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(3a*R*,7a*S*)-*N*-Triphenylmethyl-1,2,3,3a,5,6,7,7a-octahydropyrano[3,2-*b*]-pyrrol-2-one

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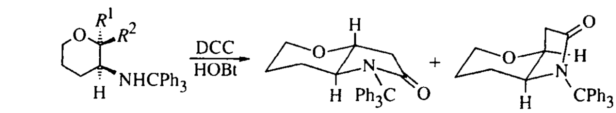
Abstract

The title compound, $C_{26}H_{25}NO_2$, is one of the two main products formed when an inseparable mixture of the diastereomeric (2*R*,3*S*)- and (2*S*,3*S*)-3-triphenylmethyl-aminooxinan-2-ylacetic acids is treated with *N*,*N*′-dicyclohexylcarbodiimide and 1-hydroxybenzotriazole. The crystal structure determination unambiguously shows that this compound has the tetrahydropyranyl and pyrrolidonyl rings fused in the *trans* configuration.

Comment

Reduction of γ-methyl (*S*)-*N*-triphenylmethylglutamate with $LiAlH_4$ (Barlos *et al.*, 1987), followed by *N*,*N*′-dicyclohexylcarbodiimide (DCC)-mediated lactonization, produced unexceptionally the (*S*)-*N*-trityl-hydroxynorvaline lactone. When this lactone was subjected to an identical sequence of reactions to that used for the preparation of (2*RS*,3*S*)-3-triphenylmethylamino-oxolan-2-ylacetic acid from (*S*)-*N*-tritylhomoserine lactone (Papaioannou *et al.*, 1991), an inseparable mixture of the diastereomeric acids (1*a*) and (1*b*) was obtained. Treatment of acid (1) with DCC in the presence of 1-hydroxybenzotriazole (HOBt), which is routinely used to prepare the corresponding 'active' hydroxy-benzotriazolyl esters (Barlos, Papaioannou & Theodoropoulos, 1984), produced, *via* TLC, a mixture (approximately 1:1) of two main products, with R_f values of 0.21 and 0.10 using the solvent system toluene/ethyl acetate (8:2). This mixture could readily be separated by flash column chromatography (FCC). Spectroscopic and analytical data for the isolated products showed them to be the diastereomeric amides (2) and (3), respectively (Papaioannou, 1997). In particular, in the 400 MHz ^{1}H NMR spectra, the H3a proton appeared at δ 4.628 and 3.916 p.p.m. for amides (3) and (2), respectively, indicating an equatorial orientation of the C3a—H3a bond in (3) and an axial orientation in (2). This is taken to mean that amide (2) has the *trans* configuration and amide (3) has the *cis* configuration. In order to establish unambiguously the mode of fusion of the two heterocyclic rings in each of the two amides, we decided to determine the structure of the less polar (as determined by TLC) amide by X-ray analysis.



(1*a*) R^1 = H; R^2 = CH_2CO_2H (2) (3)
(1*b*) R^1 = CH_2CO_2H; R^2 = H

The crystal structure determination of the title amide (2) unambiguously shows that in the amide with R_f = 0.21, the tetrahydropyranyl and pyrrolidonyl rings are indeed *trans* fused. Moreover, the six-membered ring adopts a chair conformation [atoms C3a and C6 deviate by 0.707 (3) and −0.657 (4) Å, respectively, from the plane through atoms O4, C5, C7 and C7a], whereas the pyrrolidonyl ring is found in an envelope conformation [C3a deviates by 0.618 (3) Å from the plane formed by N1, C2, C3 and C7a]. The triphenylmethyl moiety

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adopts a propeller-like conformation in order to minimize steric crowding of the phenyl rings in this group.

Fig. 1 depicts the correct absolute configuration of the molecule, which was assigned to agree with the known chirality of γ-methyl (*S*)-*N*-triphenylmethylglutamate (Barlos *et al.*, 1987) from which (2) was synthesized.

