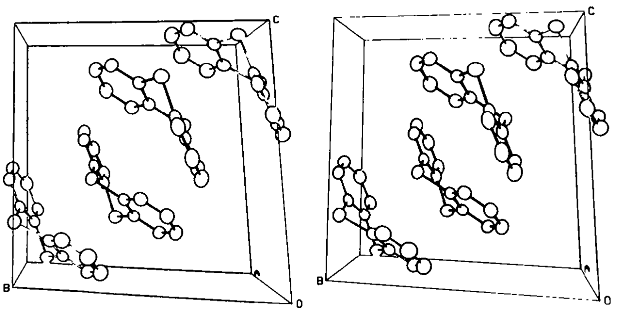

Fig. 3. Stereoview of molecular packing as viewed down the *a* axis.

The packing diagram is found in Fig. 3. One molecule appears to snuggle into the fold of the other independent molecule. The closest non-bonding contacts less than the sum of the van der Waals radii are: $S(10)\cdots H(2)B(2-x,1-y,1-z)$, 3·01 (3); $N(1)\cdots H(6)(1+x,y,z)$, 2·64 (2); $N(4)\cdots H(9)B(x,1+y,z)$, 2·67 (2); $N(1)B\cdots H(6)B(1+x,y,z)$, 2·60 (2); $N(4)B\cdots H(9)(x-1,y,1+z)$, 2·45 (3); $H(7)B\cdots H(7)B(\bar{x},\bar{y},1-z)$, 2·50 (3); $H(7)B\cdots H(8)B$, 2·43 (3); and $H(9)B\cdots H(9)B(1-x,\bar{y},1-z)$, 2·45 (3) Å.

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Structures of Umbelliferone and 7-Ethoxycoumarin

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Abstract. Umbelliferone (U), $C_9H_6O_3$, $M_r = 162\cdot1$, monoclinic, $P2_1/c$, $a = 3\cdot892$ (1), $b = 11\cdot022$ (2), $c = 16\cdot722$ (3) Å, $\beta = 90\cdot58$ (2)°, $V = 717\cdot3$ (3) Å^3, $Z = 4$, $D_m = 1\cdot50$, $D_x = 1\cdot50$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1\cdot114$ mm^{-1}, $F(000) = 336$, $T = 298$ K, $R = 0\cdot042$ for 1255 observed reflexions. 7-Ethoxycoumarin (7-*O*-ethylumbelliferone; U7E), $C_{11}H_{10}O_3$, $M_r = 190\cdot2$, monoclinic, $P2_1/n$, $a = 4\cdot001$ (1), $b = 9\cdot770$ (2), $c = 24\cdot213$ (3) Å, $\beta = 93\cdot12$ (2)°, $V = 945\cdot1$ (3) Å^3, $Z = 4$, $D_m = 1\cdot33$, $D_x = 1\cdot33$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0\cdot934$ mm^{-1}, $F(000) = 400$, $T = 298$ K, $R = 0\cdot041$ for 1691 observed reflexions. The coumarin moiety of U has a different resonance structure from coumarin itself, because the hydroxylation at the 7-position appears to change the resonance system of the coumarin moiety. The plane composed of the O—C—C atoms of the ethoxy group in U7E is approximately coplanar with the mean plane of the coumarin moiety. The torsion angle around the C_{ring}—O_{ethoxy} bond is 2·6 (3)°, and such an 'in-plane' conformation causes the C—O—C angle of the ethoxy group to expand up to 117·7 (1)°.

Introduction. It has been revealed that the structures of 6,7-dihydroxycoumarin (esculetin: E; Ueno & Saito, 1977) and 7,8-dihydroxycoumarin (daphnetin: D; Ueno & Saito, 1976) are well explained in terms of the resonance system as shown in Fig. 1. The glucosidation at the 7-hydroxy group in esculetin (E7G; Ueno, Shiraki, Sato & Saito, 1985) or daphnetin (D7G; Ueno, Sato & Saito, 1983), significantly decreases the contribution of the limiting structure (II), while the glucosidation at the 6-hydroxy group (E6G; Ueno *et al.*, 1985) or 8-hydroxy group (D8G; Ueno, Saito &

