

(+)-Methyl (4*R*,5*S*)-4-[(*R*)-1-hydroxybut-3-enyl]-5-2,2-dimethyl-trichloroacetamido-1,3-dioxane-5-carboxylate

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Key indicators

Single-crystal X-ray study

$T = 297\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$

R factor = 0.056

wR factor = 0.171

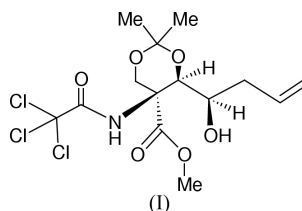
Data-to-parameter ratio = 11.0

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

The title compound, $\text{C}_{14}\text{H}_{20}\text{Cl}_3\text{NO}_6$, was prepared in a synthetic study of myriocin derivatives. There are intramolecular $\text{N}-\text{H}\cdots\text{O}$ and intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, forming one-dimensional chains along the c axis.

Comment

The title compound, (I), was prepared in a synthetic study of myriocin, which is a naturally occurring α -substituted α -amino acid derivative with potent immunosuppressive activity. Compound (I) would be a useful intermediate for the total synthesis of myriocin (Oishi *et al.*, 2002), as well as its congeners, such as mycestericins (Sasaki *et al.*, 1994). Since the geometry of (I) could not be fully determined from NMR experiments, an X-ray analysis has been carried out.



The dioxane ring of (I) shows a chair conformation, with the trichloroacetyl amino group in an axial position (Fig. 1). The absolute configuration at atom C12, derived from that at C-2 of dimethyl *L*-tartrate, was confirmed by the reasonable Flack (1983) parameter. Consequently, the absolute configurations at two other chiral centers (atoms C13 and C17) have been revealed. There are intramolecular $\text{N10}-\text{H10}\cdots\text{O6}$ and intermolecular $\text{O6}-\text{H6}\cdots\text{O9}^i$ [symmetry code: (i) $y, 1-x, z-\frac{1}{4}$] hydrogen bonds (Table 1), forming one-dimensional chains along the c axis (Fig. 2).

Experimental

Treatment of methyl (4*R*,5*S*)-4-formyl-2,2-dimethyl-5-trichloroacetamido-1,3-dioxane-5-carboxylate, prepared from dimethyl *L*-tartrate in a 14-step reaction involving an Overman rearrangement (Sato *et al.*, 2003), with allyltributyltin in the presence of MgBr_2 in CH_2Cl_2 , afforded the title compound, (I). Crystals of (I) were grown from an ethyl acetate solution by slow evaporation (m.p. 371–372 K). The specific rotation $[\alpha]_D$ of (I) at 295 K is $+56^\circ$ ($c = 1.0$, CHCl_3).

Crystal data

$\text{C}_{14}\text{H}_{20}\text{Cl}_3\text{NO}_6$
 $M_r = 404.67$
Tetragonal, $P4_1$
 $a = 9.1926$ (8) \AA
 $c = 22.724$ (2) \AA
 $V = 1920.2$ (3) \AA^3
 $Z = 4$
 $D_x = 1.400\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 25
reflections
 $\theta = 10.1\text{--}10.8^\circ$
 $\mu = 0.50\text{ mm}^{-1}$
 $T = 297\text{ K}$
Block, colourless
 $0.55 \times 0.45 \times 0.45\text{ mm}$

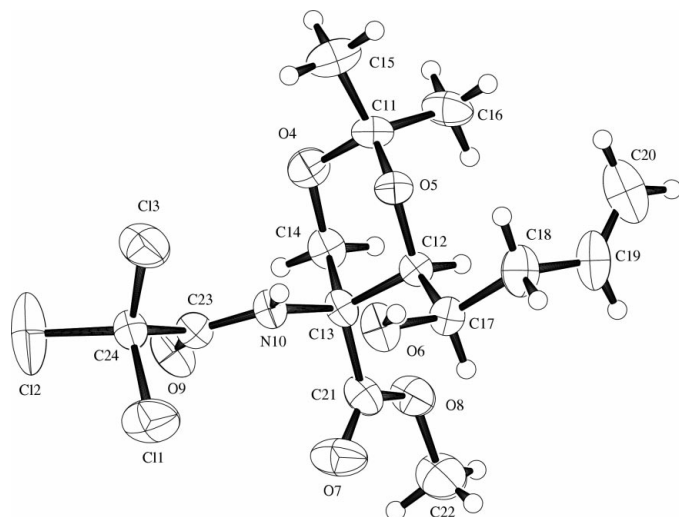


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 40% probability level.

Data collection

Rigaku AFC-7R diffractometer
 ω scans
 Absorption correction: by
 integration (Coppens *et al.*, 1965)
 $T_{\min} = 0.762$, $T_{\max} = 0.815$
 3009 measured reflections
 2388 independent reflections
 1963 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -4 \rightarrow 11$
 $k = 0 \rightarrow 11$
 $l = -12 \rightarrow 29$
 3 standard reflections
 every 150 reflections
 intensity decay: 13.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.171$
 $S = 1.05$
 2388 reflections
 218 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 1.4164P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.011$
 $\Delta\rho_{\text{max}} = 0.62 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.51 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 140 Friedel pairs
 Flack parameter = 0.16 (13)

Table 1

Hydrogen-bonding geometry (Å , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O6-H6 \cdots O9^i$	0.82	1.99	2.790 (5)	167
$N10-H10 \cdots O6$	0.95	2.05	2.709 (4)	125

Symmetry code: (i) $y, 1-x, z - \frac{1}{4}$.

The hydroxy H atom was located from a difference synthesis and allowed to ride on the O atom, with $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{O})$. The other H atoms were positioned geometrically and fixed with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

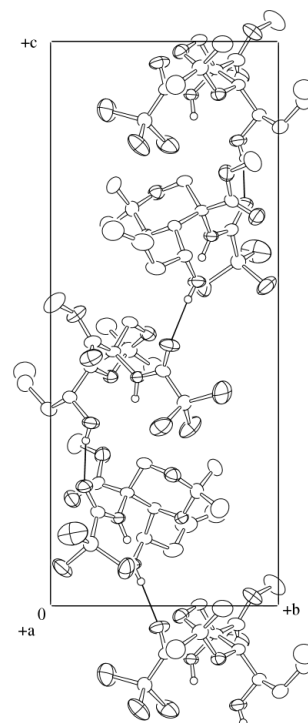


Figure 2

A projection of the crystal structure of (I) along the a axis, with thin lines indicating hydrogen bonds.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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