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Esculetin; 6,7-Dihydroxycoumarin

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Abstract. $C_9H_6O_4$, monoclinic, $P2_1/c$, $a = 8{\cdot}277(1)$, $b = 6{\cdot}884(1)$, $c = 13{\cdot}248(1)$ Å, $\beta = 103{\cdot}61(2)°$, $Z = 4$, $M_r = 178{\cdot}2$, $D_m = 1{\cdot}60$, $D_x = 1{\cdot}61$ g cm^{-3}, $R = 0{\cdot}038$ for 1055 observed reflexions. The molecules are nearly planar and stacked along the b axis.

Introduction. As part of a study on the specificity of enzymes isolated from flowers of *Daphne odora* and *Cichorium intybus* and which show high substrate specificity for hydrolysis and transglucosidation of dihydroxycoumarin glucosides (Satô & Hasegawa, 1971, 1972), the structure of daphnetin (7,8-dihydroxycoumarin) has already been determined (Ueno & Saito, 1976). The present paper deals with the structure of a compound isolated from *C. intybus*.

Crystals were prepared by slow evaporation from aqueous ethanol solution. They were colourless needles elongated along the b axis. Weissenberg photographs showed that they are monoclinic, space group $P2_1/c$, from the systematic absences $h0l$ for l odd and $0k0$ for k odd. The density was measured by flotation in a mixture of n-hexane and carbon tetrachloride. The X-ray diffraction data were obtained on a Rigaku four-circle diffractometer using Cu $K\alpha$ radiation monochromatized with graphite. A crystal of dimensions $0{\cdot}1 \times 0{\cdot}2 \times 0{\cdot}05$ mm was used. The lattice constants were obtained by a least-squares fit of the 2θ angles of 25 reflexions. Intensity data were collected by the $2\theta/\omega$ scan method with a scan rate and range of 4° (2θ) min^{-1} and $(1{\cdot}0 + 0{\cdot}5\tan\theta)°$ respectively. Background counts were measured for 10 s at the beginning and end of each scan. The reflexions with $|F_o| < 20\sigma(|F_o|)$ were measured repeatedly up to three times and the accumulated counts were used. Of 1416 independent reflexions measured, 1055 were greater than $3\sigma(|F_o|)$. No correction was made for absorption ($\mu = 12{\cdot}72$ cm^{-1}).

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) using 152 reflexions with $|E| \geq 1{\cdot}40$. Block-diagonal-matrix least-squares refinement reduced R to 0·07. A difference Fourier synthesis at this stage revealed all the H atoms. After

Table 1. *Fractional atomic coordinates and thermal parameters*

The coordinates and thermal parameters of the non-hydrogen atoms have been multiplied by 10^4. The form of the anisotropic thermal factor is $\exp[(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl) \times 10^{-4}]$. Estimated standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	8287 (2)	1480 (2)	7869 (1)	73 (2)	206 (4)	23 (1)	−16 (5)	19 (2)	−26 (3)
C(2)	6672 (3)	979 (4)	7777 (2)	68 (3)	158 (5)	36 (1)	20 (6)	11 (3)	−17 (4)
C(3)	6019 (3)	1068 (4)	8683 (2)	73 (3)	185 (5)	37 (1)	−10 (7)	29 (3)	−12 (4)
C(4)	7001 (3)	1565 (4)	9612 (2)	78 (3)	147 (5)	34 (1)	−2 (6)	38 (3)	−1 (4)
C(5)	9813 (3)	2577 (3)	10649 (2)	85 (3)	133 (5)	24 (1)	6 (6)	30 (3)	2 (4)
C(6)	11415 (3)	3102 (3)	10666 (2)	73 (3)	123 (5)	24 (1)	15 (5)	15 (3)	1 (4)
C(7)	11956 (3)	3143 (3)	9734 (2)	65 (3)	125 (5)	29 (1)	0 (5)	27 (3)	10 (3)
C(8)	10914 (3)	2575 (3)	8805 (2)	80 (3)	156 (5)	26 (1)	1 (7)	37 (3)	2 (4)
C(9)	9310 (3)	2040 (3)	8813 (2)	70 (3)	130 (5)	24 (1)	11 (6)	11 (3)	−6 (4)
C(10)	8706 (3)	2050 (3)	9708 (2)	69 (3)	106 (4)	28 (1)	14 (5)	24 (3)	4 (4)
O(2)	5883 (2)	519 (3)	6905 (1)	81 (2)	301 (5)	33 (1)	19 (6)	−2 (2)	−68 (4)
O(6)	12469 (2)	3606 (3)	11586 (1)	80 (2)	238 (4)	24 (1)	−34 (5)	8 (2)	−16 (3)
O(7)	13544 (2)	3753 (3)	9826 (1)	70 (2)	230 (4)	34 (1)	−57 (5)	30 (2)	3 (3)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(C3)	0·482 (3)	0·073 (4)	0·859 (2)	1·1 (5)	H(O6)	1·337 (4)	0·395 (5)	1·144 (2)	2·0 (6)
H(C4)	0·656 (3)	0·163 (4)	1·024 (2)	1·1 (5)	H(O7)	1·371 (4)	0·420 (5)	0·922 (2)	2·3 (7)
H(C5)	0·937 (3)	0·257 (4)	1·129 (2)	1·2 (5)	H(C8)	1·133 (3)	0·258 (4)	0·817 (2)	1·1 (5)

