Data collection

AFC-6S diffractometer
$\omega/2\theta$ scans
Absorption correction: azimuthal scans (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.79, T_{max} = 1.0
997 measured reflections
997 independent reflections
789 observed reflections [$I>2\sigma(I)$]

R_{int} = 0.065
θ_{max} = 25°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -11 \rightarrow 10$
3 standard reflections monitored every 150 reflections intensity variation: 20%

Refinement

Refinement on F
Final R = 0.036
wR = 0.044
S = 1.95
789 reflections
99 parameters
All H-atom parameters refined

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: MSC/AFC diffractometer control. Cell refinement: MSC/AFC diffractometer control. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl(1)	0.86304 (8)	0	0.05118 (10)	0.0514 (5)
Cl(8)	0.66142 (7)	0	0.55819 (10)	0.0532 (5)
C(1)	0.7913 (3)	0	0.1873 (4)	0.036 (1)
C(2)	0.7201 (2)	0.1417 (3)	0.1745 (3)	0.046 (1)
C(3)	0.6658 (2)	0.1406 (3)	0.3007 (3)	0.046 (1)
C(4)	0.5399 (2)	0.1338 (5)	0.2432 (4)	0.075 (2)
O(5)	0.5029 (2)	0	0.1598 (4)	0.087 (2)
C(8)	0.7080 (2)	0	0.3978 (3)	0.035 (1)
C(9)	0.8352 (3)	0	0.4496 (4)	0.035 (1)
N(10)	0.8731 (2)	0	0.3329 (3)	0.038 (1)
O(9)	0.8921 (2)	0	0.5789 (2)	0.046 (1)

Table 2. *Geometric parameters* (Å, °)

Cl(1)—C(1)	1.786 (4)	C(3)—C(8)	1.535 (3)
Cl(8)—C(8)	1.787 (3)	C(4)—O(5)	1.413 (4)
C(1)—C(2)	1.518 (3)	C(8)—C(9)	1.539 (4)
C(1)—N(10)	1.457 (4)	C(9)—N(10)	1.330 (4)
C(2)—C(3)	1.548 (4)	C(9)—O(9)	1.222 (4)
C(3)—C(4)	1.525 (4)		
Cl(1)—C(1)—C(2)	111.1 (2)	Cl(8)—C(8)—C(3)	111.4 (2)
Cl(1)—C(1)—N(10)	108.2 (2)	Cl(8)—C(8)—C(9)	108.0 (2)
C(2)—C(1)—C(2)	109.7 (3)	C(3)—C(8)—C(3)	106.8 (3)
C(2)—C(1)—N(10)	108.3 (2)	C(3)—C(8)—C(9)	109.6 (2)

A mixture of diallyl ether (7.01 g, 71.5 mmol) and 3,5,6-trichloro-1,2,4-triazine (2.00 g, 10.8 mmol) sealed *in vacuo* in a Rotaflo tube (*ca* 50 ml) and treated at 343 K for 4 d gave nitrogen (0.19 g, 6.8 mmol, 63%), unchanged diallyl ether (6.24 g, 64.7 mmol, 89% recovered) and a higher-boiling residue (2.28 g). The residue was extracted with diethyl ether to give a brown solution and a light-brown moisture-sensitive solid (0.71 g) which had partially hydrolysed as shown by the presence of NH bands (IR and ^{1}H NMR). The solid was dissolved in dichloromethane (5 ml), water (10 ml) was added and the mixture stirred for 3 h. The organic layer was separated, dried using $MgSO_4$ and the solvent removed *in vacuo* to afford a solid (0.68 g), which was sublimed *in vacuo* at 393-413 K to give a mixture (0.67 g, 2.8 mmol, 26%; found C 45.4, H 4.4, N 5.7, Cl 30.0%, calculated for $C_9H_{11}NO_2Cl_2$ C 45.7, H 4.6, N 5.9, Cl 30.0%) of two amide isomers in the ratio 6:1 (^{1}H NMR), which showed only one spot on the thin-layer chromatogram using a variety of solvents as eluant. Recrystallization from chloroform and then acetone gave the major isomer, 1,8-dichloro-5-oxa-10-azatricyclo[5.3.1.0^{3,8}]undecan-9-one which was formed by hydrolysis of 1,8,9-trichloro-5-oxa-10-azatricyclo[5.3.-1.0^{3,8}]undec-9-ene (0.50 g, 2.1 mmol, 19.5%; found C 45.9, H 4.7, N 5.8, Cl 30.1%, $M^{+\cdot}$ 235/237/2; $C_9H_{11}NO_2Cl_2$ requires C 45.7, H 4.6, N 5.9, Cl 30.0%, M 235/237/239), m.p. 501 K.

