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Water Molecules as a Gluing Factor in Organic Crystals. Part 2. The Crystal and Molecular Structure of 6-Acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic Acid Monohydrate

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Water molecules often play an important role in stabilizing the crystal structures, as shown by thermochemical data of simple inorganic hydrates [1]. It was also shown that water molecules encountered in organic crystal structures exhibit substantial elasticity [1] and due to their amphoteric Lewis acid/base properties [2,3] often participate in building crystal structures [4].

The aim of this report is to illustrate in detail how the water molecule in 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid monohydrate functions in the crystal lattice. The acetate of trolox (6-acetoxy-2,5,7,8-teramethylchroman-2-carboxylic acid) was obtained by a standard method. To the solution of trolox (2,5,7,8-tetramethylchroman-2-carboxylic acid, 250 mg, 1 mmol) in dry pyridine (3 ml), acetic anhydride (150 μl, 1.5 mmol) was added dropwise and allowed to stand at room temperature overnight, giving 265 mg of crude product. After two crystallizations from hexane/ethyl acetate, the pure acetate was obtained. M.p.138–139°C.

X-ray diffraction. The X-ray measurements of the monocrystal were carried out on a KM-4 KUMA diffractometer with graphite monochromated MoKα radiation. The data were collected at room temperature using the ω-2θ scan technique. The intensity of the control reflections varied by less than 3% and the linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by direct methods [5] and refined using SHELXL [6]. The refinement was based on F^2 for all reflections, except those with very negative F^2. The weight R factor, wR and all goodness-of-fit S values are based on F^2. The non-hydrogen atoms were refined anisotropically, whereas the H-atoms were placed in the calculated positions and their thermal parameters were refined isotropically. The atomic scattering factors were taken from the International Tables [7]. The details of X-ray measurements, structural computations and crystal data for the title compound (Fig. 1) are

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given in Table 1. Table 2 presents the observed bond lengths, bond angles and selected torsion angles. Atomic coordinates, and full lists of bond lengths and angles for the compound has been deposited at the Cambridge Crystallographic Data Centre (with deposition number CCDC 152556).

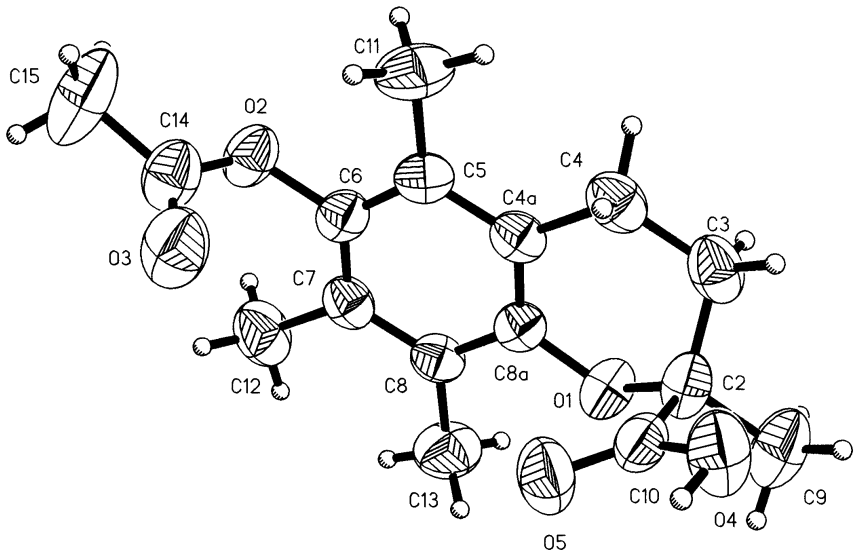

Figure 1. Molecular structure with atom numbering.

Table 1. Crystal data and structure refinement for 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid.

Empirical formula	$C_{16}H_{22}O_6$
Formula weight	310.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P*2(1)/*n*
Unit cell dimensions	*a* = 12.102(2) Å
	b = 8.683(2) Å
	c = 15.661(3) Å
	β = 105.05(3) deg.
Volume	1589.2(5) $Å^3$
Z, Calculated density	4, 1.297 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	664

Table 1 (continuation)

Crystal size	0.25 × 0.2 × 0.2 mm
Theta range for data collection	2.46 to 28.99 deg.
Index ranges	0 <= h <= 14, 0 <= k <= 11, –17 <= l <= 17
Reflections collected/unique	3883/3727 [*R*(int) = 0.0142]
Completeness to 2theta = 28.99	82.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3727/0/230
Goodness-of-fit on F^2	0.993
Final *R* indices [$I > 2\text{sigma}(I)$]	*R*1 = 0.0548, *wR*2 = 0.1384
R indices (all data)	*R*1 = 0.1317, *wR*2 = 0.1757
Largest diff. peak and hole	0.272 and –0.230 e. Å^{-3}

Table 2. Bond lengths [Å] and angles [deg], selected dihedral angles for 6-acetoxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid.

