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Ethyl (*E*)-2-(2,7-dimethyl-5-oxo-4*H*,5*H*-pyrano-[4,3-*b*]pyran-4-ylidene)acetate

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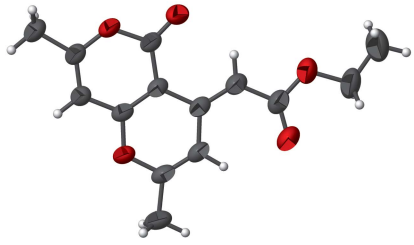
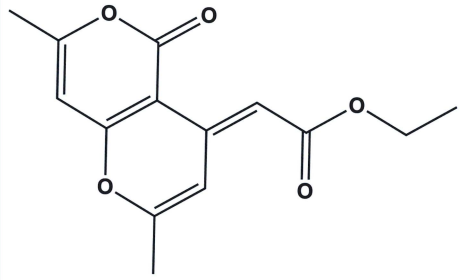
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{14}H_{14}O_5$, the two heterocyclic rings are coplanar (r.m.s. deviation = 0.008 Å), with the largest deviation from the mean plane being 0.012 (1) Å. The mean plane through the acetate group is inclined slightly with respect to the oxopyrano[4,3-*b*]pyran-4-yl system, as indicated by the dihedral angle of 1.70 (7)° between them. Two intramolecular hydrogen bonds, completing *S*(6) ring motifs, are observed in the molecule. In the crystal, molecules are linked by weak C—H···O hydrogen bonds involving the same acceptor atom, forming chains propagating along the *c*-axis direction and enclosing $R_2^1(6)$ ring motifs. The chains are linked *via* offset π–π interactions [intercentroid distance = 3.622 (1) Å], involving inversion-related oxopyrano-[4,3-*b*]pyran-4-yl ring systems, forming slabs parallel to the *bc* plane.

3D view



Chemical scheme



Structure description

Pyrones are among the most important heterocyclic structures in medicinal chemistry and specifically, 2-pyrones can be found in a wide range of medicinally significant natural products (Lee *et al.*, 2000; Fairlamb *et al.*, 2004; McGlacken & Fairlamb, 2005; Perchellet *et al.*, 1998; Defant *et al.*, 2015). As heterocyclic aromatic enols, they have a high acidity and dense functionality, which leads to a diverse reactivity profile. This means that 4-hydroxy-2-pyrones are also useful precursors to a number of other structural units and versatile intermediates in organic synthesis (Burns *et al.*, 2014; Aggarwal *et al.*, 2013).

The molecule of the title compound is build up from a bicyclic oxopyrano[4,3-*b*]-pyran-4-ylidene ring system linked to two methyl groups and one acetate group, as shown in Fig. 1. The fused heterocyclic rings are virtually coplanar with the maximum deviation from the mean plane being 0.012 (2) Å for atom C9. The oxopyrano[4,3-*b*]pyran-4-yl

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O4	0.93	2.20	2.883 (2)	130
C6—H6···O2	0.93	2.24	2.894 (2)	127
C12—H12···O4^{i}	0.93	2.59	3.283 (2)	132
C13—H13C···O4^{i}	0.96	2.59	3.398 (2)	143

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

system makes a dihedral angle of 1.70 (7)° with the mean plane through the acetate group. Two intramolecular C—H···O contacts, enclosing $S(6)$ ring motifs, are observed in the molecule (Fig. 1 and Table 1).

In the crystal, molecules are linked by weak C—H···O hydrogen bonds involving the same acceptor atom (see Table 1), forming chains propagating along the c-axis direction and enclosing $R_2^1(6)$ ring motifs (Fig. 2). The chains are linked *via* offset π–π interactions involving inversion-related oxopyrano[4,3-*b*]pyran-4-yl ring systems, [intercentroid distance = 3.622 (1) Å], forming slabs parallel to the *bc* plane (Fig. 3).

