

5,7,4'-Trimethoxyflavanone

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Abstract. C₁₈H₁₈O₅, $M_r = 314.1$, orthorhombic, $P2_12_12_1$, $a = 8.844$ (2), $b = 28.96$ (7), $c = 6.156$ (1) Å, $V = 1576.7$ Å³, $Z = 4$, $D_c = 1.32$, $D_o = 1.32$ g cm⁻³. The structure was solved by direct methods with Cu $K\alpha$ radiation and X-ray diffractometer intensities, and refined to $R = 5.0\%$ for 682 observed reflexions. The compound is a natural flavanone. The γ -pyrone ring adopts the sofa conformation.

Introduction. The compound was isolated by Kaufmann & Lam (1967) from the leaves and stems of *Dahlia lehmanni* Hieron. Apparently, this compound has not previously been isolated from any natural source but is known as a synthetic product.

A crystal $0.2 \times 0.2 \times 0.4$ mm was mounted along c . Weissenberg and precession photographs showed orthorhombic symmetry and systematic absences $h00$ where $h = 2n + 1$, $0k0$ where $k = 2n + 1$ and $00l$ where $l = 2n + 1$. Hence, the space group is $P2_12_12_1$. Cell dimensions were obtained by least squares from the setting angles of 12 reflexions centered on a Picker computer-controlled four-circle diffractometer. A graphite monochromator was employed to select Cu $K\alpha$ radiation. A scintillation counter in conjunction with a pulse-height analyzer was used. All reflexions hkl with $l \geq 0$ and $2\theta \leq 90^\circ$ were measured with the θ - 2θ scan mode, a scan rate of 1° min^{-1} and a scan width of $(1.0 + 0.692 \tan \theta)^\circ$. The background was measured for 20 s at each end of the scan range. The intensities of three standard reflexions were measured every 30 reflexions. No significant trends were observed. Intensities (I) were assigned standard deviations [$\sigma_s(I)$] according to counting statistics. The intensities were corrected for Lorentz and polarization effects but not for absorption [$\mu(\text{Cu } K\alpha) = 7.2 \text{ cm}^{-1}$]. Of the 831 independent reflexions, 682 were considered observed by the criterion $F_o^2 \geq 2\sigma_s(F_o^2)$.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Sets of phases for the 272 reflexions with $E > 1.0$ were generated. With the phases from the set with the highest combined figure of merit an E map was obtained which showed the 23 highest peaks in chemically sensible positions.

Full-matrix least-squares refinement (*LINUS*, Cop-

pens & Hamilton, 1970), initially with isotropic and finally anisotropic thermal parameters for all non-hydrogen atoms, gave $R = 9.0\%$. The 18 H atoms were located from a difference map. Refinement was continued including all atoms. For the heavy atoms anisotropic temperature factors were used; isotropic

Table 1. Final atomic coordinates ($\times 10^4$ for C and O; $\times 10^3$ for H) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(2)	5993 (9)	3333 (4)	8531 (15)
C(3)	4819 (10)	3675 (4)	9214 (18)
C(4)	4565 (9)	4034 (4)	7485 (19)
C(5)	5796 (10)	4452 (3)	4347 (17)
C(6)	7050 (10)	4554 (4)	3173 (17)
C(7)	8408 (9)	4304 (4)	3640 (19)
C(8)	8508 (9)	4003 (4)	5281 (19)
C(9)	7190 (9)	3901 (4)	6425 (17)
C(10)	5870 (4)	4117 (4)	6064 (5)
C(11)	7998 (12)	1916 (5)	16178 (21)
C(12)	4353 (12)	5006 (4)	2360 (22)
C(13)	10973 (10)	4174 (4)	2471 (26)
C(1')	6308 (9)	2982 (5)	10193 (16)
C(2')	7206 (10)	3061 (4)	11993 (20)
C(3')	7428 (11)	2703 (6)	13579 (20)
C(4')	6740 (12)	2286 (4)	13314 (19)
C(5')	5829 (13)	2217 (5)	11539 (20)
C(6')	5662 (12)	2553 (5)	10040 (21)
O(1)	7370 (6)	3560 (3)	7963 (10)
O(2)	3322 (8)	4218 (9)	7380 (14)
O(3)	6878 (8)	1903 (3)	14714 (16)
O(4)	4434 (6)	4644 (9)	3951 (13)
O(5)	9556 (7)	4432 (3)	2276 (15)
H(C2)	568 (8)	327 (2)	741 (13)
H(C3,1)	500 (11)	386 (3)	1032 (19)
H(C3,2)	395 (7)	361 (2)	973 (13)
H(C6)	706 (7)	480 (2)	201 (13)
H(C8)	895 (7)	376 (2)	542 (11)
H(C11,1)	814 (9)	167 (2)	1723 (18)
H(C11,2)	777 (10)	213 (3)	1696 (18)
H(C11,3)	911 (4)	172 (1)	1537 (8)
H(C12,1)	315 (5)	517 (1)	279 (9)
H(C12,2)	462 (8)	483 (2)	101 (14)
H(C12,3)	504 (10)	525 (3)	274 (18)
H(C13,1)	1169 (13)	417 (3)	147 (19)
H(C13,2)	1029 (11)	439 (3)	319 (21)
H(C13,3)	1055 (8)	387 (2)	288 (12)
H(C2')	770 (7)	336 (2)	1218 (11)
H(C3')	799 (5)	283 (2)	1445 (9)
H(C5')	529 (5)	191 (1)	1141 (8)
H(C6')	491 (11)	252 (3)	902 (19)

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temperature factors were assigned to the H atoms. An isotropic extinction correction was employed; the value for the isotropic extinction coefficient was $6.9(4) \times 10^{-7}$ with \bar{r} assumed to be unity; the minimum value of $F_o/F_o(\text{corr})$ was 0.72.

