Structures of Two Flavonoids from *Physalis minima*, 5-Methoxy-6,7-methylene-dioxyflavone (I) and 5,6,7-Trimethoxyflavone (II)

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Abstract. (I) 9-Methoxy-6-phenyl-8H-[1,3]dioxolo-[4,5-g][1]benzopyran-8-one, $C_{17}H_{12}O_5$, $M_r = 296.3$, monoclinic, $P2_1$, $a = 5.269$ (2), $b = 19.781$ (6), $c = 6.768$ (2) Å, $\beta = 106.46$ (2)°, $V = 676.5$ (3) Å^3, $Z = 2$, $D_x = 1.454$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.08$ cm^{-1}, $F(000) = 308$, $T = 298$ K, $R = 0.028$ for 1138 observed reflections [$I > 2\sigma(I)$]. (II) 5,6,7-Trimethoxy-2-phenyl-4H-1-benzopyran-4-one, $C_{18}H_{16}O_5$, $M_r = 312.3$, monoclinic, $P2_1/c$, $a = 13.074$ (4), $b = 14.196$ (5), $c = 8.365$ (2) Å, $\beta = 102.87$ (2)°, $V = 1513.6$ (8) Å^3, $Z = 4$, $D_x = 1.371$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.00$ cm^{-1}, $F(000) = 656$, $T = 298$ K, $R = 0.040$ for 1470 observed reflections [$I > 2\sigma(I)$]. X-ray diffraction confirmed the structures of (I) and (II) as reported based on spectroscopic and synthetic studies [Ng & Goh (1990). *J. Nat. Prod.* **53**, 747–749]. The molecules of both compounds are nearly planar. In (I), the phenyl ring is twisted at 6.7° from the plane of the fused rings and the methoxy group at C(5) is also slightly out of the plane. In (II), the phenyl is twisted at 11° from the plane of the fused rings and the three methoxy groups are slightly out of this plane. Bond lengths and angles in (I) and (II) are similar and within expected ranges.

Experimental. (I) and (II) were isolated from *Physalis minima* (Ng, 1988). D_m was not measured. Crystal sizes: (I) 0.40 × 0.35 × 0.25 mm; (II) 0.40 × 0.35 × 0.25 mm. Lattice parameters were refined using 20 reflections for both (I) and (II), in the ranges 8 < 2θ < 25° for (I) and 7.5 < 2θ < 25° for (II). A Siemens *R*3*m*/*V* 2000 diffractometer with graphite monochromator and ω scans was used for data collection. For (I), 1366 reflections in the range 3.5 < 2θ < 50° were measured for $h = 0$ to 6, $k = 0$ to 22, $l = -8$ to 7. 1233 of these reflections were independent ($R_{int} = 0.021$), and 1138 observed [$I > 2\sigma(I)$]. Three standard reflections checked every 97 reflections showed no significant intensity variation for (I); no absorption correction was made. For (II), 2847 reflections in the range 3.5 < 2θ < 50° were measured for $h = -15$ to 15, $k = -16$ to 0, $l = 0$ to 9. 2674 of these reflections were independent ($R_{int} = 0.041$), and 1470 reflections were independent ($R_{int} = 0.041$), and 1470

observed [$I > 2\sigma(I)$]. Three standard reflections checked every 97 reflections showed no significant intensity variation for (II); no absorption correction was made.

(I)   (II)
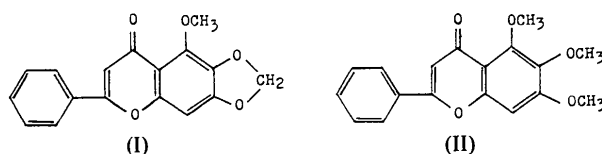
Both structures were solved by direct methods and refined by full-matrix least squares, minimizing $\Sigma w(F_o - F_c)^2$. Non-H atoms were refined with anisotropic thermal parameters. H atoms were placed at calculated positions with fixed isotropic thermal parameters. For (I), the y coordinate of O(1) was fixed during refinement and the origin was located on $P2_1$. For (I), $R = 0.028$, $wR = 0.036$ for observed reflections and 199 parameters; maximum $\Delta/\sigma = 0.096$; goodness of fit = 1.58; $\Delta\rho_{max} = 0.14$, $\Delta\rho_{min} = -0.11$ e Å^{-3}; $w = 1/(\sigma^2 + 0.0002F^2)$. For (II), $R = 0.040$, $wR = 0.056$ for observed reflections and 208
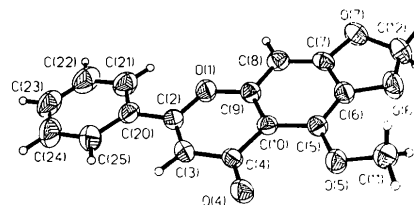