eight cycles of full-matrix refinement including H atoms R was reduced to 0·038. The final weighting scheme was $w = |F_o|/F_{\min}$ if $|F_o| < F_{\min}$, $w = F_{\max}/|F_o|$ if $|F_o| \geq F_{\max}$ and $w = 1{\cdot}0$ if $F_{\min} \leq |F_o| < F_{\max}$ where $F_{\min} = 4{\cdot}0$ and $F_{\max} = 20{\cdot}0$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1.*

Discussion. The bond lengths and angles are shown in Fig. 1. The molecular structure is close to that of daphnetin (Ueno & Saito, 1976). The coumarin ring is planar within ±0·04 Å. O(7) deviates by 0·11 Å from this plane, probably because of the hydrogen bonding. In the aromatic ring, C(5)–C(6) is shorter than C(5)–C(10) and C(6)–C(7), and the bond length C(8)–C(9) is somewhat shorter than C(7)–C(8) and C(9)–C(10). In the heterocyclic ring the C(2)=O(2) and C(3)=C(4) double bonds are longer than in coumarin (1·204, 1·344 Å; Gavuzzo, Mazza & Giglio, 1974), amyrolin (1·210, 1·320 Å; Kato, 1970) and xanthotoxin (1·198, 1·338 Å; Stemple & Watson, 1972); on the other hand, C(2)–C(3) and C(4)–C(10) are somewhat shorter than the corresponding values in these compounds (1·448, 1·431, 1·439, 1·443 and 1·441, 1·443 Å respectively). These, together with the fact that C(7)–O(7) is somewhat shorter than C(6)–O(6), indicate some tautomerism (Dean, 1963; Yakatan, Juneau & Schulman, 1972).

The crystal structure viewed along the b axis is shown in Fig. 2, and along the a axis in Fig. 3. There are two intermolecular hydrogen bonds, O(6)–H···O(2) and O(7)–H···O(2) (see Table 2, which also includes other short intermolecular contacts less than 3·3 Å). The molecules are stacked along the b axis in a similar manner to those in avicennin (Lai & Marsh, 1974). The stacking distances are 3·23 and 3·33 Å, which are comparable to values for other substituted coumarins (Shimizu, Kashino & Haisa, 1975). The hydrogen bond O(7)–O(2) forms chains along the screw axis which are linked by the hydrogen bond O(6)–O(2) to form an infinite ribbon parallel to (10$\bar{2}$). These ribbons engage each other and are connected along the c axis.

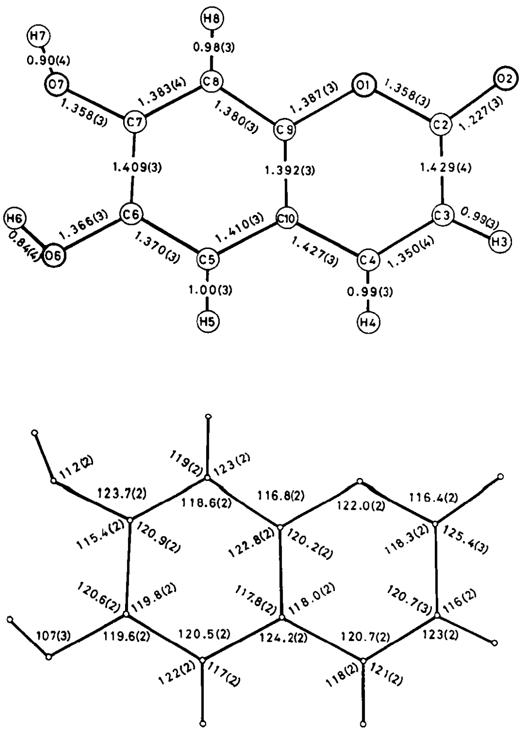

Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

Table 2. *Hydrogen bonds and other short intermolecular contacts less than* 3·3 Å

