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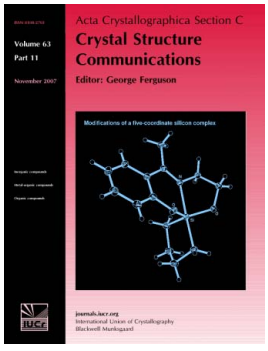

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(*E*)-Ethyl 3-(3,4-dihydroxyphenyl)-prop-2-enoate: a natural polymorph extracted from *Aristotelia chilensis* (Maqui)

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The natural title compound, $C_{11}H_{12}O_4$, extracted from the Chilean native tree *Aristotelia chilensis* (Maqui), is a polymorph of the synthetic *E* form reported by Xia, Hu & Rao [*Acta Cryst.* (2004), E**60**, o913–o914]. Both rotational conformers are identical from a metrical point of view, and only differ in the orientation of the 3,4-dihydroxyphenyl ring with respect to the rest of the molecule, which leads to completely different crystal structure arrangements and packing efficiencies. The reasons behind both reside in the different hydrogen-bonding interactions.

Comment

Aristotelia chilensis (Mol.) Stuntz (Elaeocaepaceae) is an evergreen tree distributed in central and southern Chile and in southwestern Argentina. Folk medicine attributes properties to this tree, such as anti-inflammatory, analgesic and anti-haemorrhagic activities (Bhakuni, 1976). Crushed fresh leaves are used as a poultice for treating burns and counteracting fever (Muñoz *et al.*, 2001). The fruit from *A. chilensis* (commonly known as Maqui) is an edible wild blackberry, recently reported as one of the healthiest exotic berries due to its displaying one of the highest ORAC (Oxygen Radical Absorbance Capacity) antioxidant capacities (Céspedes *et al.*, 2010; Morariou, 2007). The berry presents high concentrations of bioactive agents, such as anthocyanins (*viz*. delphinidin 3-sambubioside-5-glucoside, delphinidin 3,5-diglucoside, delphinidin 3-sambubioside, delphinidin 3-glucoside, cyanidin 3-sambubioside-5-glucoside, cyanidin 3,5-diglucoside, cyanidin 3-sambubioside and cyanidin 3-glucoside; Escribano-Bailón *et*

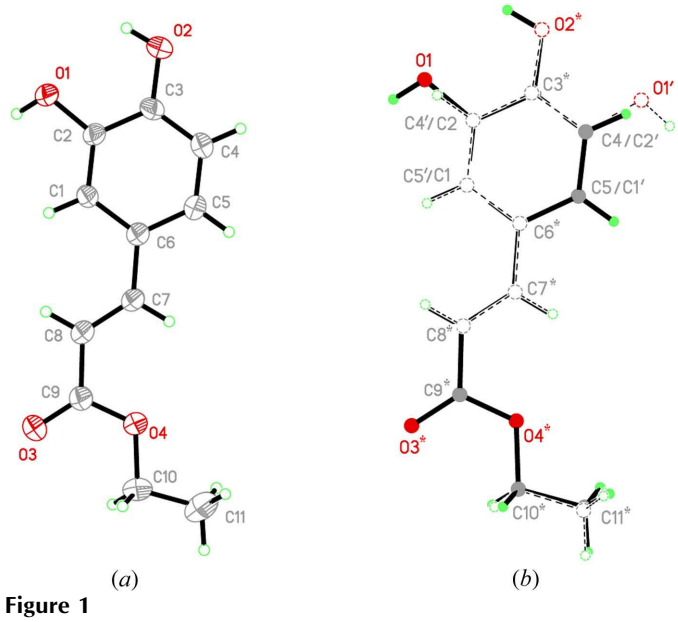

Figure 1
(*a*) The molecular structure of (I), showing he atomic numbering scheme and displacement ellipsoids at the 40% probability level. (*b*) An overlap diagram of (I) (full lines, unprimed labels) and (II) (broken lines, primed labels; Xia *et al.*, 2004). Asterisks denote overlapping similarly named atoms.

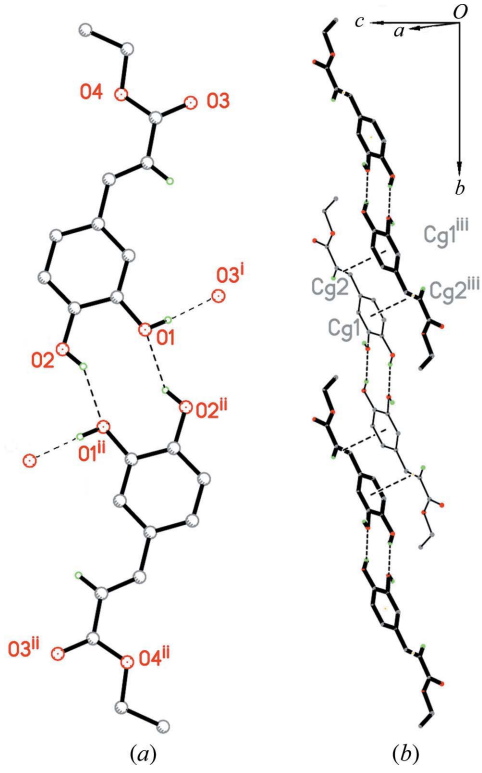

Figure 2
(*a*) The dimeric structure in (I) and (*b*) the π-bonded chain in (I). *Cg*1 is the centroid of the C1–C6 ring and *Cg*2 is the mid-point of the C7═C8 bond. [Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+2, -z$; (iii) $-x, -y+1, -z$.]

