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Daphnetin, Isolated from *Daphne odora*

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Abstract. $C_9H_6O_4.\frac{1}{2}H_2O$, orthorhombic, $Fdd2$, a = 22·990 (6), b = 36·609 (7), c = 3·711 (1) Å, Z = 16, D_x = 1·60, D_m = 1·58 g cm^{-3}, F.W. 187·2. R = 0·037 for 761 observed reflexions. The molecules are nearly planar and stacked along (001). A three-dimensional net is built up through the hydrogen bonds between two hydroxyl groups, one carbonyl group and one water molecule.

Introduction. Crystals were prepared by slow evaporation from an aqueous ethanol solution. They were colourless needles elongated along the c axis. The absences of hkl reflexions for $h+k$, $k+l$, $l+h=2n+1$, $0kl$ for $k+l=4n+1,2,3$ and $h0l$ for $h+l=4n+1,2,3$ indicate that the space group is $Fdd2$. The density was measured by flotation in a mixture of n-hexane and carbon tetrachloride. The X-ray data were collected on a Rigaku computer-controlled four-circle diffractometer. A crystal of dimensions 0·1 × 0·05 × 0·5 mm was used.

The lattice constants were obtained by least-squares refinement of the 2θ angles of 25 reflexions. Intensity data were collected by the $2\theta/\omega$ scan method to a maximum value of $2\theta = 153°$ with Cu $K\alpha$ radiation monochromatized with graphite. The scan rate was 2° min^{-1} in 2θ. Stationary background counts were measured for 20 s on each side of the diffraction peak. Of the 836 independent reflexions measured, 761 were greater than $3\sigma(F_o)$. No correction was made for absorption (μ = 12·9 cm^{-1}).

The structure was solved by inspection of the Patterson map. The initial trial structure gave an R of 0·39. Isotropic block-diagonal matrix least-squares refinement reduced the R to 0·16, and the difference synthesis at this stage revealed the water of crystallization and all hydrogen atoms. In subsequent refinements with anisotropic temperature factors for non-hydrogen atoms, all the hydrogen atoms were included, their positions and individual isotropic temperature factors being allowed to shift. The final R value was 0·037 for the observed reflexions. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are given in Table 1.*

Discussion. In the studies of the biosynthesis of courins, Sato & Hasegawa (1969, 1971, 1972) have remacently found a new enzyme from two plants which shows a high substrate specificity for the hydrolysis and transglucosylation of coumarin glucosides. In order to elucidate the nature of the specificity, the authors are seeking more detailed information on the structure of the substrates and products.

Table 1. *Fractional atomic coordinates and thermal parameters* (× 10^3)

The form of the anisotropic thermal factor is exp $(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$. Estimated standard deviations are in parentheses.

	$x(\times 10^5)$	$y(\times 10^5)$	$z(\times 10^4)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	14652 (8)	13056 (5)	1800 (8)	1·18 (4)	0·30 (1)	70 (2)	−0·04 (4)	4·3 (5)	−0·9 (3)
C(2)	12043 (13)	9731 (7)	2207 (12)	1·48 (6)	0·40 (2)	70 (3)	−0·33 (5)	0·9 (9)	−0·6 (5)
C(3)	6302 (14)	9655 (8)	3726 (12)	1·50(7)	0·53 (2)	87 (4)	−0·46 (6)	3·9 (9)	−0·6 (6)
C(4)	3482 (13)	12733 (8)	4599 (12)	1·26 (5)	0·64 (2)	67 (3)	−0·32 (6)	4·3 (8)	−0·2 (6)
C(5)	3524 (12)	19575 (8)	4880 (11)	1·07 (5)	0·63 (2)	60 (3)	0·20 (6)	2·2 (7)	−0·0 (6)
C(6)	6480 (12)	22801 (8)	4352 (11)	1·29 (6)	0·53 (2)	58 (3)	0·51 (6)	−0·8 (8)	−2·5 (5)
C(7)	12121 (12)	22735 (7)	2927 (11)	1·25 (5)	0·37 (3)	53 (3)	0·01 (5)	−1·6 (7)	−0·5 (4)
C(8)	14848 (12)	19462 (7)	2065 (10)	0·97 (5)	0·41 (2)	48 (2)	0·12 (5)	0·9 (7)	−0·5 (4)
C(9)	11796 (12)	16261 (7)	2683 (10)	1·07 (5)	0·37 (2)	46 (3)	0·06 (5)	0·8 (7)	−1·7 (5)
C(10)	6176 (12)	16229 (7)	4075 (10)	1·09 (6)	0·51 (2)	43 (3)	−0·06 (5)	1·1 (7)	−1·1 (4)
O(2)	14944 (9)	7123 (5)	1240 (9)	1·66 (5)	0·36 (1)	121 (3)	−0·15 (4)	7·2 (7)	−2·4 (4)
O(7)	15278 (8)	25842 (5)	2347 (9)	1·39 (4)	0·33 (1)	91 (2)	0·13 (4)	1·6 (6)	−0·3 (4)
O(8)	20350 (8)	19265 (5)	731 (8)	1·02 (3)	0·38 (2)	86 (2)	0·03 (4)	6·4 (6)	0·7 (4)
O(*W*)	25000	25000	6963 (13)	1·29 (6)	0·44 (2)	77 (3)	−0·14 (5)	0	0