We thank the Algerian Government for a grant (to LS).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55312 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1017]

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Oxonium (*R*)-*O*-Acetylmandelate

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Abstract

The three H atoms of the oxonium H_3O^+ cation are disordered equally over four orientations and are involved

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in an extensive three-dimensional hydrogen-bonding network with the carbonyl and carboxylate O atoms of four neighbouring (Ph)CH(OAc)COO$^-$ anions [H$\cdots$O 1.62–1.85, O$\cdots$O 2.722(3)–2.902(3) Å]; the *O*-acetyl oxygen is not involved in any hydrogen bonding. Principal bond lengths include Csp^2—$O_{carbonyl}$ 1.211(4), Csp^2—$O_{carboxylate}$ 1.234(4) and 1.246(3) Å. The main torsion angles defining the conformation in the mandelate anion are: $O_{carboxylate}$—Csp^2—Csp^3—C_{ar} 84.6(2) and −92.3(2)°; Csp^2—O—Csp^3—C_{ar} −171.6(2) and Csp^2—O—Csp^3—Csp^2 67.7(2)°.

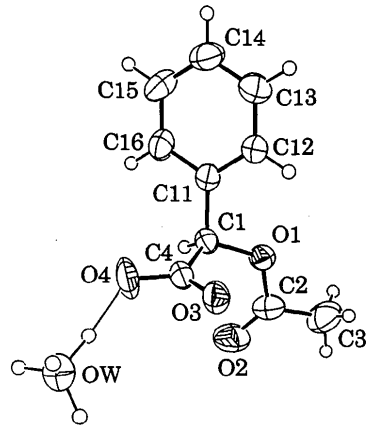

Fig. 1. A view of the asymmetric unit of H_3O^+. PhCH(OAc)CO_2^- showing the general conformation and our numbering scheme. The non-H atoms are shown with thermal ellipsoids drawn at the 50% probability level. For clarity the H atoms are drawn as small spheres of an arbitrary size. Only one of the two possible orientations for the methyl H atoms is shown.

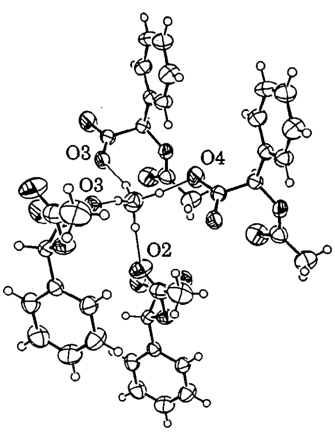

Fig. 2. A view showing the hydrogen-bonding environment around the oxonium cation with the three oxonium H atoms disordered over four sites.

Comment

(*R*)-*O*-Acetylmandelic acid has been studied thoroughly not only as a chiral derivatizing agent in ^{1}H NMR spectroscopy (Parker, 1983), but also as a chiral solvating agent (Parker & Taylor, 1987). It forms diastereoisomeric salt complexes with amines and β-amino alcohols in which large chemical shift non-equivalence is observed for certain resonances of the substrate, permitting a simple and direct measure of the enantiomeric purity of the substrate. In one attempted preparation of a salt complex, (*R*)-*O*-acetylmandelic acid was reacted with (−)-1,2-diamino-1,2-diphenylethane. The material gleaned from this reaction was recrystallized from dichloromethane and subsequently shown by our X-ray analysis to be the simple salt, oxonium (*R*)-*O*-acetylmandelate, H_3O^+.PhCH(OAc)CO_2^-.