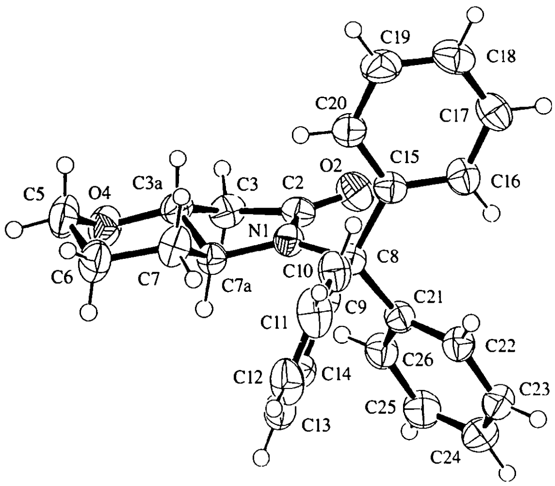

Fig. 1. View of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

To a solution of acid (1) (1.07 g, 2.66 mmol) in dioxane (10 ml), cooled to 280 K, HOBt.H_2O (0.61 g, 3.99 mmol) and DCC (0.60 g, 2.93 mmol) were added sequentially and the resulting reaction mixture was stirred at that temperature for 30 min and at ambient temperature for 24 h. Precipitated *N*,*N*′-dicyclohexylurea was filtered off and washed with ethyl acetate (30 ml). The combined filtrates were washed sequentially with 5% aqueous citric acid, water, 5% aqueous $NaHCO_3$ and water, and finally dried (Na_2SO_4). Evaporation of the solvent under reduced pressure left an oily residue which was subjected to FCC, using the solvent system toluene/ethyl acetate (8:2) as the eluant. The fractions with R_f = 0.21 for the same solvent system were pooled and gave the crystalline amide (2) (0.29 g, 28%) on evaporation of the solvents. Crystals suitable for X-ray analysis were obtained by recrystallization from ethyl acetate.

Crystal data

$C_{26}H_{25}NO_2$
M_r = 383.47
Orthorhombic
$P2_12_12_1$
a = 9.518 (2) Å
b = 14.003 (2) Å
c = 14.977 (3) Å
V = 1996.0 (6) Å^3
Z = 4
D_x = 1.276 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 44 reflections
θ = 10.49–19.81°
μ = 0.080 mm^{-1}
T = 293 (2) K
Prism
0.90 × 0.45 × 0.35 mm
Colourless

Data collection

Philips PW1100 diffractometer (updated by Stoe)
ω–2θ scans
Absorption correction: none
1970 measured reflections
1970 independent reflections
1895 reflections with $I > 2\sigma(I)$

θ_{max} = 25°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.105
S = 1.105
1970 reflections
263 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.2172P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.210 e Å^{-3}
$\Delta\rho_{min}$ = −0.189 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.026 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.372 (3)	C3a—O4	1.408 (3)
N1—C7a	1.487 (3)	C3a—C7a	1.520 (3)
C2—O2	1.215 (3)	O4—C5	1.448 (3)
C2—N1—C7a	110.5 (2)	C3a—C3—C2	100.3 (2)
O2—C2—N1	125.7 (2)	O4—C3a—C7a	112.5 (2)
O2—C2—C3	126.0 (2)	N1—C7a—C3a	100.3 (2)
N1—C2—C3	108.3 (2)		
O4—C3a—C7a—N1	164.6 (2)	O4—C3a—C7a—C7	−66.8 (2)
C3—C3a—C7a—N1	38.9 (2)	C3—C3a—C7a—C7	167.4 (2)

The data have not been been corrected for absorption effects. An extinction correction was applied. H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *DIF*4 (Stoe & Cie, 1987*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1987*b*). Program used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93. Other programs include: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1010). Services for accessing these data are described at the back of the journal.