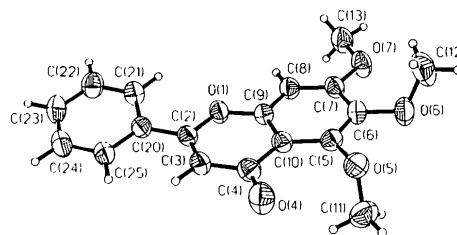Fig. 1. Perspective view of (I) with atomic numbering.

Fig. 2. Perspective view of (II) with atomic numbering.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U
Compound (I)				
O(1)	2443 (3)	6910	6369 (3)	44 (1)
O(4)	2864 (3)	5211 (1)	9839 (3)	48 (1)
O(5)	5690 (4)	4629 (1)	7580 (3)	51 (1)
O(6)	8345 (4)	4919 (1)	4257 (3)	54 (1)
O(7)	7953 (4)	5957 (1)	2619 (3)	51 (1)
C(2)	1210 (5)	6873 (2)	7883 (4)	39 (1)
C(3)	1376 (5)	6313 (2)	9023 (4)	43 (1)
C(4)	2805 (4)	5715 (1)	8750 (3)	36 (1)
C(5)	5605 (5)	5223 (1)	6573 (3)	36 (1)
C(6)	5683 (5)	5346 (1)	5034 (4)	38 (1)
C(7)	6552 (4)	5965 (1)	4026 (3)	39 (1)
C(8)	5108 (5)	6490 (1)	4446 (3)	42 (1)
C(9)	3904 (5)	6372 (1)	6002 (3)	36 (1)
C(10)	4118 (5)	5764 (2)	7099 (3)	35 (1)
C(11)	7742 (5)	4154 (2)	7614 (4)	52 (1)
C(12)	8892 (5)	5270 (2)	2585 (4)	51 (1)
C(20)	−293 (5)	7488 (2)	8024 (4)	44 (1)
C(21)	−543 (6)	8010 (2)	6623 (5)	58 (1)
C(22)	−2036 (7)	8579 (2)	6743 (6)	72 (1)
C(23)	−3285 (7)	8631 (2)	8274 (7)	74 (1)
C(24)	−3058 (7)	8120 (2)	9664 (6)	75 (1)
C(25)	−1589 (6)	7548 (2)	9558 (5)	61 (1)
Compound (II)				
C(2)	9454 (2)	2286 (2)	−105 (3)	41 (1)
C(3)	9347 (2)	1349 (2)	−109 (3)	45 (1)
C(4)	8503 (2)	876 (2)	424 (3)	45 (1)
C(5)	6827 (2)	1212 (2)	1448 (3)	41 (1)
C(6)	6147 (2)	1859 (2)	1864 (3)	45 (1)
C(7)	6358 (2)	2826 (2)	1815 (3)	43 (1)
C(8)	7237 (2)	3137 (2)	1335 (3)	43 (1)
C(9)	7909 (2)	2476 (2)	899 (3)	39 (1)
C(10)	7750 (2)	1505 (2)	952 (3)	40 (1)
C(11)	7096 (3)	−232 (2)	2867 (4)	68 (1)
C(12)	4322 (2)	1675 (3)	1124 (5)	88 (2)
C(13)	5795 (2)	4389 (2)	2234 (4)	64 (1)
C(20)	10275 (2)	2828 (2)	−658 (3)	41 (1)
C(21)	10190 (2)	3790 (2)	−889 (3)	49 (1)
C(22)	10939 (2)	4286 (2)	−1483 (4)	56 (1)
C(23)	11782 (2)	3822 (2)	−1846 (4)	60 (1)
C(24)	11885 (2)	2871 (2)	−1584 (4)	63 (1)
C(25)	11144 (2)	2359 (2)	−1005 (3)	54 (1)
O(1)	8752 (1)	2862 (1)	404 (2)	45 (1)
O(4)	8433 (2)	10 (1)	406 (3)	70 (1)
O(5)	6562 (1)	276 (1)	1456 (2)	52 (1)
O(6)	5267 (2)	1554 (1)	2357 (3)	61 (1)
O(7)	5639 (1)	3398 (1)	2279 (2)	57 (1)