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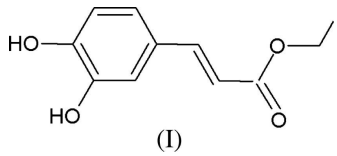
al., 2006) and polyphenols (*viz*. quercetin, rutin and derivatives of coumaric acid; Céspedes *et al.*, 2010).

On the other hand, caffeic acid and its esters have displayed antioxidant, anti-inflammatory, antiproliferative, cytostatic and, most importantly, antineoplastic properties (Ozturk *et al.*, 2012).



(I)

We present here the crystal and molecular structure of a natural derivative from caffeic acid, extracted from the Chilean tree *A. chilensis*, namely (*E*)-ethyl 3-(3,4-dihydroxyphenyl)prop-2-enoate, (I); the synthetic polymorph, also *E*, denoted (II), obtained from a Knoevenagel condensation reaction, has been described previously (Xia *et al.*, 2004). In addition, an exhaustive Raman analysis on potentially useful properties of this synthetic compound as a nonlinear optical (NLO) device has been reported (Bena Jothy *et al.*, 2009).

Fig. 1(*a*) shows the atom-numbering scheme for (I) and Fig. 1(*b*) shows a superposition of molecules (I) and (II), where all non-H atoms except O1 have been used for the least-squares overlap. The only detectable differences at a molecular level derive from the compounds being rotational conformers in the solid state, where the 3,4-dihydroxyphenyl ring is rotated by approximately 180° about the C6—C7 bond with respect to the remainder of the molecule. This puts atoms O1 and C8 in *syn* and *anti* positions in (I) and (II), respectively, as seen in the C5—C6—C7—C8 and C4—C3—O2—H2 torsion angles, with values of ∼180° in (I) and ∼0° in (II) [176.87 (17)/−178.3 (17) and −0.3 (2)/−12.0°, respectively].

Even if in both cases the main 3-(3,4-dihydroxyphenyl)-prop-2-enoate core is basically planar [maximum deviations = 0.076 (2) Å for atom O4 in (I) and 0.039 (2) Å for C7 in (II)], the pendant ethyl group deviates from this plane more significantly in (I) [by 12.1 (2)°; the deviation is only 1.2 (2)° in (II)].

Table 1 presents the hydrogen bonds in (I) and Fig. 2(*a*) shows the bimolecular arrangement generated by the centrosymmetric $R_2^2(10)$ motif built up by the second entry in Table 1. This dimeric entity is the elemental packing 'brick' in (I), as we shall see below. Since the perpendicular distance from the