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(*S*)-3-(O^{γ}-Methyl-N^{α}-triphenylmethyl-glutamyl)benzotriazole 1-Oxide

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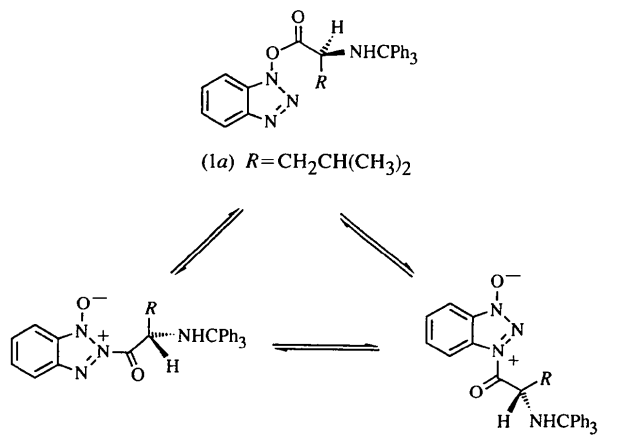
Abstract

The title compound, $C_{31}H_{28}N_4O_4$, is the product of the condensation of γ-methyl (*S*)-N^{α}-triphenylmethyl-glutamate with 1-hydroxybenzotriazole in the presence of *N*,*N*′-dicyclohexylcarbodiimide. The crystal structure determination unambiguously shows that the acyl moiety is attached to the N3 atom of the benzotriazole ring.

Comment

Condensation of N^{α}-triphenylmethylamino acids with 1-hydroxybenzotriazole (HOBt) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) results in equilibrium mixtures of an ester form (1) and two amide forms (2) and (3), which are suitable for use in peptide synthesis (Barlos, Papaioannou & Theodoropoulos, 1984). An IR investigation of these mixtures has shown the presence of three carbonyl bands at 1810–1820, 1730–1740 and 1670–1680 cm^{-1}. Subsequently, the pure ester (1*a*) (Vlassi *et al.*, 1990) and amide (3*a*) (Barlos *et al.*, 1985) forms were isolated and unambiguously characterized by X-ray crystallographic analyses. The related studies showed that the carbonyl bands at 1810–1820 and 1730–1740 cm^{-1} are associated with the carbonyl functions of the ester (1) and the amide (3) forms, respectively. Although the title compound has been obtained in an oily form, as an intermediate in the synthesis of (*S*)-4-amino-5-hydroxypentanoic acid (Barlos *et al.*, 1987), it has only quite recently been obtained in a crystalline form, during the course of an independent study on the application of the benzotriazolyl esters of N^{α}-triphenylmethylamino acids to the synthesis of amides using concentrated aqueous amines (Mamos *et al.*, 1997). The recrystallized compound showed two IR carbonyl bands at 1736 and 1722 cm^{-1}, one of which is obviously due to its γ-methyl ester function. Accordingly, we decided to determine the structure of this compound by X-ray analysis and compare it with the structure already obtained for the amide form (3*a*). The crystal structure determination of the title compound, (3*b*), unambiguously shows that the acyl moiety is also attached to the N3 atom of the benzotriazolyl ring.



(1*a*) $R=CH_2CH(CH_3)_2$

(2)

(3*a*) $R=CH_2CH_2SCH_3$
(3*b*) $R=CH_2CH_2CO_2CH_3$

A comparison of the most interesting acyl part of the crystal structures of amides (3*a*) and (3*b*) shows that the bond lengths and angles are similar (Table 1). Amides (3*a*) and (3*b*) differ, however, in the orientation of the side chain. In the former structure, the side chain is directed away from the benzotriazolyl ring, whereas in the latter, the side chain is directed towards it. It is worth noting that the bond lengths of the two carbonyl functions in amide (3*b*) are 1.200 (3) and 1.186 (4) Å, the bond length of the amide carbonyl function being the longer. For comparison, the corresponding bond length of the ester carbonyl function of (1*a*) is 1.179 (5) Å (Vlassi *et al.*, 1990). The triphenylmethyl moiety adopts the usual propeller-like conformation, which is the established means of reducing steric interaction between the phenyl rings in this group (Destro, Pilati & Simonetta, 1980). The acyl moiety of (3*b*) adopts an overall planar geometry, which is in sharp contrast to the structure of ester (1*a*), in which the ester function is perpendicular [92.9 (4)°] to the benzotriazolyl plane. This