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Redetermination of *trans*-*β*-hydromuconic acid

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The title compound (systematic name: *trans*-hex-3-enedioic acid), $C_6H_8O_4$, (I), is located on an inversion centre. A less accurate room-temperature structure has been reported previously [Ganis & Martuscelli (1966). *Ric. Sci.* **36**, 439], without the position of the H atom involved in hydrogen bonding. The carboxylic acid groups of (I) link molecules across inversion centres through O—H···O hydrogen-bonded pairs. The result of these interactions is the formation of chains with the graph-set description $C_2^2(18)$, which run along the *c* axis. The significance of this study lies in the analysis of the interactions occurring *via* hydrogen bonds, as well as in the comparison drawn between the molecular structure of (I) and the structures of several other acid derivatives possessing two carboxylic acid groups.

Comment

trans-Hex-3-enedioic acid, (I), also known as *trans*-*β*-hydromuconic acid, is a human dicarboxylic acid metabolite of unsaturated fatty acids produced by the *β*-oxidation of *trans*-oct-3-enedioic acid (Jin & Tserng, 1989). The metabolic origin of *trans*-oct-3-enedioic acid is likely to be *trans*-9,10-octadecenoic acid, an unnatural fatty acid contained in partially hydrogenated oils. Thus, the title compound is a biologically important compound, which has attracted attention in relation to metabolic disorder of fatty acid oxidation in humans [*e.g.* dicarboxylic aciduria or unexplained attacks of lethargy and hypotonia, presumably related to episodes of fever and/or insufficient food intake (Tanaka & Hine, 1982; Tserng *et al.*, 1990)] for which urinary excretions were reported to be increased. *trans*-Hex-3-enedioic acid is also of great importance for the synthesis of 3-alkylpyridine compounds, which are plausible biosynthetic precursors for the complex manzamine and related alkaloids (Baldwin *et al.*, 2000). The title compound can be used as the starting material to prepare pent-4-enoic acid, which is formed by the pyrolysis of (I) (Shulman & Osteraas, 1963).

(I)

trans-*β*-Hydromuconic acid and adipic acid were the subjects of a study of the generation mechanism of the IR spectra of hydrogen-bonded molecular crystals (Flakus & Jabłońska, 2004; Flakus *et al.*, 2006; Flakus & Hachuła, 2008; Hachuła, Nowak & Kusz, 2008; Hachuła, Pyzik, Nowak & Kusz, 2008). The IR spectra measurements of polycrystalline and monocrystalline samples of dicarboxylic acid derivatives, as well as theoretical analysis of the results, mainly focused on spectral effects corresponding to the intensity distribution, the influence of temperature, the linear dichroism and the isotopic substitution of deuterium in the above-mentioned molecules measured in the frequency range of the hydrogen and deuterium stretching vibration bands, *viz.* ν_{O-H} and ν_{O-D}, respectively. The spectral studies were preceded by analysis of the crystal X-ray structure of the measured compounds. The crystal structure of adipic acid has been described previously (Housty & Hospital, 1965). The molecules of this compound form one-dimensional chains, with graph-set description $C_2^2(18)$, along the crystallographic *c* axis, in which the carboxylic acid groups are linked to each other *via* cyclic pairs of O—H···O bonds. The 295 K structure of (I) has already been reported (Ganis & Martuscelli, 1966) with an *R* factor of 12.0%. Thus, the precision of this structure determination was limited, and additionally the position of the hydrogen-bonded H atom was not determined. In order to study interactions occurring *via* hydrogen bonding and molecular packing in this compound, we have now redetermined the structure of (I) using diffraction data collected at 298 K. Comparison of the unit-cell parameters of these structure determinations shows that there are no significant differences between them, and both the molecular packing and the crystal system remain unchanged. Ganis & Martuscelli (1966) described their structure in the standard space group $P2_1/c$, with a β angle of 134°. The matrix $(101/010/\overline{1}00)$ transforms their $P2_1/c$ cell into a comparable $P2_1/n$ cell with $a = 7.90$ Å, $b = 4.67$ Å, $c = 9.40$ Å and $\beta = 105°$, sufficiently close to the current values to be