A view of the crystal asymmetric unit is shown in Fig. 1 with our numbering scheme, and pertinent dimensions are in Table 2. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) yielded no 'hits' for an *O*-acetylmandelate fragment, but did reveal numerous structures which contain the parent mandelate [PhCH(O)CO_2] moiety. Three of these structural determinations were on the parent mandelic acid molecule [PhCH(OH)CO_2H] (Cameron & Duffin, 1974; Wei & Ward, 1977; Patil, Pennington, Paul, Curtin & Dykstra, 1987); the first two studies were on DL-mandelic acid, the last on (*S*)-(+)-mandelic acid. The conformation reported for the DL-racemate (torsion angles $O_{carboxylate}$—Csp^2—Csp^3—C_{ar} 77.3 and −102.0°; $O_{carboxylate}$—Csp^2—Csp^3—$O_{hydroxyl}$ 23.9 and −156.7°) is similar to that found here in PhCH(OAc)CO_2^- [$O_{carboxylate}$—Csp^2—Csp^3—C_{ar} 84.6(2) and −92.3(2)°; $O_{carboxylate}$—Csp^2—Csp^3—O_{acetyl} 26.4(1) and −156.7(3)°], even though the crystal environment is quite different. A different conformation was found for the two independent molecules in the (*S*)-(+)-mandelic acid structure (mean values: $O_{carboxylate}$—Csp^2—Csp^3—C_{ar} 121.7 and −59.6°; $O_{carboxylate}$—Csp^2—Csp^3—$O_{hydroxyl}$ 178.3 and −0.5°).

In the crystal structure of H_3O^+.PhCH(OAc)CO_2^- the H_3O^+ cation has its three H atoms equally disordered over four sites (in a tetrahedral arrangement) and they take part in four O—H$\cdots$O hydrogen bonds (see Fig. 2) with four neighbouring (Ph)CH(OAc)CO_2^- anions [H$\cdots$O 1.62–1.85, O$\cdots$O 2.722(3)–2.902(3) Å]; the only oxygen not involved in hydrogen bonding, O(1), is at a distance of 3.491(2) Å from the nearest intermolecular oxygen, O*W*.

The dimensions of the PhCH(OAc)CO_2^- moiety (Table 2) are as anticipated; apart from the hydrogen bonding noted above all inter-ion contacts correspond to normal van der Waals interactions.

Experimental

Crystal data

$H_3O^+.C_{10}H_9O_4^-$	Mo $K\alpha$ radiation
M_r = 212.20	λ = 0.70930 Å

Monoclinic
$P2_1$
$a = 7.6772$ (6) Å
$b = 6.2628$ (5) Å
$c = 12.4889$ (8) Å
$\beta = 104.879$ (6)°
$V = 580.34$ (7) Å^3
$Z = 2$
$D_x = 1.214$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 10.00$–20.00°
$\mu = 0.09$ mm^{-1}
$T = 293$ K
Block
$0.60 \times 0.30 \times 0.10$ mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: none
2511 measured reflections
2426 independent reflections
1893 observed reflections [$I_{net} > 3.0\sigma(I_{net})$]

$R_{int} = 0.005$
$\theta_{max} = 26.91$°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 15$
3 standard reflections frequency: 120 min intensity variation: none

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.055$
$S = 1.24$
1893 reflections
135 parameters
$w = 1/[\sigma^2(F)+0.0012F^2]$
$(\Delta/\sigma)_{max} = <0.001$