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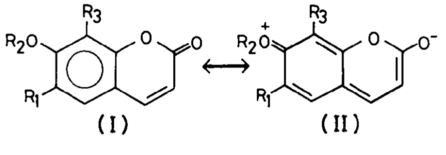
Sato, 1978), has little effect on the conjugation of the coumarin moiety. Such a change in resonance effect has been proposed to play an important role in the enzymatic transglucosidation from E7G to E6G (Sato & Hasegawa, 1972) or D7G to D8G (Sato & Hasegawa, 1971). In order to examine the resonance system more extensively, the crystal structures of 7-hydroxycoumarin (umbelliferone; U) and 7-ethoxycoumarin (U7E) have been determined.

Umbelliferone itself is considered to be the true parent of almost all the naturally occurring coumarins (Dean, 1973), and shows some characteristic properties in its chemical reactions and fluorescent behavior (Beddard, Carlin & Davidson, 1977; Moriya, 1983).

Experimental. Prismatic colorless crystals of U and U7E from aqueous ethanol solutions. D_m by flotation in CH_2Cl_2/CCl_4 (U) and potassium iodide (U7E) solutions. Systematic absences: $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$ (U); and $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$ (U7E). Crystal dimensions 0·36 × 0·18 × 0·10 (U) and 0·40 × 0·22 × 0·12 mm (U7E). Rigaku AFC-4 (U) and Nicolet $P3/F$ (U7E) diffractometers: graphite-monochromated Cu $K\alpha$. Unit-cell parameters refined by least-squares method on the basis of 25 independent 2θ values [$15 < 2\theta < 40$ (U) and $16 < 2\theta < 38°$ (U7E)]. Intensity measurement performed up to $2\theta = 150°$. hkl: 0 to 5, 0 to 13 and −21 to 21 (U), and 0 to 5, 0 to 11 and −30 to 30 (U7E). $\omega/2\theta$ scan. Scan speed 4° min^{-1} (2θ) (U), and variable speed according to prescanned peak intensities from 3 (150 Hz or below) to 8° (3000 Hz or above) min^{-1} (2θ) (U7E). Scan width 1° (ω) plus $\alpha_1 - \alpha_2$ divergence. Background 7 s before and after each scan (U), and adjusted to period of peak scan (U7E). Three standard reflexions monitored every 61 (U) and 200 (U7E) reflexions, no significant decay in intensity. 1626 (U) and 1839 (U7E) reflexions measured, 1255 (U) and 1691 (U7E) intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination. Corrections for Lorentz and polarization. Absorption ignored. Direct method and full-matrix least squares by *SHELX*76 (Sheldrick,1976) with anisotropic thermal parameters for all non-H atoms. H atoms located on a difference map, refined isotropically for U. $\sum w(|F_o| - |F_c|)^2$ minimized with weighting scheme $w = [\sigma^2(F_o) + C(F_o)^2]^{-1}$, where $C = 0{\cdot}0079$ (U) and 0·00232 (U7E). $R = 0{\cdot}042$ (U) and 0·041 (U7E), $wR = 0{\cdot}062$ (U) and 0·055 (U7E), $S = 0{\cdot}853$ (U) and 0·759 (U7E), $(\Delta/\sigma)_{max} = 0{\cdot}2$ (U) and 0·1 (U7E). $\Delta\rho < 0{\cdot}12$ (U) and 0·19 e $Å^{-3}$ (U7E). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on FACOM-HITAC system M-180 computer at this Institute.



	R1	R2	R3
U	H	H	H
U7E	H	Et	H
E	OH	H	H
D	H	H	OH

	R1	R2	R3
E6G	OGl	H	H
E7G	OH	Gl	H
D7G	H	Gl	OH
D8G	H	H	OGl

Fig. 1. Resonance structures of 7-hydroxycoumarins.

