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1-[2-(Dicarboxymethyl)-3-oxocyclopent-4-en-1-yl]-pyrrolidin-1-ium bromide hydrate

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.076
Data-to-parameter ratio = 25.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Crystallization of 6-hydroxy-2,2-dimethyl-5-[2-oxo-5-(pyrrolidin-1-yl)cyclopent-3-en-1-yl]-4*H*-1,3-dioxin-4-one from aqueous hydrobromic acid gave the title compound, $C_{12}H_{16}BrNO_5{\cdot}H_2O$. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds.

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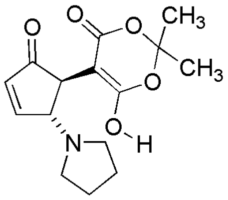
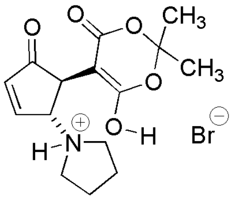
Comment

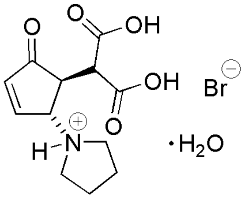
In a continuation of our studies on the synthesis of substituted cyclopentenes obtained from activated 2-substituted furan derivatives, we have reported the synthesis of (5-amino-substituted-cyclopenten-3-en-1-yl)-4*H*-1,3-dioxin-4-ones (Šafář *et al.*, 2000). It has been found that the results of the reaction of 6-hydroxy-2,2-dimethyl-5-[2-oxo-5-(pyrrolidin-1-yl)cyclopent-3-en-1-yl]- 4*H*-1,3-dioxin-4-one, (I), with hydrobromic acid are strongly dependent on the nature of the solvent. While reaction of (I) with hydrobromic acid in methanol resulted in the formation of the cyclopentenone hydrobromide (II), treatment of (I) with 10% hydrobromic acid afforded the substituted malonic acid hydrobromide (III), having the molecular formula $C_{12}H_{16}BrNO_5$ and a molecular ion ($M^{+\cdot} - 80$) having m/z = 253 in the mass spectrum.



(I)



(II)



(III)

Spectral data (^{1}H and ^{13}C NMR) were not sufficient to determine the position of the pyrrolidine ring and malonic acid on the cyclopentene ring, so an X-ray diffraction study of (III) was undertaken.

The crystal structure of (III) consists of a 2-[2-oxo-5-(pyrrolidin-1-yl)cyclopent-3-en-1-yl]malonic acid cation and a Br^- anion, and is stabilized by the presence of a water molecule (Fig. 1). The positions of the bulky substituents are *trans* and the cation consists of a cyclopentene ring substituted in the 5-position by a pyrrolidine ring and in the 1-position by a malonic acid moiety. The pyrrolidine ring adopts a half-chair conformation, and the cyclopentene ring is nearly planar (χ^2 = 5.99 at the 95% probability level) with the main displacement for C1 and C5 atoms of 0.056 (1) and −0.062 (2) Å, respec-

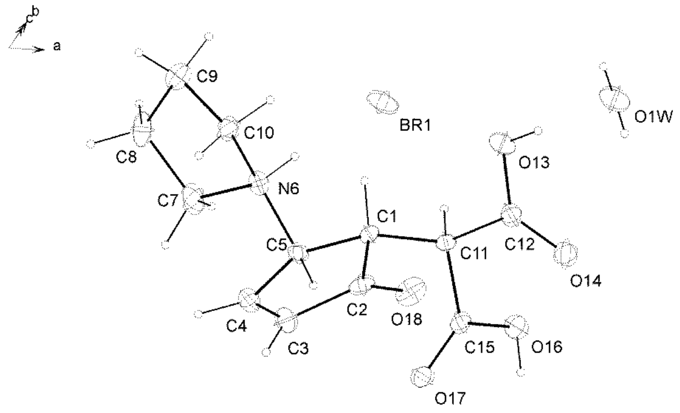


Figure 1
The numbering scheme of (III). Displacement ellipsoids are shown at the 50% probability level.

tively. The distance C3—C4 of 1.336 (2) Å clearly indicates double-bond character, while all other C—C and C—N bonds are single. The system of hydrogen bonds (see Fig. 2 and Table 2) between the cation, the Br$^-$ anion and the water molecule form a three-dimmensional framework and stabilize the crystal structure.

Experimental

See above for synthesis details.