parameters; maximum $\Delta/\sigma = 0.040$; goodness of fit $= 0.65$; $\Delta\rho_{max} = 0.15$, $\Delta\rho_{min} = -0.19\,\mathrm{e\,Å^{-3}}$, $w = 1/(\sigma^2 + 0.0053F^2)$. All calculations were performed with SHELXTL-Plus (Sheldrick, 1990) on a Micro-VAX 2000 computer. Atomic scattering factors were obtained from International Tables for X-ray Crystallography (1974, Vol. IV). Figs. 1 and 2 were prepared by SHELXTL-Plus graphics programs. The structure of (I) is shown in Fig. 1, which also shows the atomic numbering. The structure with atomic numbering of (II) is shown in Fig. 2. Atomic coordinates of non-H atoms are given in Table 1.* Bond lengths, angles and selected torsion angles are given in Table 2.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55455 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1008]

Table 2. Bond lengths (Å), bond angles (°) and torsion angles (°)

Compound (I)

O(1)—C(2)	1.362 (3)	O(1)—C(9)	1.375 (3)
O(4)—C(4)	1.234 (3)	O(5)—C(5)	1.353 (4)
O(5)—C(11)	1.427 (4)	O(6)—C(6)	1.382 (4)
O(6)—C(12)	1.425 (4)	O(7)—C(7)	1.360 (3)
O(7)—C(12)	1.448 (4)	C(2)—C(3)	1.338 (4)
C(2)—C(20)	1.470 (4)	C(3)—C(4)	1.442 (4)
C(4)—C(10)	1.475 (4)	C(5)—C(6)	1.377 (4)
C(5)—C(10)	1.428 (4)	C(6)—C(7)	1.391 (4)
C(7)—C(8)	1.364 (4)	C(8)—C(9)	1.394 (4)
C(9)—C(10)	1.403 (4)	C(20)—C(21)	1.382 (4)
C(20)—C(25)	1.400 (5)	C(21)—C(22)	1.389 (5)
C(22)—C(23)	1.380 (7)	C(23)—C(24)	1.363 (6)
C(24)—C(25)	1.385 (5)		

C(2)—O(1)—C(9)	120.4 (2)	C(5)—O(5)—C(11)	119.8 (2)
C(6)—O(6)—C(12)	106.3 (2)	C(7)—O(7)—C(12)	106.2 (2)
O(1)—C(2)—C(3)	120.7 (2)	O(1)—C(2)—C(20)	112.7 (2)
C(3)—C(2)—C(20)	126.6 (3)	C(2)—C(3)—C(4)	123.8 (3)
O(4)—C(4)—C(3)	120.8 (2)	O(4)—C(4)—C(10)	124.5 (3)
C(3)—C(4)—C(10)	114.7 (2)	O(5)—C(5)—C(6)	125.2 (3)
O(5)—C(5)—C(10)	117.8 (2)	C(6)—C(5)—C(10)	117.0 (2)
O(6)—C(6)—C(5)	128.7 (3)	O(6)—C(6)—C(7)	109.3 (2)
C(5)—C(6)—C(7)	122.0 (3)	O(7)—C(7)—C(6)	110.0 (2)
O(7)—C(7)—C(8)	127.0 (3)	C(6)—C(7)—C(8)	123.0 (2)
C(7)—C(8)—C(9)	115.5 (2)	O(1)—C(9)—C(8)	113.9 (2)
O(1)—C(9)—C(10)	122.2 (2)	C(8)—C(9)—C(10)	123.9 (3)
C(4)—C(10)—C(5)	123.3 (2)	C(4)—C(10)—C(9)	118.2 (2)
C(5)—C(10)—C(9)	118.5 (2)	O(6)—C(12)—O(7)	107.3 (2)
C(2)—C(20)—C(21)	121.5 (3)	C(2)—C(20)—C(25)	120.1 (3)
C(21)—C(20)—C(25)	118.4 (3)	C(20)—C(21)—C(22)	120.7 (3)
C(21)—C(22)—C(23)	120.2 (3)	C(22)—C(23)—C(24)	119.7 (4)
C(23)—C(24)—C(25)	120.8 (4)	C(20)—C(25)—C(24)	120.2 (3)