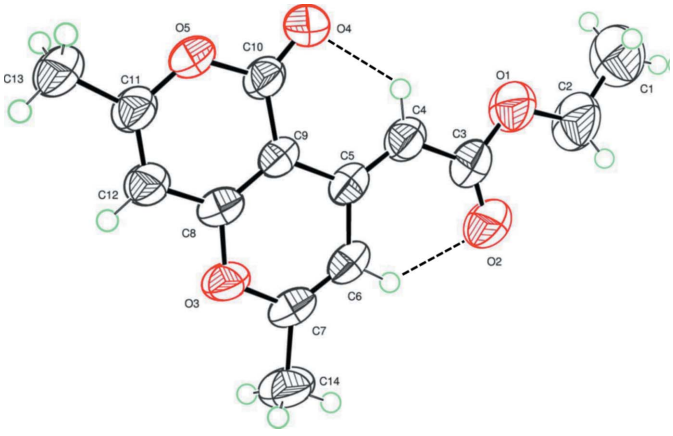


Figure 1
A view of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular C—H···O contacts are shown as dashed lines (see Table 1).

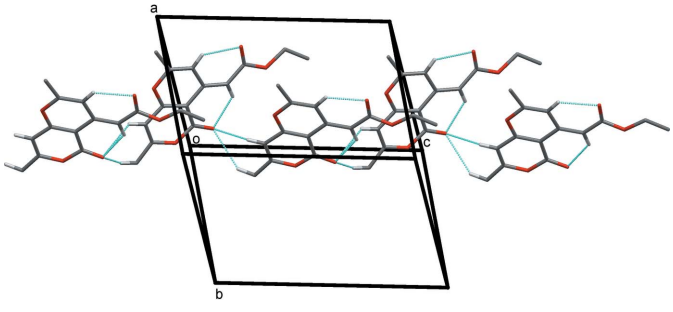


Figure 2
A partial view, normal to (110), of the crystal packing for the title compound, with hydrogen bonds shown as dashed lines (see Table 1; only H atoms H4, H6, H12 and H13*C* have been included).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{14}O_5$
M_r	262.25
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	9.5679 (12), 11.4330 (13), 12.7993 (15)
β (°)	108.257 (4)
V (Å^3)	1329.6 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.32 × 0.26 × 0.21
Data collection	
Diffractometer	Bruker X8 *APEX*
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.663, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16353, 2939, 1909
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.137, 1.03
No. of reflections	2939
No. of parameters	180
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.15

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Synthesis and crystallization

To a solution of 6-aminouracil (1 mmol) in 25 ml of ethanol, 4-hydroxy-6-methyl-2-pyrone (1.1 mmol) and drops of tri-

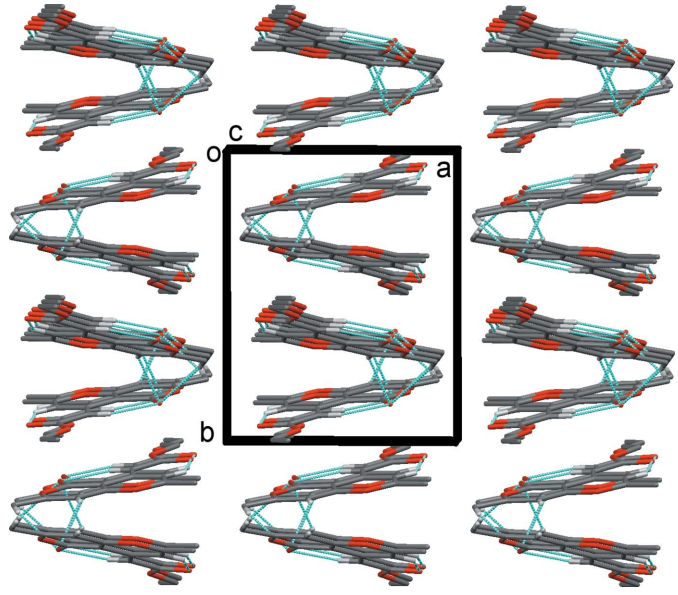


Figure 3
A view along the c axis of the crystal packing for the title compound, with the hydrogen bonds shown as dashed lines (see Table 1; only H atoms H4, H6, H12 and H13*C* have been included).