Discussion. Atomic parameters are listed in Table 1.* The *ORTEP* (Johnson, 1976) drawings of the molecules with the atom numbering are shown in Fig. 2. Both molecules are nearly planar. Bond distances are listed in Table 2, in which those of coumarin (Gavuzzo, Mazza & Giglio, 1974) are also given for comparison. The C(2)—O(11), C(5)—C(10) and C(6)—C(7) bonds in U are longer than the corresponding ones in coumarin, whereas the C(2)—C(3), C(4)—C(10) and C(8)—C(9) bonds are shorter. This indicates that the hydroxylation at the 7-position brings about the contribution of resonance form (II) shown in Fig. 1. When the 7-hydroxy group is replaced by the ethoxy group as in U7E, C(7)—O(12), C(8)—C(9) and C(4)—C(10) become longer, and C(2)—O(11) becomes shorter than the corresponding ones of U. Their values approach those of coumarin. The contribution of the limiting structure (II) apparently decreases with the ethoxylation at C(7), which was also observed with the glucosidation at the 7-hydroxy group in dihydroxycoumarins, E7G and D7G.

The torsion angle C(6)—C(7)—O(12)—C(13) is 2·6 (3)°. Such an 'in-plane' conformation has been found in E7G and D7G, in which the corresponding angles are 9·9 (8) and 13·8 (3)° respectively. The π electrons of the linking O atom can participate in the resonance of the coumarin moiety. However, the intramolecular repulsion between the coumarin moiety and the ethyl group may increase: As shown in Table 2, the C(7)—O(12)—C(13) angle, 117·7 (1)°, is comparable to 119·6 (6) and 118·5 (2)° in E7G and D7G, respectively, and is significantly larger than that in E6G, 113·7 (7)°, and D8G, 114·4 (2)°. The latter two molecules take the 'out-of-plane' conformation and appear to be released from the intramolecular repulsion. The resonance energy brought about by the 'in-plane' conformation would probably be compensated by the distortion energy due to the intramolecular repulsion.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, equations of best planes and atomic parameters for H atoms of the two crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42422 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The C(3)–C(2)–O(11) and C(4)–C(10)–C(5) angles in U are larger by 10·0 and 7·5° than O(1)–C(2)–O(11) and O(1)–C(9)–C(8), respectively, which is observed in U7E and other coumarins as a common feature. These differences may be due to the intramolecular repulsions between H(C3) and O(11) [separation 2·57 (1) Å] or H(C4) and H(C5) [separation 2·57 (2) Å].

Table 1. *Fractional coordinates and equivalent isotropic temperature factors*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{i,j}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Umbelliferone				
O(1)	0·1658 (3)	0·19726 (10)	0·27477 (7)	3·22 (5)
C(2)	0·0843 (5)	0·25939 (17)	0·20639 (11)	3·25 (5)
C(3)	0·1921 (5)	0·38329 (18)	0·20015 (11)	3·50 (6)
C(4)	0·3640 (5)	0·43689 (17)	0·26041 (11)	3·44 (6)
C(5)	0·6232 (5)	0·42213 (17)	0·39808 (11)	3·52 (7)
C(6)	0·6849 (5)	0·35418 (18)	0·46514 (11)	3·61 (7)
C(7)	0·5792 (5)	0·23330 (17)	0·46836 (11)	3·33 (6)
C(8)	0·4063 (5)	0·18044 (16)	0·40385 (10)	3·14 (6)
C(9)	0·3433 (4)	0·25099 (16)	0·33740 (10)	2·77 (6)
C(10)	0·4464 (4)	0·37213 (16)	0·33177 (10)	2·99 (6)
O(11)	−0·0804 (4)	0·20292 (13)	0·15594 (8)	4·59 (6)
O(12)	0·6378 (4)	0·16319 (15)	0·53332 (8)	4·72 (6)
7-Ethoxycoumarin				
O(1)	−0·05431 (19)	0·37257 (7)	0·22081 (3)	4·49 (3)
C(2)	−0·09917 (26)	0·25393 (10)	0·25071 (4)	4·74 (3)
C(3)	0·01771 (27)	0·12862 (11)	0·22786 (5)	4·94 (3)
C(4)	0·16952 (27)	0·12667 (10)	0·17937 (4)	4·75 (3)
C(5)	0·35891 (26)	0·25934 (10)	0·09716 (4)	4·70 (3)
C(6)	0·37854 (26)	0·38129 (11)	0·06983 (4)	4·73 (3)
C(7)	0·25354 (23)	0·50043 (9)	0·09349 (4)	4·13 (3)
C(8)	0·10932 (22)	0·49733 (9)	0·14448 (3)	4·07 (3)
C(9)	0·09175 (22)	0·37089 (9)	0·17047 (4)	3·82 (3)
C(10)	0·21156 (22)	0·25053 (9)	0·14889 (4)	4·06 (3)
O(11)	−0·23301 (25)	0·26838 (9)	0·29411 (3)	6·51 (3)
O(12)	0·28475 (20)	0·61734 (7)	0·06341 (3)	5·06 (3)
C(13)	0·14832 (27)	0·74042 (11)	0·08473 (4)	4·89 (3)
C(14)	0·19588 (31)	0·85042 (13)	0·04260 (5)	5·88 (3)