O(1)–C(8A)	1.364(3)	C(6)–O(2)	1.399(3)
O(1)–C(2)	1.407(3)	C(7)–C(8)	1.374(3)
C(2)–C(3)	1.489(4)	C(7)–C(7A)	1.490(4)
C(2)–C(2A)	1.496(3)	C(8)–C(8A)	1.369(3)
C(2)–C(2B)	1.498(3)	C(8)–C(8B)	1.497(3)
C(3)–C(4)	1.492(4)	C(2B)–O(5)	1.177(3)
C(4)–C(4A)	1.480(3)	C(2B)–O(4)	1.287(3)
C(4A)–C(8A)	1.363(3)	O(2)–C(14)	1.334(3)
C(4A)–C(5)	1.375(3)	C(14)–O(3)	1.165(3)
C(5)–C(6)	1.358(3)	C(14)–C(15)	1.464(4)
C(5)–C(11)	1.492(3)		
C(6)–C(7)	1.362(3)		
C(8A)–O(1)–C(2)	116.7(2)	C(7)–C(6)–O(2)	118.4(2)
O(1)–C(2)–C(3)	109.6(2)	C(6)–C(7)–C(8)	117.6(2)
O(1)–C(2)–C(2A)	104.9(2)	C(6)–C(7)–C(7A)	120.9(2)
C(3)–C(2)–C(2A)	112.7(2)	C(8)–C(7)–C(7A)	121.5(2)
O(1)–C(2)–C(2B)	108.4(2)	C(8A)–C(8)–C(7)	118.8(2)
C(3)–C(2)–C(2B)	111.1(2)	C(8A)–C(8)–C(8B)	119.8(2)
C(2A)–C(2)–C(2B)	109.9(2)	C(7)–C(8)–C(8B)	121.4(2)
C(2)–C(3)–C(4)	111.8(2)	C(4A)–C(8A)–O(1)	122.1(2)

Table 2 (continuation)

C(4A)–C(4)–C(3)	112.5(2)	C(4A)–C(8A)–C(8)	122.8(2)
C(8A)–C(4A)–C(5)	118.6(2)	O(1)–C(8A)–C(8)	115.0(2)
C(8A)–C(4A)–C(4)	120.6(2)	O(5)–C(2B)–O(4)	123.3(2)
C(5)–C(4A)–C(4)	120.8(2)	O(5)–C(2B)–C(2)	124.5(2)
C(6)–C(5)–C(4A)	118.0(2)	O(4)–C(2B)–C(2)	112.2(2)
C(6)–C(5)–C(11)	121.1(2)	C(14)–O(2)–C(6)	115.84(18)
C(4A)–C(5)–C(11)	120.9(2)	O(3)–C(14)–O(2)	122.1(2)
C(5)–C(6)–C(7)	124.2(2)	O(3)–C(14)–C(15)	126.5(3)
C(5)–C(6)–O(2)	117.3(2)	O(2)–C(14)–C(15)	111.4(3)
C(8A)–O(1)–C(2)–C(3)	–50.5(3)	C(4)–C(4A)–C(8A)–O(1)	–1.1(3)
C(8A)–O(1)–C(2)–C(2A)	–71.7(2)	C(5)–C(4A)–C(8A)–C(8)	0.8(3)
C(8A)–O(1)–C(2)–C(2B)	70.9(2)	C(4)–C(4A)–C(8A)–C(8)	179.0(2)
O(1)–C(2)–C(3)–C(4)	58.7(3)	C(2)–O(1)–C(8A)–C(4A)	22.4(3)
C(2A)–C(2)–C(3)–C(4)	175.1(2)	C(2)–O(1)–C(8A)–C(8)	–157.72(19)
C(2B)–C(2)–C(3)–C(4)	–61.0(3)	C(5)–C(6)–O(2)–C(14)	–89.6(3)
C(2)–C(3)–C(4)–C(4A)	–38.5(3)	C(7)–C(6)–O(2)–C(14)	92.9(3)
C(3)–C(4)–C(4A)–C(8A)	10.3(3)	C(6)–O(2)–C(14)–O(3)	–6.4(4)
C(3)–C(4)–C(4A)–C(5)	–171.5(2)	C(6)–O(2)–C(14)–C(15)	172.5(3)
C(5)–C(4A)–C(8A)–O(1)	–179.29(19)		

Figure 2 presents the scheme of the dimer of 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid monohydrate, showing clearly that despite the presence of a carboxylic group, no typical cyclic dimer is formed [8], but instead the water molecule becomes a center of the intermolecular interactions, keeping two of 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid molecules together in the crystal structure. Table 3 presents the geometric parameters of this region.