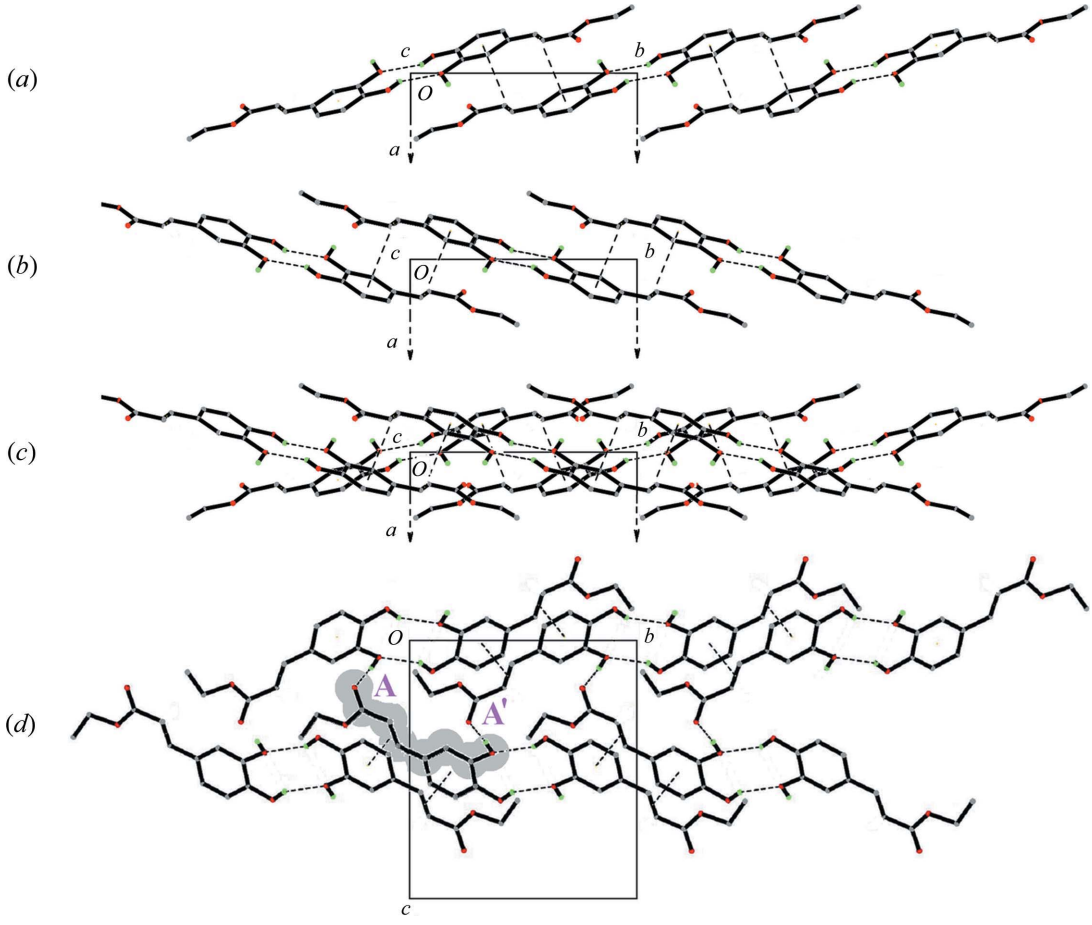


Figure 3
(*a*),(*b*) Packing diagrams of (I) projected down [001], showing two neighbouring chains, *viz*. at $z \sim 0$ in part (*a*) and at $z \sim 0.5$ in part (*b*). (*c*) The complete planar array, showing a superposition of (*a*) and (*b*). (*d*) Similar to part (*c*), but viewed down [100], with the *C*(9) hydrogen-bonding motif highlighted.

dihydroxyphenyl plane in (I) to the nearby centre of inversion is 0.272 (2) Å, the generated dimer presents a 0.54 Å interplanar shift between both parallel aromatic planes.

The packing sequence can be viewed as a two-step process: (i) an initial concatenation of dimers *via* the π–π interaction between the benzene ring and the central double bond of the propenyl group (Table 2 and Fig. 2*b*) generating chains along [010]; (ii) a strong lateral interaction between neighbouring chains related by a 2_1 axis running parallel to, but external from, the chains themselves. Figs. 3(*a*) and 3(*b*) show lateral views of two neighbouring chains ($z \sim 0, \frac{1}{2}$, respectively); dimers in vicinal chains are rotated by 180°, subtending angles of 40.12 (2)° to each other. Figs. 3(*c*) and 3(*d*) show two overlapping views when both types of chains are considered (Fig. 3*c* sideways and Fig. 3*d* normal to the plane). The linkage between chains is achieved through the strong O1—H1···O3^{i} hydrogen bond [symmetry code: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; Table 1, first entry], giving rise to a *C*(9) transverse chain (see **A**···**A′** in Fig. 3*d*).

Fig. 3(*c*) shows that the central core is composed of hydrophilic nuclei, shielded from significant interplanar interactions, with an outer hydrophobic cover of methyl groups. The plane width, as defined by the outermost C11 methyl atoms, is ∼6.35 Å, which with *a* = 7.7326 (9) Å leaves ∼1.40 Å for the interplanar region.

Table 3 presents the hydrogen-bonding interactions for (II) (Xia *et al.*, 2004). There are some analogies with those in (I) but, despite these formal similarities, the final packing arrays are entirely different. The hydrogen bonds involving O2—H2 (entries 2 and 3) generate an $R_1^2(5)$ ring and define, as in (I), the elemental packing 'brick' in the crystal structure, but here it consists of a broad strip running along [010], halved by a 2_1 axis acting as its 'backbone' (Fig. 4*a*). These roughly planar structures (∼19 Å wide and ∼1 Å thick) are almost parallel to the (601) plane. The hydrogen bond involving atom H1 (first entry in Table 3) serves *via* a *C*(9) chain to connect strips into the final packing array, *i.e.* a very broad two-dimensional structure (∼13.68 Å thick) parallel to (001) (Fig. 4*b*). Considering that there are two of these structures (2 × 13.68 = 27.36 Å) per unit-cell *c* translation [25.992 (7) Å], it is apparent that in this case the particular planes interpenetrate, with no interplanar spacing left.

This suggests a better packing efficiency for (II), as shown by the larger calculated densities [1.315 *versus* 1.375 Mg m^{-3} for (I)], as well as packing indices [67.6 for (II) *versus* 70.8 for (I); calculated with *PLATON* (Spek, 2009)].