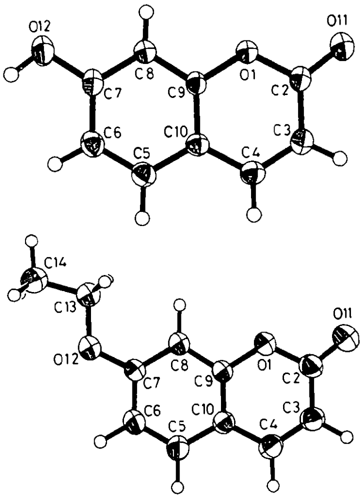

Fig. 2. Perspective drawings of U (upper) and U7E (lower).

Table 2. *Bond distances* (Å) *and angles* (°) *including the e.s.d.'s in parentheses*

	U	U7E	Coumarin (Gavuzzo *et al.*, 1974)
O(1)–C(2)	1·367 (2)	1·383 (1)	1·367 (4)
O(1)–C(9)	1·382 (2)	1·380 (1)	1·378 (4)
C(2)–C(3)	1·433 (3)	1·432 (1)	1·448 (5)
C(2)–O(11)	1·224 (2)	1·213 (1)	1·204 (4)
C(3)–C(4)	1·341 (2)	1·351 (2)	1·344 (5)
C(4)–C(10)	1·424 (2)	1·432 (1)	1·431 (5)
C(5)–C(6)	1·368 (3)	1·367 (1)	1·369 (5)
C(5)–C(10)	1·411 (2)	1·416 (1)	1·390 (5)
C(6)–C(7)	1·396 (3)	1·402 (1)	1·368 (6)
C(7)–C(8)	1·393 (2)	1·391 (1)	1·391 (5)
C(7)–O(12)	1·351 (2)	1·364 (1)	
C(8)–C(9)	1·376 (2)	1·390 (1)	1·383 (5)
C(9)–C(10)	1·398 (2)	1·383 (1)	1·395 (4)
O(12)–C(13)		1·429 (1)	
C(13)–C(14)		1·501 (2)	

	U	U7E
C(2)–O(1)–C(9)	121·9 (1)	121·7 (1)
O(1)–C(2)–C(3)	118·2 (2)	117·4 (1)
O(1)–C(2)–O(11)	115·9 (2)	115·6 (1)
C(3)–C(2)–O(11)	125·9 (2)	127·1 (1)
C(2)–C(3)–C(4)	120·6 (2)	121·3 (1)
C(3)–C(4)–C(10)	121·0 (2)	120·5 (1)
C(6)–C(5)–C(10)	120·7 (2)	121·3 (1)
C(5)–C(6)–C(7)	120·3 (2)	119·7 (1)
C(6)–C(7)–C(8)	120·6 (2)	121·3 (1)
C(6)–C(7)–O(12)	122·0 (2)	115·6 (1)
C(8)–C(7)–O(12)	117·4 (2)	123·1 (1)
C(7)–C(8)–C(9)	118·0 (2)	117·1 (1)
O(1)–C(9)–C(8)	117·0 (2)	115·1 (1)
O(1)–C(9)–C(10)	120·0 (1)	121·1 (1)
C(8)–C(9)–C(10)	123·0 (2)	123·9 (1)
C(4)–C(10)–C(5)	124·5 (2)	125·0 (1)
C(4)–C(10)–C(9)	118·2 (2)	118·1 (1)
C(5)–C(10)–C(9)	117·3 (2)	116·9 (1)
C(7)–O(12)–C(13)		117·7 (1)
O(12)–C(13)–C(14)		107·0 (1)