Hydrogen bonds

Donor atom (D)	Acceptor atom (A)	$D\cdots A$ (Å)	H$\cdots A$ (Å)	∠O–H···O (°)
O(6)	O(2)$^{\rm i}$	2·833	2·06	151
O(7)	O(2)$^{\rm ii}$	2·734	1·84	172

Other short intermolecular contacts (Å)

O(7)···O(2)$^{\rm i}$	3·015
C(5)···C(9)$^{\rm iii}$	3·300
C(2)···O(6)$^{\rm iii}$	3·300

Symmetry code: (i) $1+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (ii) $2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (iii) $2-x$, $-y$, $2-z$.

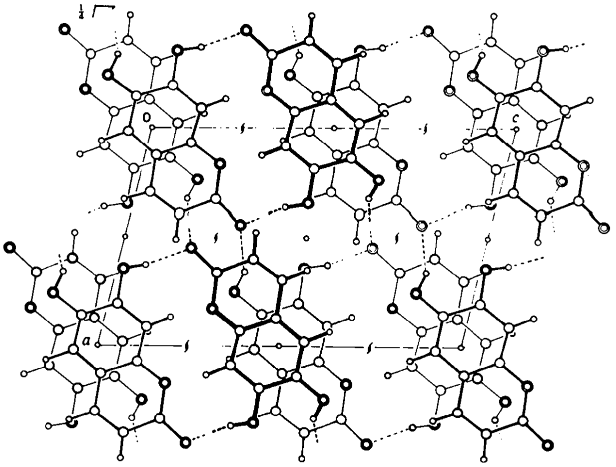

Fig. 2. The crystal structure viewed along the b axis. The hydrogen bonds are represented by broken lines.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32104 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

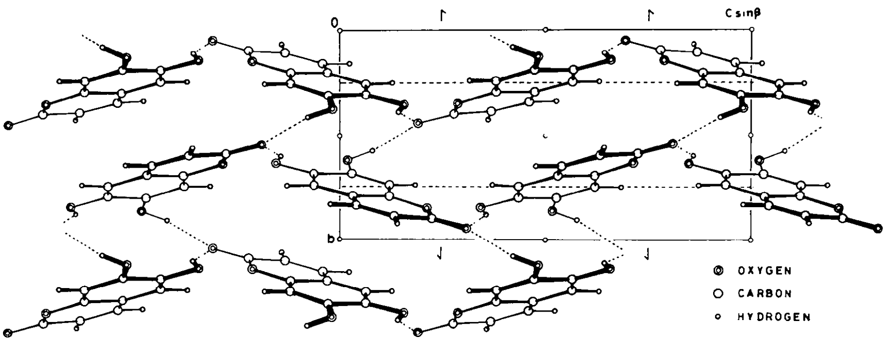

Fig. 3. The crystal structure viewed along the *a* axis.

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L'orthothiophosphate de Chrome

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Abstract. $CrPS_4$, monoclinic, space group $B2/m$; $a = 10{\cdot}859\,(5)$, $b = 6{\cdot}128\,(3)$, $c = 7{\cdot}244\,(4)$ Å, $\gamma = 91{\cdot}90\,(5)°$; $Z = 4$. The structure was refined by least squares from single-crystal diffractometer data (656 independent reflexions) to a final R value of 0·036. The layered structure is developed parallel to the (010) plane and consists of octahedral units of CrS_6 connected to slightly distorted tetrahedral PS_4 units. The mean bond lengths are Cr–S 2·42 and P–S 2·05 Å.

Introduction. $CrPS_4$ a été préparé à partir des éléments. Dans la méthode utilisée, chrome, phosphore et soufre, pris en proportions calculées, sont placés dans une ampoule de silice scellée sous vide; on maintient la température vers 400 °C jusqu'à absorption complète du soufre, puis on porte à 700 °C pendant deux semaines et on refroidit lentement jusqu'à la température ambiante. Le produit ainsi obtenu contient des cristaux noirs de forme lamellaire qui se clivent très facilement en de nombreux feuillets. Nous avons d'abord vérifié, par analyse à la microsonde électronique, que le cristal étudié contient bien les éléments chrome, phosphore et soufre, dans des proportions compatibles, aux erreurs d'experiences près, avec la formule $CrPS_4$.

Le cristal utilisé mesure approximativement 160 × 120 × 25 μm. Les diagrammes de cristal tournant et de Weissenberg, réalisés en l'irradiant avec le rayonne-