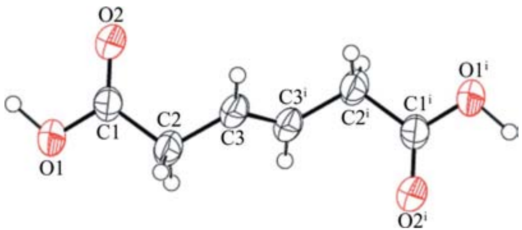

Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x$, $-y$, $-z$.]

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identical to the current unit cell. It can be mentioned that the present redetermination provides a much lower *R* value (3.58%) and the precision of the geometric parameters considerably increases [*viz.* σ(C—C) = 0.002 Å].

Compound (I) crystallizes with only one half-molecule in the asymmetric unit (Fig. 1). The molecule of (I) is in an extended conformation, so that atoms C2, C3, C3^{i} and C2^{i} are planar [symmetry code: (i) $-x, -y, -z$]. This planarity of the carbon chain is typical for even dicarboxylic acids (Thalladi *et al.*, 2000). The single C—C bond lengths (Table 1) are similar to those in another saturated dicarboxylic acid possessing six C atoms (*i.e.* in adipic acid; C1—C2 = 1.487 Å and C2—C3 = 1.506 Å; Housty & Hospital, 1965). The ethylene bond length (C3═C3^{i}) differs slightly from the values found in similar structures, for example, maleic acid (1.337 Å; James & Williams, 1974), α-fumaric acid (1.348 Å; Brown, 1966), β-fumaric acid (1.315 Å; Bednowitz & Post, 1966), and other unsaturated carboxylic acid derivatives, such as acrylic acid [1.3285 (11) Å; Boese *et al.*, 1999] or crotonic acid (1.293 Å; Shimizu *et al.*, 1974). Moreover, this bond distance in (I) is considerably shorter than the value reported by Sutton (1965) for simple C═C double bonds (1.335 Å).

The crystal structure of (I) differs slightly from those in other even, saturated and unsaturated, dicarboxylic acids, for example, maleic acid (James & Williams, 1974), α-fumaric acid (Brown, 1966), β-fumaric acid (Bednowitz & Post, 1966), adipic acid (Housty & Hospital, 1965) and suberic acid (Gao *et al.*, 1994). Firstly, the plane of the carboxyl group in (I) is twisted out of the plane of the chain zigzag (see the torsion angles given in Table 1). In some even diacids, the carboxylic acid groups are almost coplanar with the carbon chain, for example, in β-fumaric acid (O2—C1—C2—C3 = 179.26° and O1—C1—C2—C3 = 0.69°; Bednowitz & Post, 1966) or *trans*,*trans*-muconic acid (O2—C1—C2—C3 = 2.34° and O1—C1—C2—C3 = 177.96°; Bernstein & Leiserowitz, 1972). Secondly, the dihedral angle between the plane of the carbon chain and the plane of the O1/C1/O2 carboxylic acid group is 52.85 (20)°. By comparison, this angle is about 2.32° in maleic acid (James & Williams, 1974), 1.47° in α-fumaric acid (Brown, 1966), 1.36° in β-fumaric acid (Bednowitz & Post, 1966) and 0.51° in *trans*,*trans*-muconic acid (Bednowitz & Post, 1966). Similar values of this angle can be found in saturated dicarboxylic acids, for example, 6.19° in adipic acid (Housty & Hospital, 1965), 6.43° in suberic acid (Gao *et al.*, 1994) and 2.07° in sebacic acid (Bond *et al.*, 2001). Thus, the twisting of the carboxylic acid group in (I) seems to cause the distortion of the molecule as a whole and introduces severe torsions into the carbon chains (Thalladi *et al.*, 2000). The C—O and C═O bond distances in (I) are similar to those in other structures, for example, maleic acid (C1—O1 = 1.3 Å and C1—O2 = 1.222 Å; James & Williams, 1974), α-fumaric acid (C1—O1 = 1.287 Å and C1—O2 = 1.234 Å; Brown, 1966), β-fumaric acid (C1—O1 = 1.289 Å and C1—O2 = 1.228 Å; Bednowitz & Post, 1966) or *trans*,*trans*-muconic acid (C1—O1 = 1.297 Å and C1—O2 = 1.234 Å; Bernstein & Leiserowitz, 1972). Thus, these C—O and C═O bond distances in (I) are in normal ranges and are also comparable to the mean values given by Allen *et al.* (1987) for a variety of carboxylic acid groups (C—OH = 1.308 Å and C═O = 1.214 Å). The bond-angle values at the central C atom in the carboxylic acid group also agree with the mean values specified by Borthwick (1980) for a typical carboxylic acid group [O2—C1—C2 = 123 (2)° and O1—C1–C2 = 112 (2)°].