ethylamine were added. The mixture was refluxed for 8 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified on silica gel using hexane:ethyl acetate (2/8) as eluent. The title compound was recrystallized from ethanol giving colourless block-like crystals (yield: 54%, m.p. 376 K). It should be noted that in the reaction of 6-aminouracil with 4-hydroxy-6-methyl-2-pyrone, under reflux of ethanol in the presence of Et3N, we observed another competitive reaction between two molecules of 4-hydroxy-6 -methyl-2-pyrone, this reaction is kinetically favored over the first reaction. Details are given in the Supporting information.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Funding information

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References

Aggarwal, R., Rani, C., Kumar, R., Garg, G. & Sharmab, J. (2013). *ARKIVOC*, **II**, 120–134.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burns, M. J., Ronson, T. O., Taylor, R. J. K. & Fairlamb, I. J. S. (2014). *Beilstein J. Org. Chem.* **10**, 1159–1165.
Defant, A., Mancini, I., Tomazzolli, R. & Balzarini, J. (2015). *Arch. Pharm. Chem. Life Sci.* **348**, 23–33.
Fairlamb, I. J. S., Marrison, L. R., Dickinson, J. M., Lu, F.-J. & Schmidt, J. P. (2004). *Bioorg. Med. Chem.* **12**, 4285–4299.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Lee, Y. S., Kim, S. N., Lee, Y. S., Lee, J. Y., Lee, C.-K., Kim, H. S. & Park, H. (2000). *Arch. Pharm. Pharm. Med. Chem.* **333**, 319–322.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
McGlacken, G. P. & Fairlamb, I. J. S. (2005). *Nat. Prod. Rep.* **22**, 369–385.
Perchellet, E. M., Ladesich, J. B., Chen, Y., Sin, H.-S., Hua, D. H., Kraft, S. L. & Perchellet, J.-P. (1998). *Anticancer Drugs*, **9**, 565–576.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). **2**, x170208 [https://doi.org/10.1107/S2414314617002085]