O(1)—C(2)—C(20)—C(21)	5.0 (3)	C(11)—O(5)—C(5)—C(10)	−160.3 (2)

Compound (II)

C(2)—C(3)	1.337 (4)	C(2)—C(20)	1.476 (4)
C(2)—O(1)	1.367 (3)	C(3)—C(4)	1.444 (4)
C(4)—C(10)	1.469 (4)	C(4)—O(4)	1.233 (3)
C(5)—C(6)	1.375 (4)	C(5)—C(10)	1.422 (4)
C(5)—O(5)	1.374 (3)	C(6)—C(7)	1.403 (4)
C(6)—O(6)	1.376 (3)	C(7)—C(8)	1.372 (4)
C(7)—O(7)	1.363 (3)	C(8)—C(9)	1.389 (4)
C(9)—C(10)	1.395 (4)	C(9)—O(1)	1.374 (3)
C(11)—O(5)	1.426 (3)	C(12)—O(6)	1.433 (4)
C(13)—O(7)	1.424 (3)	C(20)—C(21)	1.380 (4)
C(20)—C(25)	1.402 (4)	C(21)—C(22)	1.385 (4)
C(22)—C(23)	1.375 (4)	C(23)—C(24)	1.371 (4)
C(24)—C(25)	1.382 (4)		

C(3)—C(2)—C(20)	126.9 (3)	C(3)—C(2)—O(1)	121.2 (2)
C(20)—C(2)—O(1)	111.8 (2)	C(2)—C(3)—C(4)	123.3 (3)
C(3)—C(4)—C(10)	114.8 (2)	C(3)—C(4)—O(4)	121.4 (3)
C(10)—C(4)—O(4)	123.9 (3)	C(6)—C(5)—C(10)	121.1 (2)
C(6)—C(5)—O(5)	117.8 (2)	C(10)—C(5)—O(5)	121.0 (2)
C(5)—C(6)—C(7)	120.2 (2)	C(5)—C(6)—O(6)	119.8 (2)
C(7)—C(6)—O(6)	120.0 (2)	C(6)—C(7)—C(8)	120.5 (2)
C(6)—C(7)—O(7)	114.9 (2)	C(8)—C(7)—O(7)	124.5 (2)
C(7)—C(8)—C(9)	118.6 (2)	C(8)—C(9)—O(1)	123.5 (2)
C(8)—C(9)—O(1)	113.9 (2)	C(10)—C(9)—O(1)	122.6 (2)
C(4)—C(10)—C(5)	125.4 (2)	C(4)—C(10)—C(9)	118.4 (2)
C(5)—C(10)—C(9)	116.1 (2)	C(2)—C(20)—C(21)	121.2 (2)
C(2)—C(20)—C(25)	119.8 (2)	C(21)—C(20)—C(25)	118.9 (3)
C(20)—C(21)—C(22)	120.8 (3)	C(21)—C(22)—C(23)	120.1 (3)
C(22)—C(23)—C(24)	119.4 (3)	C(23)—C(24)—C(25)	121.5 (3)
C(20)—C(25)—C(24)	119.2 (3)	C(2)—O(1)—C(9)	119.6 (2)
C(5)—O(5)—C(11)	114.5 (2)	C(6)—O(6)—C(12)	113.0 (2)
C(7)—O(7)—C(13)	118.0 (2)		