The molecules of (I) lie on inversion centres with an all-*trans* conformation. Each of these molecules has two terminal carboxylic acid groups, which link the molecules across an inversion centre through two O—H···O hydrogen bonds. Atom O1 of the OH group in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H1, to carbonyl atom O2 belonging to the molecule at ($-x, -y, -z + 1$), and in turn carbonyl atom O2 in the molecule at (x, y, z) is an acceptor in a hydrogen bond to the OH group of the molecule at ($-x, -y, -z + 1$) (Fig. 2 and Table 2). These interactions lead to the formation of cyclic dimers with a graph-set motif of $R_2^2(8)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999). The carboxy dimer motifs connect lateral molecules in an end-to-end manner to generate infinite hydrogen-bonded chains [graph-set $C_2^2(18)$] that run along the *c* axis. The same graph-set motif of $C_2^2(18)$ is found in most, saturated as well as unsaturated, dicarboxylic acids, with some exceptions (such as the α form of oxalic acid or some 1,2-disubstituted acids). The

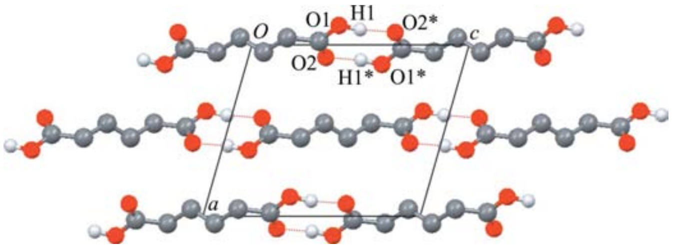

Figure 2
Part of the crystal structure of (I), viewed along the *b* axis, showing the $R_2^2(8)$ rings. Atoms marked with an asterisk (*) are at the symmetry position ($-x, -y, -z + 1$). The dashed lines indicate the hydrogen-bond interactions. For the sake of clarity, all H atoms bonded to C atoms have been omitted.

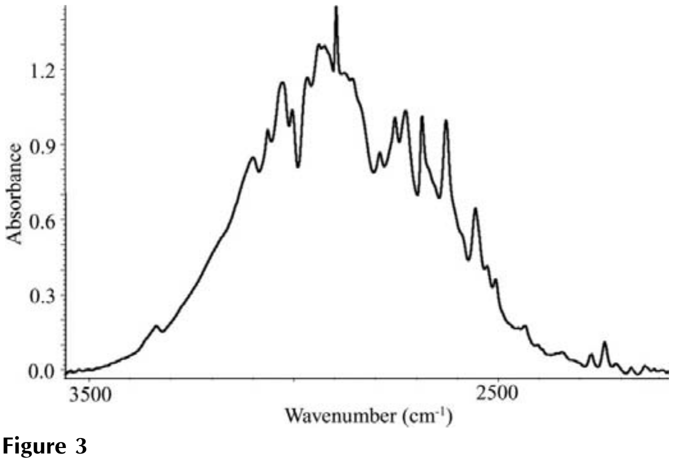

Figure 3
The IR spectrum of the *trans*-β-hydromuconic acid sample dispersed in a KBr pellet.

