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(2*R*,3*R*)-2-(4-Methoxyphenyl)-3-{1-[(3a*S*)-(3a*α*,6*α*,7a*α*)-hexahydro-8,8-dimethyl-3*H*-3a,6-methano-2,2-dioxo-2,1-benzoisothiazolyl]carbonyl}-4-isopropoxycarbonyl-5-methyl-2,2-dihydrofuran

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The title compound, $C_{27}H_{35}NO_7S$, is selectively formed by the oxidative addition of a *β*-keto ester to a chiral *N*-cinnamoyl derivative. The determination from X-ray analysis of the absolute configuration of two newly created stereogenic centres allows us to understand the facial selectivity of the addition.

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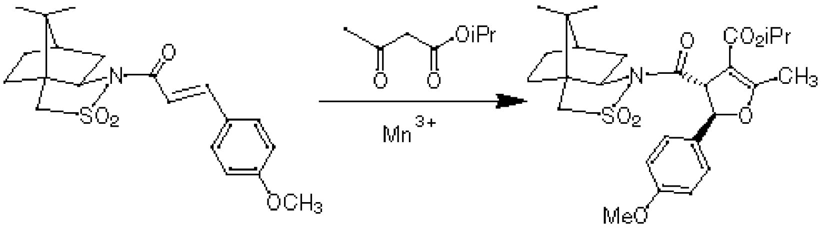
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.057
wR factor = 0.127
Data-to-parameter ratio = 19.3

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

Comment

The addition of isopropyl 3-oxobutanoate to compound (1) [(1*S*,2*R*)-*N*-[(*E*)-4-methoxycinnamoyl]-10,2-camphorsultam] in the presence of $Mn(OAc)_3$, using a previously described method, affords the title molecule, (2), as a major isomer, the reaction being totally regio- and diastereoselective (Garzino *et al.*, 2000). The facial selectivity of the Mn^{III}-mediated addition of *β*-keto esters to olefins can be controlled by introduction of a chiral auxiliary on the substrate (Curran *et al.*, 1996). This reaction thereby provides an entry to chiral dihydrofurans. The structures of the starting compound (Garzino *et al.*, 2002) and of the dihydrofuran adduct were thus elucidated in order to establish their relative configurations and to understand how the diastereoselection is controlled. When using compound (1) as substrate, dihydrofuran (2) was selectively formed.



(1) (2)

The absolute configurations of the two stereogenic centres were determined by X-ray analysis. It appears that, when (−)-10,2-camphorsultam was used as the chiral inductor, the (2*R*,3*R*)-dihydrofuran (−)-(2) was selectively obtained, with a specific rotation of −229.0° in chloroform for a concentration $c = 0.7$ (2*R* is atom C9 and 3*R* is atom C13). As it is known that in such radical reactions the transition state resembles the substrate, the explanation of such a facial selectivity can be provided by the crystal structure of the starting compound (−)-(1). Indeed it can be seen that, in this compound, the *anti s-cis* conformation is favoured by dipolar interactions between the cinnamate C═O group and the equatorial S═O group of the sulfonyl moiety. In this conformation, the approach by the lower face is hindered by the axial S═O, thus enabling the facial stereoselectivity to be controlled. It is interesting to note

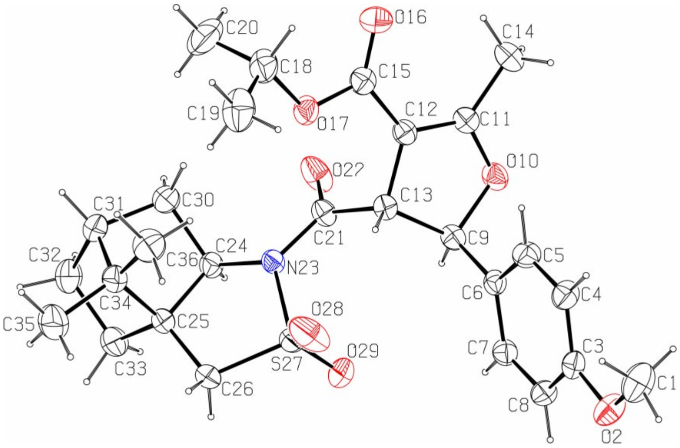


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (2) with displacement ellipsoids drawn at the 50% level.

that the addition of isopropyl 3-oxobutanoate to compound (1) affects considerably the conjugation of the π sytem. The value of the torsion angle C9—C10—C11—O12 changes from 19.8 (2) to 76.40 (3)°.

Experimental

Colourless square-platelet-shaped crystals of (2) were obtained by evaporation of an ethanol solution.

Crystal data

$C_{27}H_{35}NO_7S$
$M_r = 517.62$
Monoclinic, $P2_1$
$a = 12.1894$ (7) Å
$b = 8.9921$ (3) Å
$c = 13.0425$ (8) Å
$\beta = 107.97$ (1)°
$V = 1359.83$ (12) Å^3
$Z = 2$

$D_x = 1.264$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12731 reflections
$\theta = 1.8$–28.6°
$\mu = 0.16$ mm^{-1}
$T = 293$ (2) K
Square platelet, colourless
0.42 × 0.41 × 0.32 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
12731 measured reflections
6413 independent reflections
5079 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.082$
$\theta_{\rm max} = 28.6°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 11$
$l = -17 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.128$
$S = 1.02$
6413 reflections
332 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.2323P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Absolute structure: Flack (1983); 6327 Friedel pairs
Flack parameter = 0.03 (8)

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 1990).

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