978). Several coordination compounds of the ligand memi have been prepared and characterized (Bouwman, Westheide, Driessen & Reedijk, 1989). To gain insight into the precise stereochemistry of the uncomplexed ligand its X-ray crystal structure has been determined.

Experimental. Colorless needle, grown from ethanol at room temperature, with approximate dimensions 0·5 × 0·3 × 0·3 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromatized Mo $K\alpha$. Cell constants from setting angles of 24 reflections, $10 < \theta < 12^\circ$. Corrections for Lorentz and polarization effects. Transmission coefficients 0·97 to

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