A check in the Cambridge Structural Database (CSD, Version 5.33; Allen, 2002) for structures closely related to (I) and (II) uncovered a whole family of 3-(3,4-dihydroxyphenyl)prop-2-enoate derivatives, in particular, with pendant alkyl groups (C_nH_{2n+1}), a family in which (I) and (II) would be the *n* = 2 (ethyl) members. Fig. 5 shows schematic views of the complete set, all of them synthetic [which makes (I) the first naturally occurring member]. Inspection of Fig. 5 shows that there are, in addition to the *n* = 2 case herein discussed, other reported cases of polymorphism associated with conformational isomerism [*viz.* the *n* = 1 (methyl) case]. Surprisingly, these particular situations seem to appear only for the shortest chains (*n* = 1 and 2), as if the existence of longer 'tails' would reduce the number of favourable spatial arrangements into a

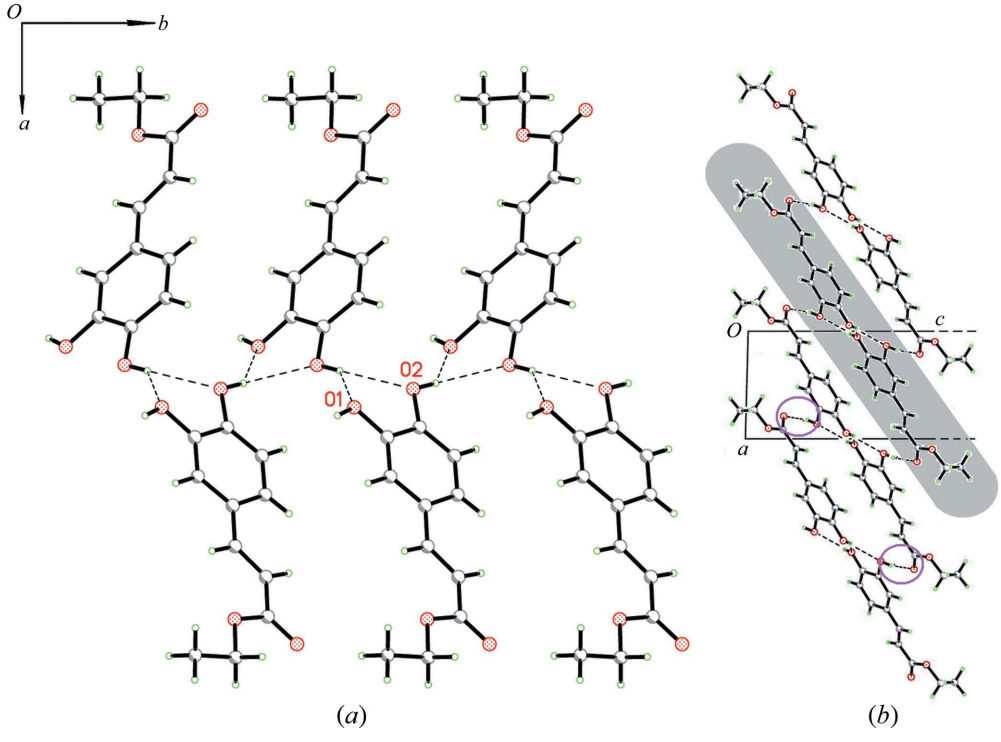


Figure 4
Packing diagrams of (II), showing (*a*) the elemental hydrogen-bonded strip, viewed down *c*. (*b*) A view down [010] of the broad planar array formed by strips connected by the (encircled) O—H···O hydrogen bonds (first entry in Table 3). One of the strips, viewed in projection, is highlighted.

