Crystal Structure of Ethyl(3-methyl-7-coumaryloxy)acetate

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$C_{14}H_{14}O_5$, contains four molecules in the monoclinic unit cell. The coumarin moiety forms a dimer structure by π - π interaction around the inversion centre. The distance between two coumarins is 3.4241(3) Å. The structure is stabilized by one intramolecular and five intermolecular hydrogen-bonding interactions.

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It has been found that coumarin is one of the most interesting molecules, since it shows a wide spectrum of chemical reactivity.¹ Heterocycles containing the coumarin ring system involve some novel pharmacologically active compounds, such as dicumarol, warfarin, mercumatin and novobiocin.²

Synthesis of the coumarin base organic compound is well-known in the literature. In our literature investigation, we found no x-ray study about a coumarin base compound like in this work. The title compound was prepared according to a literature method.¹⁻³ Similar complexes have recently been studied in our laboratories.^{4,5}

7-Hydroxy-3-methyl-coumarin (5.8 mmol) was dissolved in 100 mL of acetone and 0.66 mL of ethylbromoacetate (d : 1.506 g/cm³, 6.0 mmol) was added. The reaction mixture was refluxed for 8 h. The solution was evaporated under a vacuum to half its volume and poured into ice water to precipitate. The

residue was filtered off and recrystallized from aqueous 1,4-dioxane (yield 85%). A chemical diagram of the complex in Fig. 1.

The present study showed that, $C_{14}H_{14}O_5$, contain four molecules in the monoclinic unit cell. The coumarin moiety forms a dimer structure by a π - π interaction around the inversion centre. The distance between two coumarins is 3.4241(3) Å. An ethyl group is connected to the coumaryloxy moiety with acetate group. The linked distance between these group O(3)-C(6) is 1.3714(16) Å. The torsion angles between the ethyl-acetate [C(14)-C(13)-O(5)-C(12)] and acetate-coumaryloxy [C(12)-C(11)-O(3)-C(6)] are 89.6(3) and 76.3(2)°, respectively. The distances of the O(3) and C(10) atoms from the plane of the coumaryloxy moiety are 0.066(1) and -0.0087(1)°, respectively. The dihedral angles between the coumaryloxy moiety and acetate group is 78.41(2)°.

The structure is stabilized by one intramolecular and five intermolecular hydrogen-bonding interactions. The crystal

Fig. 1 Chemical diagram.

Fig. 2 Structure of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small circles of arbitrary radii.

Table 1 Crystal and experimental data

Formula:	$C_{14}H_{14}O_5$
Formula weight:	262.25
Crystal system:	monoclinic
Space group:	$P2_1/n$
Z :	4
a :	12.546(2) Å
b :	8.101(1) Å
c :	13.390(1) Å
β :	115.670(4)°
V :	1226.6(3) Å ³
D_x :	1.420 g/cm ³
No. of reflection used:	2921
θ range for data collection:	3.38 to 27.87°
R :	0.053
Goodness-of-fit:	1.06
$(\Delta/\sigma)_{\max}$:	0.001
$(\Delta\rho)_{\max}$:	0.35 e Å ⁻³
$(\Delta\rho)_{\min}$:	-0.29 e Å ⁻³
Measurement:	Nonius Kappa CCD diffractometer
Program system:	SHELXTL
Structure determination:	SHELXTL
Refinement:	full matrix least-square SHELXTL
CCDC number:	285743

Table 2 Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for non-hydrogen atoms

Atom	x	y	z	U_{eq}^*
O(1)	6660(1)	6957(1)	6178(1)	15(1)
O(2)	8255(1)	5595(1)	6354(1)	20(1)
O(3)	3237(1)	9829(1)	5975(1)	18(1)
O(4)	3335(1)	7329(1)	7430(1)	21(1)
O(5)	4203(1)	9084(1)	8872(1)	20(1)
C(1)	5522(1)	6133(2)	3922(1)	14(1)
C(2)	6647(1)	5637(2)	4554(1)	16(1)
C(3)	7258(1)	6014(2)	5722(1)	15(1)
C(4)	5511(1)	7480(2)	5555(1)	13(1)
C(5)	5011(1)	8383(2)	6127(1)	14(1)
C(6)	3850(1)	8907(2)	5538(1)	15(1)
C(7)	3215(1)	8531(2)	4411(1)	17(1)
C(8)	3736(1)	7645(2)	3867(1)	17(1)
C(9)	4912(1)	7086(2)	4431(1)	14(1)
C(10)	4892(1)	5685(2)	2716(1)	19(1)
C(11)	3773(1)	10151(2)	7132(1)	17(1)
C(12)	3732(1)	8664(2)	7801(1)	16(1)
C(13)	4372(1)	7784(2)	9684(1)	19(1)
C(14)	5578(1)	7015(2)	10042(1)	23(1)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

O(1)-C(4)	1.3825(15)
O(1)-C(3)	1.3845(16)
O(2)-C(3)	1.2153(17)
O(3)-C(6)	1.3714(16)
O(3)-C(11)	1.4201(16)
O(4)-C(12)	1.2036(17)
O(5)-C(12)	1.3374(16)
O(5)-C(13)	1.4619(17)
C(4)-O(1)-C(3)	121.67(10)
C(6)-O(3)-C(11)	118.49(10)
C(12)-O(5)-C(13)	117.96(11)
O(2)-C(3)-O(1)	115.97(12)
O(2)-C(3)-C(2)	126.70(13)
O(1)-C(3)-C(2)	117.33(11)
O(1)-C(4)-C(5)	115.44(11)
O(1)-C(4)-C(9)	120.97(12)
O(3)-C(6)-C(5)	124.62(12)
O(3)-C(6)-C(7)	114.58(12)
O(3)-C(11)-C(12)	112.18(11)
O(4)-C(12)-O(5)	125.65(13)
O(4)-C(12)-C(11)	125.74(13)
O(5)-C(12)-C(11)	108.61(11)
O(5)-C(13)-C(14)	109.62(12)

Table 4 Hydrogen bonding geometry ($\text{\AA}$, $^\circ$)

D-H...A	D-H	H...A	D-A	D-H...A
C(8)-H(8)...O(1) ⁱ	0.95	2.55	3.4241	152
C(10)-H(10B)...O(4) ⁱⁱ	0.99	2.47	3.3651	150
C(11)-H(11A)...O(4) ⁱⁱⁱ	0.96	2.53	3.4355	156
C(11)-H(11B)...O(2) ^{iv}	0.98	2.49	3.4054	156
C(13)-H(13A)...O(4)	0.98	2.41	2.7456	100
C(13)-H(13B)...O(2) ^v	0.98	2.48	3.3770	153

Symmetry codes: (i) $1/2+x$, $1/2-y$, $1/2+z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $3/2-x$, $-1/2+y$, $1/2-z$; (iv) $1/2-x$, $-1/2+y$, $1/2-z$; (v) $1/2+x$, $1/2-y$, $-1/2+z$

structure has all intermolecular and intramolecular C-H...O hydrogen contacts (Table 4). The crystal and experimental data are given in Table 1. The final atomic parameters are presented in Table 2, and the selected bond distances and angles in Table 3.

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