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31530 (4 pp.). Copies can be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 (*cont.*)

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^2$)	B (Å^2)
H(3)	42 (2)	72 (1)	40 (1)	3·4 (10)
H(4)	−6 (2)	126 (1)	58 (1)	3·2 (10)
H(5)	−7 (2)	195 (1)	61 (1)	2·6 (9)
H(6)	43 (1)	252 (1)	49 (1)	0·8 (6)
H(7)	131 (2)	280 (1)	28 (1)	2·6 (9)
H(8)	217 (2)	217 (1)	−1 (2)	3·7 (10)
H(*W*)	216 (2)	357 (1)	55 (2)	5·5(10)

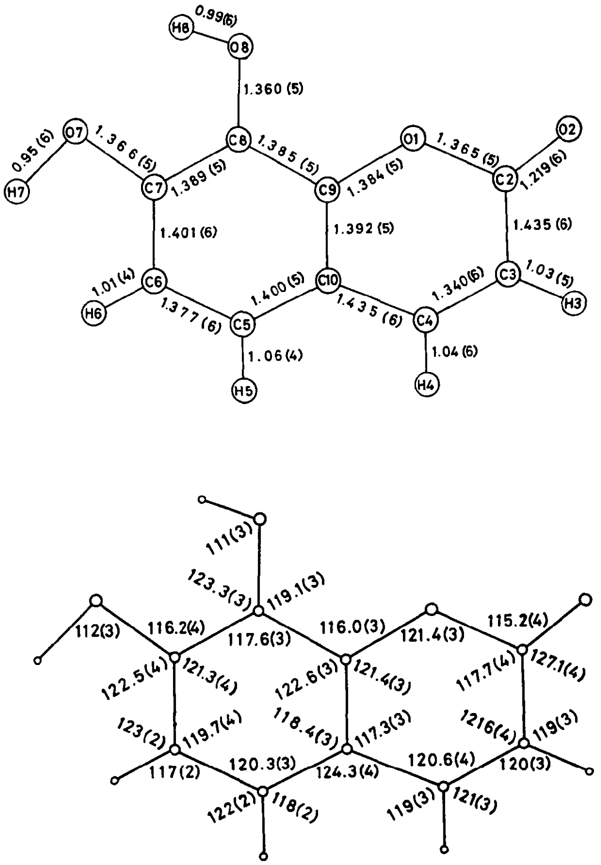

Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

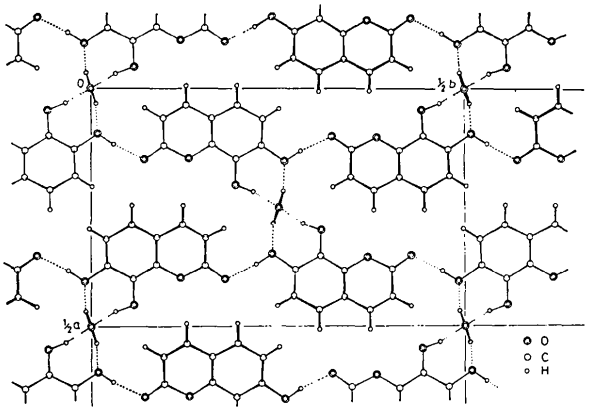

Fig. 2. The crystal structure viewed along the c axis. The hydrogen bonds are represented by broken lines.

Fig. 1 shows the bond lengths and angles in daphnetin with estimated standard deviations. In the aromatic ring, the bond lengths agree with the normally accepted value except for C(5)–C(6). On the other hand, the bond angles C(7)–C(8)–C(9) and C(8)–C(7)–O(7) are small, and C(8)–C(9)–C(10) is somewhat large. In the heterocyclic ring, the C–O bond lengths are identical with those in coumarin (1·379, 1·366 Å; Myasnikova, Davydova & Simonov, 1973), in xanthotoxin (1·383, 1·371 Å; Stemple & Watson, 1972) and in 4-methylumbelliferone (1·383, 1·363 Å; Shimizu, Kashino & Haisa, 1975). C(2)–C(3) and C(4)–C(10) are somewhat short. These distances may indicate conjugation along this chain of atoms. The molecule is nearly planar within the largest deviation of 0·035 Å [O(2) atom].

Water molecules, located on a twofold axis, are hydrogen bonded with hydroxyl groups, O(7) and O(8). Intermolecular distances less than 3·4 Å are given in Table 2. All the hydrogen bonds are indicated with broken lines in Fig. 2 and also listed in Table 2.

The hydrogen bond O(7)···O(2) forms an infinite chain along the b axis, and hydrogen bonds O(W)···O(7) and O(8)···O(W) also form a chain along the c axis.