Weights were chosen as $w = 1/\sigma^2(F_o)$ with $\sigma(F_o) = [\sigma_s(F_o^2) + 1.03F_o^2]^{1/2} - |F_o|$. A final difference map showed no significant features, establishing that the refinement was complete. The scattering factors were those of Cromer & Mann (1968) for the heavy atoms, and of Stewart, Davidson & Simpson (1965) for H. The final atomic positions are given in Table 1.*

Discussion. This analysis was undertaken to determine the correct molecular structure of this natural product. The structure obtained is shown in Fig. 1. Bond lengths and angles are given in Table 2.

The first published conformational reproduction of the chromon ring system was the half-chair conformation analogous to that of cyclohexene (Geissman, 1962). A further modification of the half-chair to a sofa has been suggested (Philbin & Wheeler, 1958) which is more in accord with infrared absorption data of the 2- and 3-substituted chromones.

The chromon ring system does indeed adopt the sofa conformation where O(1), C(3) and C(4) are coplanar with the aromatic nucleus. The least-squares equation of the plane passing through the aromatic ring [O(1), C(3) and C(4)] is $28.81x + 257.88y + 48.292z - 152.6 = 0$. The maximum deviation from the plane is 0.03 Å for C(3); C(2) deviates from this plane by 0.11 Å. The phenyl ring is in the equatorial position, H(C2) in the axial position.

The phenyl ring is planar; C(3') shows the maximum

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33451 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

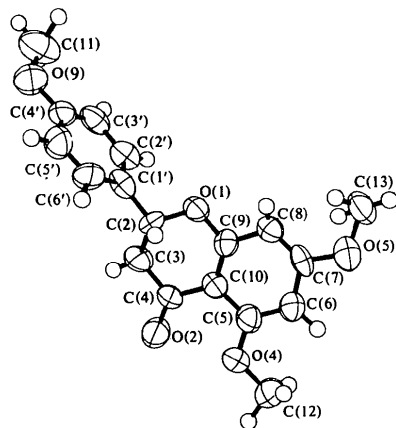


Fig. 1. A view of the molecule showing the numbering of the atoms.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

O(1)—C(2)	1.428 (9)	C(2)—C(11)	1.469 (12)
C(2)—C(3)	1.496 (11)	C(1')—C(2')	1.383 (12)
C(3)—C(4)	1.503 (13)	C(2')—C(3')	1.437 (11)
C(4)—C(10)	1.468 (9)	C(3')—C(4')	1.361 (14)
C(10)—C(9)	1.343 (9)	C(4')—C(5')	1.372 (14)
C(9)—O(1)	1.378 (10)	C(5')—C(6')	1.347 (14)
C(9)—C(8)	1.393 (11)	C(6')—C(11)	1.371 (12)
C(8)—C(7)	1.368 (10)	C(4')—O(3)	1.410 (11)
C(7)—C(6)	1.431 (13)	O(3)—C(11)	1.340 (12)
C(6)—C(5)	1.356 (11)	C(5)—O(4)	1.350 (9)
C(5)—C(10)	1.436 (9)	O(4)—C(13)	1.437 (15)
C(4)—O(2)	1.224 (8)	C(7)—O(5)	1.368 (12)
		O(5)—C(14)	1.463 (11)
C(2)—H(C2)	0.77 (1)	C(11)—H(C11,1)	0.97 (1)
C(3)—H(C3,1)	0.85 (1)	C(11)—H(C11,2)	0.80 (1)
C(3)—H(C3,2)	0.87 (1)	C(11)—H(C11,3)	1.2 (1)
C(6)—H(C6)	1.0 (1)	C(13)—H(C13,1)	1.1 (1)
C(2')—H(C2')	0.97 (1)	C(13)—H(C13,2)	1.0 (1)
C(3')—H(C3')	0.82 (1)	C(13)—H(C13,3)	0.96 (1)
C(5')—H(C5')	1.0 (1)	C(14)—H(C14,1)	0.88 (1)
C(6')—H(C6')	0.92 (1)	C(14)—H(C14,2)	0.97 (1)
		C(14)—H(C14,3)	0.98 (1)
C(2)—O(1)—C(9)	113.6 (6)	C(3)—C(2)—C(1')	113.3 (7)
O(1)—C(2)—C(3)	110.8 (8)	C(1')—C(2')—C(3')	120.2 (10)
C(2)—C(3)—C(4)	111.2 (7)	C(2')—C(3')—C(4')	119.7 (10)
C(3)—C(4)—C(10)	114.7 (6)	C(3')—C(4')—C(5')	119.2 (10)
C(4)—C(10)—C(9)	120.5 (5)	C(4')—C(5')—C(6')	120.3 (10)
C(10)—C(9)—O(1)	123.2 (7)	C(5')—C(6')—C(1')	124.1 (10)
C(3)—C(4)—O(2)	118.2 (8)	C(5)—O(4)—C(13)	118.0 (7)
C(10)—C(4)—O(2)	127.1 (9)	C(6)—C(5)—O(4)	122.9 (9)
C(9)—C(8)—C(7)	117.6 (8)	C(10)—C(5)—O(4)	116.9 (7)
C(7)—C(6)—C(5)	117.9 (9)	C(1')—C(2)—O(2)	109.1 (7)
C(8)—C(7)—C(6)	122.5 (8)	C(2')—C(1')—C(2)	125.5 (10)
C(6)—C(5)—C(10)	120.1 (8)	C(6')—C(1')—C(2)	120.0 (9)
C(5)—C(10)—C(9)	118.4 (6)	C(4')—O(3)—C(1')	117.0 (10)
C(10)—C(9)—C(8)	123.1 (9)	C(5')—C(4')—O(3)	115.0 (12)
O(1)—C(2)—C(1')	109.1 (7)	C(10)—C(5)—C(7)	116.6 (9)