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Crystal data

$C_{14}H_{14}O_5$
M_r = 262.25
Monoclinic, $P2_1/c$
a = 9.5679 (12) Å
b = 11.4330 (13) Å
c = 12.7993 (15) Å
β = 108.257 (4)°
V = 1329.6 (3) Å^3
Z = 4
$F(000)$ = 552
D_x = 1.310 Mg m^{-3}
Melting point: 376 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2939 reflections
θ = 2.5–27.1°
μ = 0.10 mm^{-1}
T = 296 K
Block, colourless
0.32 × 0.26 × 0.21 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.663, T_{max} = 0.746
16353 measured reflections
2939 independent reflections
1909 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.1°, θ_{min} = 2.5°
h = −12→12
k = −14→14
l = −13→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.137
S = 1.03
2939 reflections
180 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2 + 0.1184P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7176 (3)	0.4822 (2)	1.10578 (18)	0.1053 (9)
H1A	0.7896	0.5034	1.1742	0.158*
H1B	0.6384	0.5376	1.0884	0.158*
H1C	0.6801	0.4055	1.1122	0.158*
C2	0.7864 (2)	0.4820 (2)	1.01765 (16)	0.0901 (7)
H2A	0.8250	0.5590	1.0105	0.108*
H2B	0.8670	0.4263	1.0345	0.108*
C3	0.7183 (2)	0.43027 (15)	0.82769 (14)	0.0584 (5)
C4	0.59172 (17)	0.40172 (14)	0.73274 (13)	0.0523 (4)
H4	0.5000	0.3988	0.7433	0.063*
C5	0.59770 (16)	0.37903 (12)	0.62997 (12)	0.0442 (4)
C6	0.73205 (17)	0.38065 (13)	0.60097 (14)	0.0496 (4)
H6	0.8198	0.3960	0.6563	0.060*
C7	0.73778 (16)	0.36155 (14)	0.50021 (14)	0.0508 (4)
C8	0.48137 (16)	0.33460 (12)	0.43348 (13)	0.0453 (4)
C9	0.46732 (15)	0.35306 (12)	0.53543 (12)	0.0420 (4)
C10	0.31964 (17)	0.34808 (14)	0.54336 (13)	0.0488 (4)
C11	0.22563 (17)	0.30720 (14)	0.34851 (13)	0.0515 (4)
C12	0.35992 (17)	0.31137 (14)	0.33862 (14)	0.0519 (4)
H12	0.3739	0.2993	0.2707	0.062*
C13	0.08513 (19)	0.2864 (2)	0.26002 (16)	0.0752 (6)
H13A	0.0281	0.3571	0.2461	0.130 (10)*
H13B	0.0310	0.2259	0.2824	0.109 (8)*
H13C	0.1052	0.2627	0.1942	0.100 (7)*
C14	0.8690 (2)	0.36234 (18)	0.46180 (18)	0.0702 (6)
H14A	0.8813	0.2865	0.4338	0.109 (8)*
H14B	0.9548	0.3815	0.5222	0.100 (7)*
H14C	0.8558	0.4196	0.4046	0.102 (8)*
O1	0.67347 (14)	0.44936 (12)	0.91578 (10)	0.0756 (4)
O2	0.84654 (14)	0.43692 (14)	0.83266 (11)	0.0822 (5)
O3	0.61171 (11)	0.33840 (10)	0.41328 (9)	0.0557 (3)
O4	0.28225 (13)	0.36313 (13)	0.62435 (10)	0.0714 (4)
O5	0.20544 (11)	0.32427 (10)	0.44793 (9)	0.0546 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.110 (2)	0.129 (2)	0.0675 (13)	0.0096 (16)	0.0138 (14)	−0.0315 (14)
C2	0.0758 (15)	0.1147 (18)	0.0611 (12)	0.0024 (13)	−0.0055 (11)	−0.0259 (12)
C3	0.0485 (11)	0.0619 (11)	0.0556 (10)	0.0028 (8)	0.0030 (8)	−0.0001 (8)
C4	0.0406 (9)	0.0584 (10)	0.0531 (10)	−0.0007 (7)	0.0079 (7)	0.0046 (7)
C5	0.0348 (8)	0.0411 (8)	0.0515 (9)	0.0014 (6)	0.0061 (7)	0.0063 (6)
C6	0.0318 (8)	0.0524 (9)	0.0573 (10)	0.0009 (6)	0.0034 (7)	0.0027 (7)
C7	0.0304 (8)	0.0516 (9)	0.0676 (11)	0.0000 (6)	0.0111 (8)	−0.0013 (8)
C8	0.0329 (8)	0.0445 (8)	0.0577 (10)	−0.0009 (6)	0.0132 (7)	−0.0020 (7)

C9	0.0326 (8)	0.0417 (8)	0.0484 (9)	0.0006 (6)	0.0079 (7)	0.0046 (6)
C10	0.0350 (8)	0.0586 (10)	0.0495 (9)	−0.0038 (7)	0.0084 (8)	0.0085 (7)
C11	0.0386 (9)	0.0580 (10)	0.0532 (9)	−0.0056 (7)	0.0075 (7)	−0.0067 (7)
C12	0.0400 (9)	0.0636 (10)	0.0510 (9)	−0.0047 (7)	0.0125 (7)	−0.0103 (7)
C13	0.0416 (10)	0.1101 (17)	0.0657 (12)	−0.0123 (11)	0.0050 (9)	−0.0200 (11)
C14	0.0401 (10)	0.0861 (15)	0.0874 (14)	−0.0025 (9)	0.0243 (10)	−0.0080 (12)
O1	0.0609 (8)	0.1019 (10)	0.0552 (7)	0.0007 (7)	0.0055 (6)	−0.0196 (7)
O2	0.0457 (8)	0.1220 (12)	0.0674 (9)	−0.0020 (7)	0.0014 (7)	−0.0103 (8)
O3	0.0336 (6)	0.0732 (8)	0.0607 (7)	−0.0042 (5)	0.0151 (5)	−0.0125 (5)
O4	0.0439 (7)	0.1199 (11)	0.0522 (7)	−0.0059 (7)	0.0176 (6)	0.0078 (7)
O5	0.0321 (6)	0.0744 (8)	0.0546 (7)	−0.0077 (5)	0.0097 (5)	−0.0009 (5)