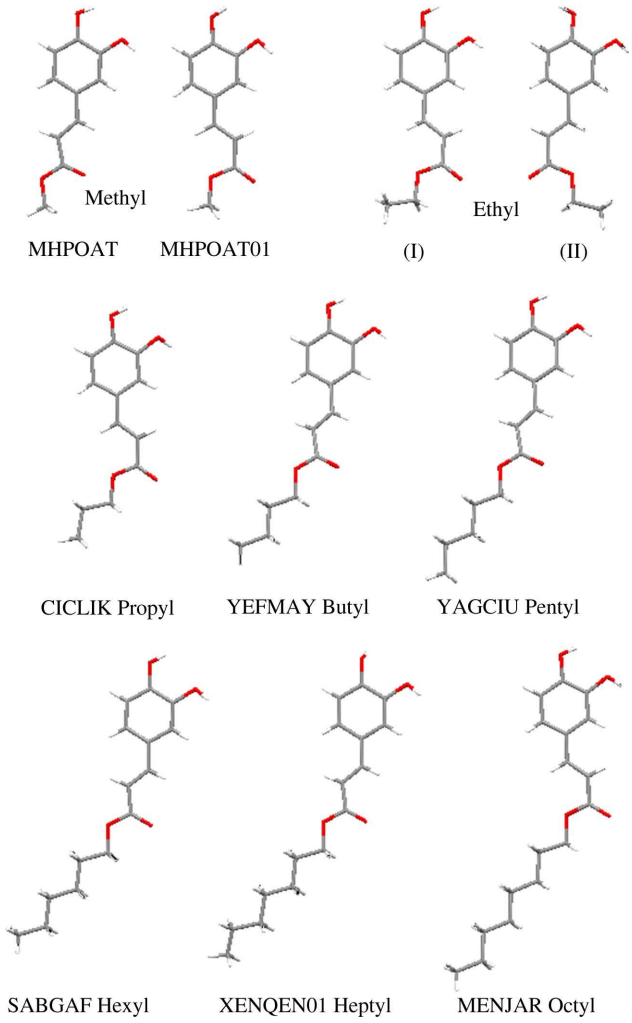


Figure 5
Structural schemes for all members of the (C_nH_{2n+1}) 3-(3,4-dihydroxyphenyl)prop-2-enoate family. (For CSD refcodes, see Table 5.)

single feasible one. This latter assumption seems to be supported by the fact that structures with n = 4–7 are isostructural (Table 4), with identical conformations (Fig. 5). Regarding the main difference between structures (I) and (II), *viz*. the relative orientation of the O—H groups, there seems to be a marked preference for the conformation present in (I); that in (II) appears to be highly unusual.

Experimental

Aristotelia chilensis (Maqui) was collected in Concepción, VIII Region of Chile (36° 50′ 00″ S and 73° 01′ 54″ W) in February 2012.

Leaves (2 kg) were dried at 313 K, powdered and extracted with ethyl acetate three times (6 l). The solvent was concentrated in a vacuum, producing 40 g of a dark gum which was purified by silica-gel column chromatography, eluting with increasing polarity solvents from hexane to ethyl acetate. This was followed by thin-layer chromatography and similar fractions were concentrated together giving five fractions. A white solid was obtained from the 30% EtOAc–70% hexane fraction and this was recrystallized from ethyl acetate producing large colourless crystals which were suitable for X-ray diffraction analysis.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.86 (2)	1.82 (2)	2.6801 (18)	175 (2)
O2—H2···O1^{ii}	0.85 (2)	2.07 (2)	2.8189 (17)	145 (2)

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

Table 2
π–π contacts (Å, °) for (I).

*Cg*1 is the centroid of the C1–C6 ring and *Cg*2 is the mid-point of the C7═C8 bond. ccd is the center-to-center distance (distance between centroids), ipd is the interplanar distance (distance from one plane to the neighbouring centroid) and sa is the mean slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000).

Group 1···Group 2	ccd	ipd	sa
*Cg*1···*Cg*2^{iii}	3.435	3.4201	5.3

Symmetry code: (iii) $-x, -y+1, -z$.

Table 3
Hydrogen-bond geometry (Å, °) for (II) (Xia *et al.*, 2004).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.82	1.92	2.7308 (17)	170
O2—H2···O2^{ii}	0.82	2.30	3.0364 (18)	150
O2—H2···O1^{ii}	0.82	2.22	2.8699 (17)	135

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

Crystal data

$C_{11}H_{12}O_4$
M_r = 208.21
Monoclinic, $P2_1/c$
a = 7.7326 (9) Å
b = 10.9427 (10) Å
c = 12.6997 (13) Å
β = 101.948 (11)°
V = 1051.3 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 291 K
0.42 × 0.34 × 0.28 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.95, T_{max} = 0.98
4801 measured reflections
2416 independent reflections
1699 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.119
S = 1.03
2416 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

All H atoms were found in a difference map, but C-bound H atoms were repositioned at their ideal values, with methylene C—H = 0.97 Å, aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å, and allowed to ride, with U_{iso}(H) = kU_{eq}(C), where k = 1.2 for methylene and aromatic H atoms, and k = 1.5 for methyl H atoms. Hydroxy H atoms were freely refined.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*;

Table 4
Comparative data for the (C_nH_{2n+1}) 3-(3,4-dihydroxyphenyl)prop-2-enoate family.