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Table 2. *Hydrogen bond distances* (Å) *and angles* (°) *and shortest intermolecular contacts less than* 3·4 Å

Donor atom Acceptor atom	Position of acceptor atom	$D\cdots A$	$H\cdots A$	O–H···O
O(W)···O(7)	$x,\ y,\ z$	2·833	1·86	167
O(8)····O(W)	$x,\ y,\ -1+z$	2·740	1·80	157
O(7)····O(2)	$\frac{1}{4}-x,\ \frac{1}{4}+y,\ \frac{1}{4}+z$	2·645	1·70	173
Other shortest intermolecular contacts				
O(8)···O(W)	$x,\ y,\ z$	3·301		
O(7)···O(W)	$x,\ y,\ -1+z$	3·014		
O(8)···C(3)	$\frac{1}{4}+x,\ \frac{1}{4}-y,\ -\frac{3}{4}+z$	3·346		

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Hydrazinium(1+) Tetrafluoroaquoindate(III)

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Abstract. $N_2H_5[InF_4H_2O]$, orthorhombic, $P2_12_12_1$, $a=6{\cdot}768\ (2)$, $b=8{\cdot}632\ (2)$, $c=9{\cdot}249\ (2)$ Å, $Z=4$, $D_m=2{\cdot}99$, $D_c=2{\cdot}97$ g cm^{-3}, $V=540{\cdot}339$ Å^3, Mo $K\alpha$ ($\mu=43{\cdot}98$ cm^{-1}). Indium atoms are in pentagonal bipyramidal coordination with six fluorine atoms and one oxygen atom. The bipyramids share their edges to form chains which are linked by hydrogen bonds.

Introduction. There are a number of fluorometallate(III) hydrates known in the literature, with the stoichiometries $M^{I}_2M^{III}F_5.H_2O$ and $M^{I}M^{III}F_4.2H_2O$. However, the only crystallographic studies reported are for $K_2AlF_5.H_2O$ (Brosset, 1942), $K_2MnF_5.H_2O$ (Edwards, 1971) and $K_2FeF_5.H_2O$ (Edwards, 1972). In the first two compounds there are octahedrally coordinated anions linked through *trans*-bridging fluorine atoms and separate water molecules. In the last case the structure consists of isolated $[FeF_5.H_2O]^{2-}$ anions.

In our first report dealing with fluorometallates(III) (Šiftar & Bukovec, 1970) we described the compound $N_2H_5[InF_4.H_2O]$. As there are no complete crystal structures known for fluoroindates and because of the unusual stoichiometry of our compound, we decided to investigate it by means of single-crystal X-ray diffraction.

Crystals of hydrazinium(1+) tetrafluoroaquoindate(III) were obtained in the form of colourless needles by isothermal evaporation of an aqueous solution containing equivalent quantities of indium trifluoride and hydrazinium(1+) fluoride.

Unit-cell dimensions were determined from $h0l$ and $hk0$ Weissenberg photographs calibrated with superimposed Al ($a_0=4{\cdot}04907$ Å) powder lines, using Cu $K\alpha_1$ radiation. Systematic absences, $h00$ with h odd, $0k0$ with k odd and $00l$ with l odd indicated the orthorhombic space group $P2_12_12_1$. The crystal density was measured by the flotation method in a mixture of methylene iodide and bromoform.

The intensities were collected on an Enraf–Nonius CAD-4 single-crystal automatic diffractometer, equipped with a graphite monochromator and Mo $K\alpha$ radiation. ω–2θ scan was used in the sphere with $\theta \leq 45°$. A spherical crystal with a diameter of 0·2 mm was used for intensity measurements. A total of 5061 reflexions were collected from the hkl and $\bar{h}\bar{k}\bar{l}$ octants and were merged into a unique set of 2525 reflexions. Of these 2315 were observed and 210 were unobserved (less than $3\sigma(I_o)$ above background). Structure amplitudes were derived by application of Lorentz, polarization and absorption ($\mu=0{\cdot}88$) corrections.

The position of the indium atom was obtained from a three-dimensional Patterson function. The positions of all non-hydrogen atoms were located by Fourier synthesis. All atomic positions, together with individual isotropic temperature factors were refined by a number of least-squares cycles with all the collected data included to $R=0{\cdot}071$. The structure was then refined with anisotropic temperature factors to $R=0{\cdot}019$. Hy-

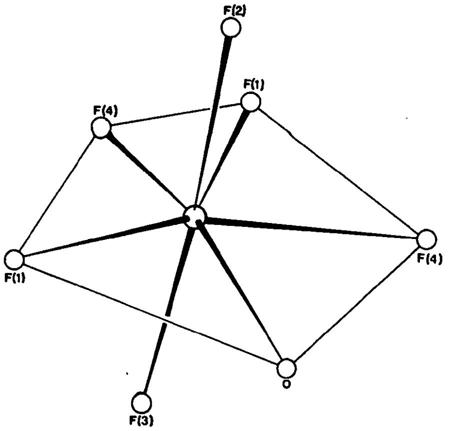

Fig. 1. Coordination polyhedron of indium.