Geometric parameters (Å, º)

C1—C2	1.473 (3)	C7—C14	1.485 (2)
C1—H1A	0.9600	C8—O3	1.3513 (18)
C1—H1B	0.9600	C8—C9	1.369 (2)
C1—H1C	0.9600	C8—C12	1.418 (2)
C2—O1	1.458 (2)	C9—C10	1.449 (2)
C2—H2A	0.9700	C10—O4	1.2102 (19)
C2—H2B	0.9700	C10—O5	1.3869 (18)
C3—O2	1.211 (2)	C11—C12	1.331 (2)
C3—O1	1.344 (2)	C11—O5	1.3596 (19)
C3—C4	1.459 (2)	C11—C13	1.481 (2)
C4—C5	1.359 (2)	C12—H12	0.9300
C4—H4	0.9300	C13—H13A	0.9600
C5—C6	1.446 (2)	C13—H13B	0.9600
C5—C9	1.471 (2)	C13—H13C	0.9600
C6—C7	1.326 (2)	C14—H14A	0.9600
C6—H6	0.9300	C14—H14B	0.9600
C7—O3	1.3864 (18)	C14—H14C	0.9600
C2—C1—H1A	109.5	C9—C8—C12	123.09 (14)
C2—C1—H1B	109.5	C8—C9—C10	116.72 (14)
H1A—C1—H1B	109.5	C8—C9—C5	120.27 (13)
C2—C1—H1C	109.5	C10—C9—C5	123.00 (14)
H1A—C1—H1C	109.5	O4—C10—O5	114.81 (14)
H1B—C1—H1C	109.5	O4—C10—C9	127.65 (15)
O1—C2—C1	107.53 (19)	O5—C10—C9	117.54 (14)
O1—C2—H2A	110.2	C12—C11—O5	120.55 (14)
C1—C2—H2A	110.2	C12—C11—C13	127.24 (17)
O1—C2—H2B	110.2	O5—C11—C13	112.20 (14)
C1—C2—H2B	110.2	C11—C12—C8	118.81 (16)
H2A—C2—H2B	108.5	C11—C12—H12	120.6
O2—C3—O1	122.03 (16)	C8—C12—H12	120.6
O2—C3—C4	128.38 (18)	C11—C13—H13A	109.5
O1—C3—C4	109.59 (15)	C11—C13—H13B	109.5
C5—C4—C3	124.97 (16)	H13A—C13—H13B	109.5

C5—C4—H4	117.5	C11—C13—H13C	109.5
C3—C4—H4	117.5	H13A—C13—H13C	109.5
C4—C5—C6	123.81 (14)	H13B—C13—H13C	109.5
C4—C5—C9	123.55 (14)	C7—C14—H14A	109.5
C6—C5—C9	112.62 (14)	C7—C14—H14B	109.5
C7—C6—C5	123.96 (15)	H14A—C14—H14B	109.5
C7—C6—H6	118.0	C7—C14—H14C	109.5
C5—C6—H6	118.0	H14A—C14—H14C	109.5
C6—C7—O3	121.42 (14)	H14B—C14—H14C	109.5
C6—C7—C14	128.16 (16)	C3—O1—C2	116.73 (16)
O3—C7—C14	110.42 (15)	C8—O3—C7	118.41 (12)
O3—C8—C9	123.32 (14)	C11—O5—C10	123.28 (13)
O3—C8—C12	113.58 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry code: (i) x, $-y+1/2$, $z-1/2$.