The water molecule exhibits a substantially opened HOH angle, 108.7°, which may be compared with this quantity for the gas phase 104.52° [9] and for liquid 102.8° [10]. Evidently, optimization for the H-bond formation between both OH bonds of the water molecule with O3a and O5a oxygen atoms in 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid monohydrate causes the opening of the OHO bond angle. The water molecule is strongly H-bonded in three ways; two as mentioned above and one in which water is an H-bond acceptor. Application of the rough estimation of H…O interaction energy *via* the exponential approximation [11], based on Pauling's bond numbers [12], leads to the values given in Table 3. A sum of all the H–O interaction energies of water molecule with neighbours is 34.3 kJ/mole, which may be compared with such a value for a water molecule on ice, equal to 62 kJ/mole. The interatomic distance between the oxygen atom in water (as H-bond acceptor) and ox-

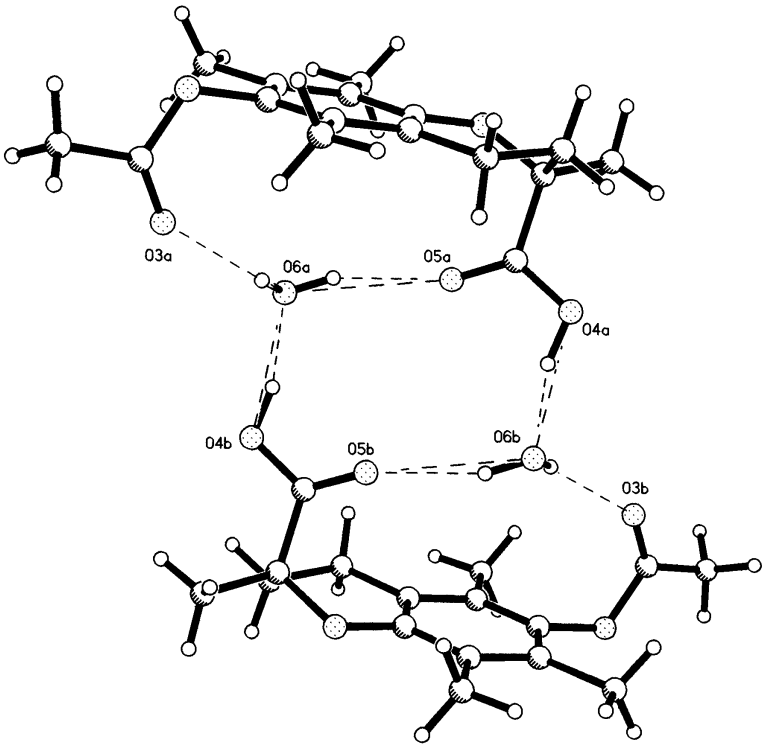

Figure 2. 6-Acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid monohydrate – dimer with a water molecule as a gluing factor.

ygen O4b (as a donor) is 2.559 Å, which may be compared with the O…O distance in ice 2.75 Å [13]. Thus, it may be concluded that the water molecule plays a very important role in the architecture of crystals of the 6-acetoxy-2,5,7,8-tetramethylchroman-2-carboxylic acid monohydrate.

Table 3. Structural parameters of hydrogen bonds.

Hydrogen bond D–H....A Symm. Code	Donor- H D–H [Å]	Acceptor...H A....H [Å]	Donor..Acceptor D...A [Å]	D–H...A [°]	E(O...H) kJ/mol
O(6)–H(63)...O(5)	O(6)–H(63) 0.85	H(63)....O(5) 2.01	O(6)–O(5) 2.835 (3)	162	O(5)...H(63) 4.8
O(6)–H(62)...O(3)	O(6)–H(62) 0.91	H(62)....O(3) 2.09	O(6)–O(3) 2.891 (4)	147	O(3)...H(62) 4.1
O(4)–H(4)...O(6) –X, –Y, 1 – Z	O(4)–H(4) 0.96	H(4)....O(6) 1.62	O(4)–O(6) 2.559 (3)	165	O(6)...H(4) 26.1

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