Crystal data

$C_{12}H_{16}NO_5^+ \cdot Br^- \cdot H_2O$
$M_r = 352.18$
Triclinic, $P\bar{1}$
$a = 8.7253$ (1) Å
$b = 8.9271$ (1) Å
$c = 11.5975$ (2) Å
$\alpha = 72.68$ (1)°
$\beta = 71.25$ (1)°
$\gamma = 61.01$ (1)°
$V = 737.12$ (2) Å^3

$Z = 2$
$D_x = 1.587$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7513 reflections
$\theta = 1.9$–32.6°
$\mu = 2.81$ mm^{-1}
$T = 183$ (2) K
Block, colourless
1.00 × 0.40 × 0.30 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.148$, $T_{\max} = 0.486$
9194 measured reflections

4871 independent reflections
4148 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 32.6°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.076$
$S = 0.97$
4871 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0060 (15)

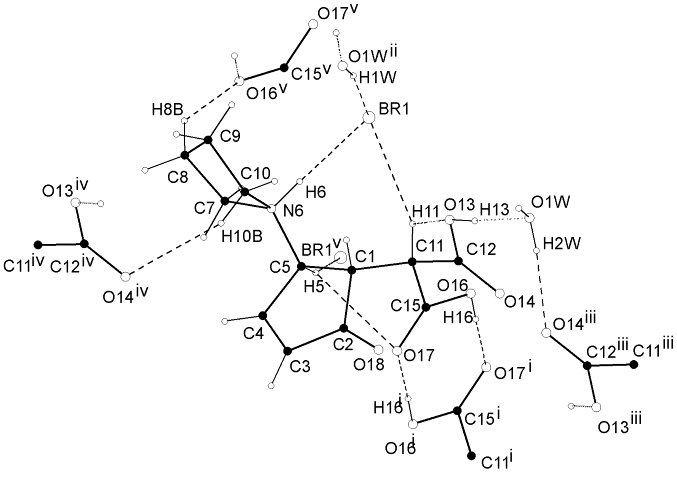


Figure 2
The system of hydrogen bonds and short contacts in (III). The symmetry code used is the same as in Table 2.

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.534 (2)	C7—C8	1.528 (2)
C1—C11	1.540 (2)	C8—C9	1.538 (3)
C1—C5	1.543 (2)	C9—C10	1.527 (2)
C2—O18	1.221 (2)	C11—C15	1.521 (2)
C2—C3	1.476 (2)	C11—C12	1.532 (2)
C3—C4	1.336 (2)	C12—O14	1.221 (2)
C4—C5	1.514 (2)	C12—O13	1.320 (2)
C5—N6	1.513 (2)	C15—O17	1.225 (2)
N6—C10	1.508 (2)	C15—O16	1.315 (2)
N6—C7	1.516 (2)		
C2—C1—C5	104.13 (11)	C12—C11—C1	111.20 (11)
C15—C11—C12	110.42 (11)	O14—C12—O13	124.70 (14)
C15—C11—C1	112.63 (11)	O17—C15—O16	124.54 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O13	1.00	2.53	2.891 (2)	101
C5—H5···O17	1.00	2.63	3.094 (2)	108
N6—H6···Br1	0.93	2.32	3.247 (1)	173
C11—H11···Br1	1.00	2.79	3.731 (1)	156
O13—H13···O1W	0.84	1.74	2.578 (2)	177
O16—H16···O17^{i}	0.84	1.81	2.645 (2)	173
O1W—H1W···Br1^{ii}	0.82 (3)	2.45 (3)	3.263 (1)	170 (2)
O1W—H2W···O14^{iii}	0.82 (2)	2.06 (2)	2.874 (2)	171 (2)
C10—H10B···O14^{iv}	0.99	2.57	3.417 (2)	144
C8—H8B···O16^{v}	0.99	2.64	3.451 (2)	139
C5—H5···Br1^{v}	1.00	2.84	3.803 (1)	162

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

Data were collected at 183 K using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low temperature device. Slightly more than a hemisphere of reciprocal space was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm. A preliminary orientation matrix was obtained from the first 100 frames using *SMART* (Siemens, 1995). Exposure time was 4.5 s

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per frame. The collected frames were integrated using the preliminary orientation matrix which was updated every 100 frames. Final cell parameters were obtained by refinement on the position of 7513 reflections with $I > 10\sigma(I)$ after integration of all the frames data using *SAINT* (Siemens, 1995). The data were empirically corrected for absorption and other effects using *SADABS* (Sheldrick, 1996) based on the method of Blessing (1995). H atoms (with the exception of those of the water molecule) were refined freely in an isotropic approximation and were constrained to ideal geometry using an appropriate riding model. For hydroxyl groups, the O—H distances (0.84 Å) and C—O—H angles (109.5°) were fixed.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL*.

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