deviation of 0.09 Å. The angle between this plane and that of the chromon ring is 70.8°.

The lengths of C(9)—O(1) and C(2)—O(1) correspond to that of C—O in pyranoses (Mariezcurrena & Rasmussen, 1973). C(9)—C(10) in the aromatic ring is significantly shortened. The carbonyl group has a bond length of 1.22 Å.

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8-[(2-Aminoethyl)amino]adenosine Cyclic 3',5'-Monophosphate Tetrahydrate

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Abstract. $C_{12}H_{18}N_7O_6P \cdot 4H_2O$ (I), orthorhombic, $P2_12_12_1$, $a = 13.180$ (2), $b = 22.439$ (7), $c = 6.661$ (1) Å, $M_r = 459.4$, $D_x = 1.55$ g cm⁻³. The adenine base displays a *syn* conformation ($\chi = -107.0^\circ$) with respect to the glycosyl bond, the furanose ring a twist $_4T^3$ [C(3')-endo–C(4')-exo] conformation relative to the glycosyl N(9). The adenine heterocycles form base stacks of 2_1 symmetry with an interplanar distance of 3.17 Å. Base overlap is limited to only 5.9% of the maximum possible as a result of steric contact, 2.94 Å, between N(6) and O(1') of the sugar ring of the screw-related molecule.

Introduction. Adenosine cyclic 3',5'-monophosphate (cAMP) dependent protein kinases occur in a wide variety of animal tissues. Their highly specific recognition of the cAMP, which is important for control and regulatory mechanisms of the human body, suggests that affinity chromatography should provide a convenient means for their purification. In this method a column containing a cAMP derivative bonded to an inert matrix is used to separate chromatographically the coordinate protein from impurities. In (I), which was specifically synthesized for this purpose, the purine base of the nucleotide is connected to the inert matrix *via* the C(8) side chain (Fig. 1). A knowledge of the molecular geometry of (I) and thereby the conformational preference at the glycosyl bond should provide an insight into the spatial characteristics of the specific cAMP binding site of the coordinate protein.

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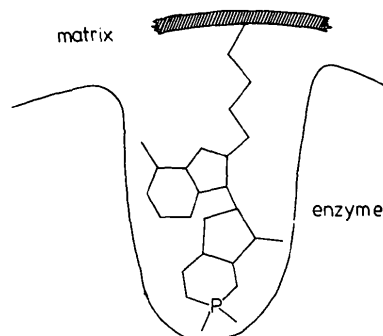


Fig. 1. The principle of affinity chromatography.

1 ml of ethylenediamine (14.8 mmol) was added to a suspension of 200 mg (490 μ mol) of 8-bromo-cAMP (Boehringer, Mannheim) in 10 ml of ethanol and heated to 100°C in a bomb for 2 h (Muneyama, Bauer, Shuman & Robins, 1971). After cooling, the reaction mixture was added at a pH of 11.5 to a Dowex 1-X2 column (Serva, Feinbiochemica, Heidelberg) and washed with water to remove the residual ethylenediamine. 8-(2-Aminoethyl)amino-cAMP (I) was eluted with water/0.5 M acetic acid (1:1, v/v). The product fractions were reduced to 10 ml and, after dilution with 10 ml of methanol, added to a Sephadex LH 20 column (Pharmacia, Frankfurt/Main) equilibrated with methanol/water (1:1, v/v). (I) was crystallized as long prisms from the methanol/water solution of the appropriate fractions (yield 81%): 100 MHz ¹H NMR (D_2O), $\delta = 8.06$ [s, H(2)], 5.88 [s, H(1')] and 4.23