n	CSD refcode (reference)	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ*(°)	D_c (Mg m^{-3})	Conformational isomer
1	MHPOAT (Chen *et al.*, 1979)	$P2_1/n$	11.377 (9)	11.561 (5)	7.146 (2)	90.00	104.50 (5)	90.00	1.417	*anti*
1	MHPOAT01 (Wang, Meng *et al.*, 2011)	$P\overline{1}$	5.129 (5)	9.969 (8)	10.586 (9)	117.63 (2)	97.92 (2)	94.32 (2)	1.375	*syn*
2	(I) (this work)	$P2_1/c$	7.7326 (9)	10.9427 (10)	12.6997 (13)	90.00	101.948 (11)	90.00	1.315	*anti*
2	(II) (Xia *et al.*, 2004)	$P2_1/c$	6.659 (2)	5.811 (2)	25.992 (7)	90.00	91.51 (2)	90.00	1.376	*syn*
3	CICLIK (Xia *et al.*, 2007)	$C2/c$	18.883 (3)	10.965 (2)	12.478 (2)	90.00	116.95 (2)	90.00	1.282	*syn*
4	YEFMAY (Xia *et al.*, 2006*a*)	$P\overline{1}$	5.282 (5)	10.490 (5)	11.558(7	83.95 (6)	84.31 (7)	81.14 (6)	1.251	*syn*
5	YAGCIU (Wang, Gu *et al.*, 2011)	$P\overline{1}$	5.307 (2)	10.567 (2)	11.816 (2)	90.96 (3)	91.84 (3)	98.60 (3)	1.270	*syn*
6	SABGAF (Wang *et al.*, 2012)	$P\overline{1}$	5.292 (2))	10.689 (2)	12.732 (3)	95.45 (3)	92.76 (3)	96.84 (3)	1.235	*syn*
7	XENQEN01 (Xia *et al.*, 2008)	$P\overline{1}$	5.296 (3)	10.711 (13)	13.870 (4)	98.84 (7)	90.97 (4)	96.77 (7)	1.198	*syn*
8	MENJAR (Xia *et al.*, 2006*b*)	$P\overline{1}$	5.454 (2)	12.152 (5)	12.584 (5)	87.76 (2)	80.56 (2)	81.39 (2)	1.194	*anti*

program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3110). Services for accessing these data are described at the back of the journal.

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supplementary materials

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(*E*)-Ethyl 3-(3,4-dihydroxyphenyl)prop-2-enoate: a natural polymorph extracted from *Aristotelia chilensis* (Maqui)

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Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(*E*)-Ethyl 3-(3,4-dihydroxyphenyl)prop-2-enoate

Crystal data

$C_{11}H_{12}O_4$
$M_r = 208.21$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.7326$ (9) Å
$b = 10.9427$ (10) Å
$c = 12.6997$ (13) Å
$\beta = 101.948$ (11)°
$V = 1051.3$ (2) Å^3
$Z = 4$
$F(000) = 440$
$D_x = 1.315$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1254 reflections
$\theta = 3.7$–29.2°
$\mu = 0.10$ mm^{-1}
$T = 291$ K
Block, colourless
0.42 × 0.34 × 0.28 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans, thick slices (1°)
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{min} = 0.95$, $T_{max} = 0.98$
4801 measured reflections
2416 independent reflections
1699 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 29.2°$, $\theta_{min} = 3.7°$
$h = -6 \rightarrow 9$
$k = -13 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
$S = 1.03$
2416 reflections
146 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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.1986P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.014 (3)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.00655 (17)	0.86442 (10)	0.06502 (10)	0.0485 (3)
H1	−0.071 (3)	0.8341 (18)	0.1062 (16)	0.063 (6)*
O2	0.10857 (18)	0.90070 (11)	−0.12009 (10)	0.0520 (4)
H2	0.054 (3)	0.952 (2)	−0.0881 (19)	0.092 (9)*
O3	0.21251 (16)	0.26008 (10)	0.31465 (10)	0.0531 (4)
O4	0.32630 (16)	0.21932 (10)	0.17089 (9)	0.0505 (3)
C1	0.11952 (19)	0.66131 (13)	0.08159 (12)	0.0354 (3)
H1A	0.0810	0.6479	0.1453	0.042*
C2	0.08573 (19)	0.77133 (12)	0.02941 (12)	0.0344 (3)
C3	0.1441 (2)	0.79284 (13)	−0.06617 (12)	0.0383 (4)
C4	0.2359 (2)	0.70332 (15)	−0.10765 (14)	0.0468 (4)
H4	0.2757	0.7175	−0.1708	0.056*
C5	0.2686 (2)	0.59272 (15)	−0.05538 (13)	0.0447 (4)
H5	0.3301	0.5326	−0.0842	0.054*
C6	0.21149 (19)	0.56917 (13)	0.03981 (12)	0.0351 (4)
C7	0.24649 (19)	0.44970 (13)	0.09088 (12)	0.0366 (4)
H7	0.3013	0.3924	0.0547	0.044*
C8	0.2086 (2)	0.41411 (13)	0.18329 (13)	0.0395 (4)
H8	0.1537	0.4700	0.2208	0.047*
C9	0.2475 (2)	0.29288 (14)	0.22975 (13)	0.0394 (4)
C10	0.3621 (3)	0.09494 (15)	0.20958 (16)	0.0573 (5)
H10A	0.2563	0.0586	0.2261	0.069*
H10B	0.4541	0.0945	0.2744	0.069*
C11	0.4198 (3)	0.02527 (18)	0.12296 (18)	0.0673 (6)
H11A	0.3307	0.0307	0.0581	0.101*
H11B	0.4373	−0.0588	0.1440	0.101*
H11C	0.5286	0.0588	0.1106	0.101*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0682 (8)	0.0298 (6)	0.0568 (7)	0.0073 (5)	0.0345 (6)	0.0050 (5)
O2	0.0750 (9)	0.0359 (6)	0.0516 (7)	0.0062 (6)	0.0280 (6)	0.0122 (6)
O3	0.0727 (8)	0.0459 (7)	0.0485 (7)	0.0054 (6)	0.0304 (6)	0.0081 (6)
O4	0.0697 (8)	0.0386 (6)	0.0498 (7)	0.0166 (5)	0.0278 (6)	0.0089 (5)
C1	0.0434 (8)	0.0320 (7)	0.0333 (8)	−0.0017 (6)	0.0139 (6)	0.0006 (7)