molecules of the α form of oxalic acid are connected through O—H···O hydrogen bonds, forming a catemer motif (Derissen & Smith, 1974). 1,2-Disubstituted acids, such as maleic acid or furan-3,4-dicarboxylic acid, are linked by both intra- and intermolecular hydrogen bonds, resulting in infinite chains (Leiserowitz, 1976).

The polycrystalline spectrum of (I) is shown in Fig. 3. From the values of the H—O and O···O distances as well the O—H···O angle recorded in Table 2, it can be seen that the hydrogen bond in (I) is of medium strength (Desiraju & Steiner, 1999; Steiner, 2002). In addition, the $\nu_{\rm O-H}$ stretching vibration band of (I) covers a broad frequency range of 3500–2100 cm^{-1}, and the polycrystalline OH band is shifted towards lower frequencies by *ca* 620 cm^{-1} in relation to the unperturbed value of 3570 cm^{-1}. This shift in the OH stretching frequency proves that the O—H···O hydrogen bond is medium strong. A familiar correlation between the hydrogen-bond energy and the frequency shift of the hydrogen (or deuteron) stretching vibration band is used to justify this statement (Hadži & Bratos, 1976; Libowitzky, 1999). Judging from the O···O bond length, the O—H···O hydrogen bond between two *trans*-β-hydromuconic acid molecules appears to be slightly weaker than the hydrogen bond involving two adipic acid molecules (O···O = 2.642 Å). However, this O—H···O bond is stronger than those in α-fumaric acid (O···O = 2.684 Å) or β-fumaric acid (O···O = 2.673 Å). Consequently, the stronger O—H···O hydrogen bonds correspond to a larger frequency shift. It can also be noted that the O—H bond length in the title compound is comparable to the mean value reported by Allen *et al.* (1987) for the hydroxy group in carboxylic acid systems (O—H = 1.015 Å).

Experimental

trans-β-Hydromuconic acid (98% pure) was purchased from Sigma–Aldrich. Slow crystallization from an acetone solution over a period of several days at room temperature afforded single crystals of (I) suitable for X-ray diffraction.

Crystal data

$C_6H_8O_4$
M_r = 144.12
Monoclinic, $P2_1/n$
a = 7.781 (2) Å
b = 4.665 (1) Å
c = 9.516 (2) Å
β = 106.01 (3)°
V = 332.01 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 298 (2) K
0.28 × 0.14 × 0.08 mm

Data collection

Oxford Diffraction KM-4 diffractometer with a Sapphire3 CCD detector
1971 measured reflections
582 independent reflections
441 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.108
S = 1.00
582 reflections
50 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3022 (18)	C2—C3	1.484 (2)
O2—C1	1.2109 (19)	C3—C3$^{\rm i}$	1.306 (3)
C1—C2	1.493 (2)		
O2—C1—C2	123.20 (14)	O1—C1—C2	113.72 (14)
O2—C1—C2—C3	−8.2 (2)	C1—C2—C3—C3$^{\rm i}$	−124.0 (2)
O1—C1—C2—C3	171.94 (14)		

Symmetry code: (i) $-x, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2$^{\rm ii}$	1.02 (2)	1.66 (2)	2.6680 (16)	174 (2)

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

The one H atom of the asymmetric unit that takes part in hydrogen bonding was located in a difference Fourier map and was refined freely with an isotropic displacement parameter. Other H atoms were introduced in geometrically idealized positions and allowed for with an appropriate riding model, with C—H distances of 0.99 (CH_2) and 0.96 Å (CH), and with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3251). Services for accessing these data are described at the back of the journal.

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