O(1)—C(2)—C(20)—C(21)	−10.9 (3)	C(10)—C(5)—O(5)—C(11)	81.5 (3)
C(7)—C(6)—O(6)—C(12)	76.2 (3)	C(8)—C(7)—O(7)—C(13)	1.3 (3)

Related literature. For isolation and spectroscopic study of (I) and (II) see Ng (1988) and Ng & Goh (1990). Compound (II) has also been isolated from other plant species (Kutney & Hansson, 1971; Hosozawa, Kato & Munakata, 1972; Pinar, 1973; Panichpol & Waterman, 1978).

We wish to thank the National University of Singapore for financial support.

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Acta Cryst. (1993). C49, 107–109

Structure of 2-[N-(2-Hydroxyethyl)]aminomethyl-3-phenylthioindole

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Abstract. $C_{17}H_{18}N_2OS$, $M_r = 298.4$, orthorhombic, *Pbca*, $a = 36.276\,(7)$, $b = 10.469\,(3)$, $c = 8.229\,(3)$ Å, $V = 3125.2\,(5)$ Å^3, $Z = 8$, $D_x = 1.27$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.73$ mm^{-1}, $F(000) = 1264$, $T = 293$ K, $R = 0.060$, $wR = 0.063$ for 1709 reflections. The indole moiety is planar with the S atom $-0.051\,(1)$ Å out of the plane. The phenyl ring is oriented at an angle of $82.3\,(1)°$ to the indole moiety. The structure is stabilized by an intra- and two intermolecular hydrogen bonds [N—H···O 2.858 (5) Å and O—H···N 2.766 (6) Å].

Experimental. Colourless rectangular needle-shaped crystals were grown by slow evaporation in ethanol. The preliminary details of the crystal were obtained by oscillation and Weissenberg photographs. A crystal with dimensions 0.1 × 0.25 × 0.3 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined from setting angles of 25 reflections having $15 \leq \theta \leq 22°$. Intensity data were collected by $\omega/2\theta$-scan technique using Cu $K\alpha$ radiation between 2 and 130° in 2θ; range in *hkl*: $0 \leq h \leq 42$; $0 \leq k \leq 12$; $0 \leq l \leq 9$. Two standard reflections were monitored after every 200 reflections and showed 2.2% intensity variation for which correction was applied. A total of 2389 reflections were measured of which 1709 reflections with $I \geq 3\sigma(I)$ were used for refinement. The intensities were corrected for background, Lorentz and polarization effects and absorption (maximum/minimum transmission factors 0.987/0.923). The structure was solved by Patterson and difference Fourier synthesis using *SHELXS*86 (Sheldrick, 1986), all the H atoms were located from difference Fourier syntheses. Full-

matrix least-squares refinement for 262 parameters was with anisotropic thermal parameters for the non-H atoms and isotropic for the H atoms using the *SHELX*76 (Sheldrick, 1976) program. Final $R = 0.060$ and $wR = 0.063$, $w = 2.22/[\sigma^2(F) + gF^2]$, where $g = 0.0013$; the refinement terminated when shift/ e.s.d. for non-H atoms was less than 0.002; goodness of fit $S = 1.5$. The maximum and minimum electron densities in the final ΔF map were 0.59 and -0.26 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structural geometry and graphics were obtained using *PARST* (Nardelli, 1983) and *PLUTO* (Motherwell & Clegg, 1978). All calculations were performed on a MicroVAX II computer. The final positional parameters of the non-H atoms with B_{eq} values are given in Table 1.* A perspective view of the molecule with numbering scheme and unit-cell packing are shown in Figs. 1 and 2 respectively. Bond lengths, bond angles, selected torsion angles and the hydrogen-bonding scheme are given in Table 2.

Related literature. The title compound is the key intermediate for the synthesis of tetrahydro-pyrazino[1,2-*a*]indole. The importance of these

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