C2	0.0397 (8)	0.0270 (7)	0.0383 (8)	−0.0015 (6)	0.0125 (6)	−0.0027 (6)
C3	0.0456 (9)	0.0323 (8)	0.0388 (8)	−0.0039 (6)	0.0126 (7)	0.0044 (7)
C4	0.0603 (10)	0.0438 (9)	0.0430 (9)	0.0028 (8)	0.0259 (8)	0.0051 (8)
C5	0.0550 (10)	0.0393 (9)	0.0448 (9)	0.0072 (7)	0.0221 (8)	−0.0008 (8)
C6	0.0379 (8)	0.0322 (8)	0.0363 (8)	0.0007 (6)	0.0099 (6)	−0.0007 (6)
C7	0.0404 (8)	0.0308 (7)	0.0400 (8)	0.0029 (6)	0.0116 (6)	−0.0019 (7)
C8	0.0468 (9)	0.0321 (8)	0.0416 (9)	0.0029 (6)	0.0139 (7)	−0.0025 (7)
C9	0.0428 (8)	0.0375 (8)	0.0403 (8)	0.0000 (6)	0.0140 (7)	0.0006 (7)
C10	0.0714 (13)	0.0425 (9)	0.0603 (11)	0.0181 (9)	0.0189 (10)	0.0138 (9)
C11	0.0697 (13)	0.0522 (11)	0.0771 (14)	0.0152 (9)	0.0085 (11)	−0.0103 (10)

Geometric parameters (Å, º)

O1—C2	1.3730 (17)	C5—C6	1.394 (2)
O1—H1	0.86 (2)	C5—H5	0.9300
O2—C3	1.3637 (18)	C6—C7	1.460 (2)
O2—H2	0.85 (2)	C7—C8	1.326 (2)
O3—C9	1.2189 (18)	C7—H7	0.9300
O4—C9	1.3289 (18)	C8—C9	1.458 (2)
O4—C10	1.4540 (19)	C8—H8	0.9300
C1—C2	1.373 (2)	C10—C11	1.481 (3)
C1—C6	1.400 (2)	C10—H10A	0.9700
C1—H1A	0.9300	C10—H10B	0.9700
C2—C3	1.400 (2)	C11—H11A	0.9600
C3—C4	1.377 (2)	C11—H11B	0.9600
C4—C5	1.378 (2)	C11—H11C	0.9600
C4—H4	0.9300		
C2—O1—H1	108.7 (13)	C8—C7—C6	127.01 (14)
C3—O2—H2	113.5 (16)	C8—C7—H7	116.5
C9—O4—C10	117.02 (13)	C6—C7—H7	116.5
C2—C1—C6	120.62 (14)	C7—C8—C9	124.11 (15)
C2—C1—H1A	119.7	C7—C8—H8	117.9
C6—C1—H1A	119.7	C9—C8—H8	117.9
O1—C2—C1	123.47 (13)	O3—C9—O4	122.06 (14)
O1—C2—C3	116.34 (13)	O3—C9—C8	124.12 (14)
C1—C2—C3	120.18 (13)	O4—C9—C8	113.82 (13)
O2—C3—C4	119.33 (14)	O4—C10—C11	107.24 (15)
O2—C3—C2	120.90 (13)	O4—C10—H10A	110.3
C4—C3—C2	119.76 (14)	C11—C10—H10A	110.3
C3—C4—C5	119.89 (14)	O4—C10—H10B	110.3
C3—C4—H4	120.1	C11—C10—H10B	110.3
C5—C4—H4	120.1	H10A—C10—H10B	108.5
C4—C5—C6	121.35 (14)	C10—C11—H11A	109.5
C4—C5—H5	119.3	C10—C11—H11B	109.5
C6—C5—H5	119.3	H11A—C11—H11B	109.5
C5—C6—C1	118.19 (13)	C10—C11—H11C	109.5
C5—C6—C7	119.20 (13)	H11A—C11—H11C	109.5
C1—C6—C7	122.59 (13)	H11B—C11—H11C	109.5