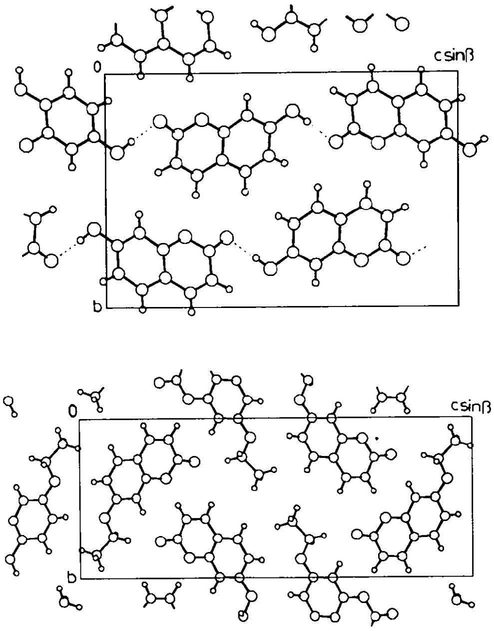

Fig. 3. The crystal structures of U (upper) and U7E (lower). The hydrogen bonds in U are indicated by broken lines.

The crystal structures viewed along each *a* axis are shown in Fig. 3. In both crystals the coumarin moieties are stacked along the *a* axes. In U, the hydrogen bond O(12)—H···O(11) forms a ribbon along the *c* axis. The O(12)···O(11) distance and O(12)—H···O(11) angle are 2·746 (2) Å and 175 (1)° respectively.

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Structure of 3-Phenyl-4-(1-phenylethyl)-5-(2-thienyl)-4,5-dihydro-1,2,4-oxadiazole

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Abstract. $C_{20}H_{18}N_2OS$, $M_r = 334{\cdot}4$, monoclinic, $P2_1/n$, $a = 8{\cdot}84\ (1)$, $b = 12{\cdot}235\ (1)$, $c = 15{\cdot}903\ (3)$ Å, $\beta = 91{\cdot}90\ (5)^\circ$, $V = 1719\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}29$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}872$ cm^{-1}, $F(000) = 704$, $T = 290$ K, $R = 0{\cdot}052$ for 1750 observed reflexions. The configuration of the title compound has been established. Bond lengths and angles are normal. The dihydrooxadiazole ring is not planar, maximum deviation 0·098 (4) Å from the least-squares plane.

Introduction. The title compound has been prepared and studied by spectroscopy by Arjona, Plumet, Ossorio & Carreiro (1985).

In order to establish unequivocally the configuration of this compound, which was difficult to resolve by conventional techniques such as ^{1}H NMR and ^{13}C NMR spectroscopy, its crystal structure has been determined.

Experimental. Colourless, prismatic crystal 0·4 × 0·2 × 0·6 mm. Enraf–Nonius CAD-4*F* automatic diffractometer; cell dimensions refined by least-squares fitting of θ values of 25 reflexions; intensities of 3742 unique reflexions, $1 < \theta < 27^\circ$, *hkl* −11,0,0 to 11,15,20, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans; three reflexions monitored periodically during data collection showed no crystal decomposition; intensities corrected for Lorentz and polarization effects; 1750 considered observed $[I > 2\sigma(I)]$. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Structure solved with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977); best *E* map revealed all non-H atoms. An empirical absorption correction (Walker & Stuart, 1983) was applied at the end of the isotropic refinement; anisotropic full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized; unit weights; a difference synthesis calculated with reflexions having $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1} showed all H atoms as highest peaks; final refinement with fixed isotropic temperature factors for H atoms led to $R = 0{\cdot}052$; max. and average Δ/σ in final LS cycle 0·018 and 0·005; final difference synthesis had no electron density $>0{\cdot}21$ or $<-0{\cdot}18$ e Å^{-3}. No correction for secondary extinction. Most of the calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Least-squares planes computed with *PARST*5 (Nardelli, Musatti, Domiano & Andreetti, 1965).

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