$\Delta\rho_{max} = 0.12$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.72312 (18)	0.24910	0.73775 (12)	0.0457 (7)
O(2)	0.48918 (24)	0.0515 (5)	0.65104 (17)	0.0764 (12)
O(3)	0.86806 (20)	0.0492 (4)	0.58554 (12)	0.0470 (8)
O(4)	0.8980 (3)	−0.2502 (4)	0.68155 (16)	0.0787 (14)
O(*W*)	0.84868 (23)	−0.5338 (4)	0.51118 (15)	0.0603 (10)
C(1)	0.82823 (25)	0.0561 (4)	0.76964 (16)	0.0389 (10)
C(2)	0.5539 (3)	0.2254 (5)	0.67886 (20)	0.0531 (13)
C(3)	0.4592 (4)	0.4352 (6)	0.6535 (3)	0.0777 (18)
C(4)	0.8652 (3)	−0.0576 (4)	0.66919 (18)	0.0426 (11)
C(11)	1.0032 (3)	0.1224 (4)	0.84925 (16)	0.0378 (10)
C(12)	1.0803 (3)	0.3199 (4)	0.84185 (19)	0.0477 (11)
C(13)	1.2419 (3)	0.3736 (5)	0.91500 (24)	0.0614 (15)
C(14)	1.3269 (3)	0.2329 (6)	0.99679 (22)	0.0617 (14)
C(15)	1.2507 (3)	0.0351 (6)	1.00337 (21)	0.0632 (14)
C(16)	1.0890 (3)	−0.0198 (5)	0.93026 (19)	0.0496 (12)
HO*W*(1)	0.728	−0.506	0.449	0.0707
HO*W*(2)	0.964	−0.512	0.480	0.0707
HO*W*(3)	0.847	−0.678	0.550	0.0707
HO*W*(4)	0.854	−0.420	0.580	0.0707

Table 2. *Bond lengths* (Å), *bond angles* (°), *torsion angles* (°) *and contact distances* (Å)

O(1)—C(1)	1.451 (3)	O(4)—C(4)	1.234 (4)
O(1)—C(2)	1.326 (3)	C(1)—C(4)	1.531 (3)
O(2)—C(2)	1.211 (4)	C(1)—C(11)	1.510 (3)
O(3)—C(4)	1.246 (3)	C(2)—C(3)	1.496 (5)
C(1)—O(1)—C(2)	117.09 (17)	O(2)—C(2)—C(3)	126.01 (23)
O(1)—C(1)—C(4)	111.70 (17)	O(3)—C(4)—O(4)	125.69 (23)
O(1)—C(1)—C(11)	106.85 (20)	O(3)—C(4)—C(1)	118.94 (23)
C(4)—C(1)—C(11)	110.27 (16)	O(4)—C(4)—C(1)	115.29 (21)
O(1)—C(2)—O(2)	122.1 (3)	C(11)—C(16)—C(15)	120.1 (3)
O(1)—C(2)—C(3)	111.9 (3)		
C2—O1—C1—C4	67.7 (2)	C11—C1—C4—O3	−92.3 (2)
C2—O1—C1—C11	−171.6 (2)	C11—C1—C4—O4	84.6 (2)
C1—O1—C2—O2	−1.0 (1)	O1—C1—C11—C12	−31.1 (1)
C1—O1—C2—C3	178.7 (2)	O1—C1—C11—C16	149.8 (2)
O1—C1—C4—O3	26.4 (1)	C4—C1—C11—C12	90.5 (2)
O1—C1—C4—O4	−156.7 (3)	C4—C1—C11—C16	−88.6 (2)
O*W*—O(2)^{i}	2.902 (3)	O*W*—O(3)^{iii}	2.763 (3)
HO*W*(1)—O(2)^{i}	1.85	HO*W*(3)—O(3)^{iii}	1.76
O*W*—O(3)^{ii}	2.794 (2)	O*W*—O(4)	2.722 (3)
HO*W*(2)—O(3)^{ii}	1.74	HO*W*(4)—O(4)	1.62

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

Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction, program used to solve and refine structure, software used to prepare material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). The H atoms of the H_3O^+ ion appeared as four clear maxima of equal size in a difference map computed at an intermediate stage of the refinement. They were included (at the coordinates obtained from the difference map) in subsequent structure-factor calculations but were not refined. The H atoms attached to the C atoms were positioned geometrically (C—H 0.95 Å), and included as riding atoms in the structure-factor calculations (the three methyl H atoms were disordered equally over six sites). We were not able to determine the absolute configuration of the material studied by X-ray methods because of the small anomalous scattering values for O and C (refinement with both *R* and *S* models yielded the same *R* factors and dimensions); the absolute configuration was known in any case from the initial starting material. The diagrams were prepared using *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55364 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1019]

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