C6—C1—C2—O1	178.75 (14)	C2—C1—C6—C5	0.7 (2)
C6—C1—C2—C3	−0.6 (2)	C2—C1—C6—C7	−178.33 (14)
C1—C2—C3—O2	178.73 (15)	C5—C6—C7—C8	176.87 (17)
O1—C2—C3—O2	−0.7 (2)	C1—C6—C7—C8	−4.1 (3)
C1—C2—C3—C4	0.1 (2)	C6—C7—C8—C9	−179.98 (15)
O1—C2—C3—C4	−179.30 (15)	C10—O4—C9—O3	2.7 (2)
O2—C3—C4—C5	−178.36 (16)	C10—O4—C9—C8	−177.25 (15)
C2—C3—C4—C5	0.3 (3)	C7—C8—C9—O3	−179.93 (17)
C3—C4—C5—C6	−0.2 (3)	C7—C8—C9—O4	0.1 (2)
C4—C5—C6—C1	−0.3 (3)	C9—O4—C10—C11	170.22 (16)
C4—C5—C6—C7	178.76 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.86 (2)	1.82 (2)	2.6801 (18)	175 (2)
O2—H2···O1^{ii}	0.85 (2)	2.07 (2)	2.8189 (17)	145 (2)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1/2; (ii) −*x*, *y*+5/2, −*z*+1/2.

Table 2. π–π contacts (Å, °) for (I)

Group 1···Group 2	ccd	ipd	sa
Cg1···Cg2^{iii}	3.435	3.4201	5.3

Symmetry code: (iii) -x, -y+1, -z *Cg*1 is the centroid of the C1–C6 ring and *Cg*2 is the mid-point of the C7═C8 bond. Notes: ccd is the center-to-center distance (distance between centroids), ipd is the interplanar distance (distance from one plane to the neighbouring centroid) and sa is the mean slippage angle (angle subtended by the intercentroid vector to the plane normal). For details, see Janiak (2000).

Table 3. Hydrogen-bond geometry (Å, °) for (II)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.82	1.92	2.7308 (17)	170
O2—H2···O2^{ii}	0.82	2.30	3.0364 (18)	150
O2—H2···O1^{ii}	0.82	2.22	2.8699 (17)	135

Symmetry codes: (i) -x-2, y+1/2, -z+1/2; (ii) x+1, y-1, z.

Table 4. Comparative data for the (C_nH_{2n+1})-3-(3,4-dihydroxyphenyl)prop-2-enoate family.

n	CSD refcode (reference)	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ*(°)	D_c (Mg Mm^{-3})	Conformational isomer
1	MHPOAT (Chen *et al.*, 1979)	$P2_1/n$	11.377 (9)	11.561 (5)	7.146 (2)	90.00	104.50 (5)	90.00	1.417	*Z*
1	MHPOAT01 (Wang, Meng *et al.*, 2011)	$P\bar{1}$	5.129 (5)	9.969 (8)	10.586 (9)	117.63 (2)	97.92 (2)	94.32 (2)	1.375	*E*
2	(I) (this work)	$P2_1/c$	7.7326 (9)	10.9427 (10)	12.6997 (13)	90.00	101.948 (11)	90.00	1.315	*Z*
2	(II) (Xia *et al.*, 2004)	$P2_1/c$	6.659 (2)	5.811 (2)	25.992 (7)	90.00	91.51 (2)	90.00	1.376	*E*

3	CICLIK (Xia *et al.*, 2007)	*C*2/*c*	18.883 (3)	10.965 (2)	12.478 (2)	90.00	116.95 (2)	90.00	1.282 *E*
4	YEFMAY (Xia *et al.*, 2006a)	$P\overline{1}$	5.282 (5)	10.490 (5)	11.558(7	83.95 (6)	84.31 (7)	81.14 (6)	1.251 *E*
5	YAGCIU (Wang, Gu *et al.*, 2011)	$P\overline{1}$	5.307 (2)	10.567 (2)	11.816 (2)	90.96 (3)	91.84 (3)	98.60 (3)	1.270 *E*
6	SABGAF (Wang *et al.*, 2012)	$P\overline{1}$	5.292 (2))	10.689 (2)	12.732 (3)	95.45 (3)	92.76 (3)	96.84 (3)	1.235 *E*
7	XENQEN01 (Xia *et al.*, 2008)	$P\overline{1}$	5.296 (3)	10.711 (13)	13.870 (4)	98.84 (7)	90.97 (4)	96.77 (7)	1.198 *E*
8	MENJAR (Xia *et al.*, 2006b)	$P\overline{1}$	5.454 (2)	12.152 (5)	12.584 (5)	87.76 (2)	80.56 (2)	81.39 (2)	1.194 *Z*