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3-(7,7-Dimethyl-2-oxobicyclo[2.2.1.]hept-1-yl-methanesulfonyloxy)-2-methyl-2-(toluene-4-sulfonyl-oxymethyl)propyl 4-chlorobenzoate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.006 Å
R factor = 0.038
wR factor = 0.078
Data-to-parameter ratio = 14.0

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

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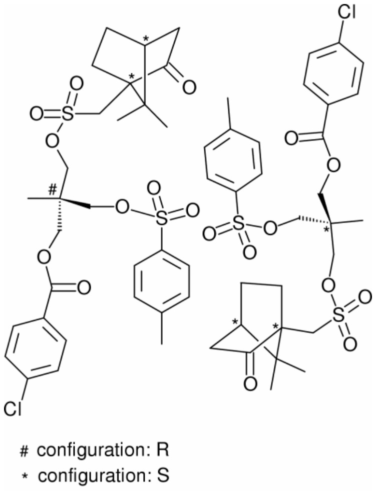
The title compound, $C_{29}H_{35}ClO_9S_2$, is a tris(hydroxymethyl)ethane derivative with an asymmetric carbon in the propane skeleton. Surprisingly, in the unit cell, two stereoisomers with different configuration at this centre are present. Their relative orientation gives a nearly centrosymmetric arrangement, and all corresponding bond lengths and angles are comparable in the two molecules. Two additional chiral centres with *S*-configurations present in the camphorsulfonic acid group have to be the same in both molecules, rendering the two compounds diastereomers.

Comment

2-Hydroxymethyl-2-methyl-3-(toluene-4-sulfonyloxy)propyl 4-chlorobenzoate with high enantiomeric purity was treated with (1*S*)-camphorsulfonic acid chloride to yield the title compound, (I) (von Matt *et al.*, 1995). ^{1}H NMR analysis of the resulting colourless solid showed a high diastereomeric excess. Treatment with a 4:1 mixture of hexane and methanol yielded a small amount of crystals suitable for X-ray diffraction. The structure given in Fig. 1 shows that there are actually two compounds present in the unit cell. Removal of the camphorsulfonic acid group would leave two centrosymmetrically related molecules with the tosylate groups facing each other. The corresponding bond lengths and angles of both molecules are nearly identical and the configuration at both C114 and C214 is *S*. They differ only in the configuration of their central asymmetric carbon, this being *R* for C12 and *S* for C22. It has not yet been possible to obtain crystals for X-ray diffraction of a single diastereomer.



(I)

Experimental

0.95 g (2.29 mmol) of 2-hydroxymethyl-2-methyl-3-(toluene-4-sulfonyloxy)propyl 4-chlorobenzoate was dissolved in 50 ml of dichloromethane and treated with 0.86 g (3.44 mmol) of camphorsulfonic acid chloride in 35 ml of dichloromethane and 5 ml of triethylamine. After stirring overnight at room temperature, the reaction mixture was washed with 60 ml of 10% $NaHCO_3$ solution and 60 ml of water, and dried with Na_2SO_4. The crude product was purified by column chromatography (2:1 cyclohexane/ethyl acetate) to yield 1.12 g (1.78 mmol, 78%) of the title compound. The colourless oil was crystallized from petroleum ether (65–90)/MTBE (2:1) to give a colourless solid (m.p. 346–348 K). Treatment with methanol/hexane (1:4) gave crystals after four weeks suitable for X-ray diffraction; m.p. 347–349 K.

Crystal data

$C_{29}H_{35}ClO_9S_2$
$M_r = 627.14$
Triclinic, $P1$
$a = 8.5321$ (3) Å
$b = 12.0941$ (4) Å
$c = 16.6243$ (6) Å
$\alpha = 70.7225$ (14)°
$\beta = 85.0894$ (14)°
$\gamma = 71.5179$ (14)°
$V = 1535.38$ (9) Å^3

$Z = 2$
$D_x = 1.357$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15324 reflections
$\theta = 3.3$–27.5°
$\mu = 0.31$ mm^{-1}
$T = 291$ (1) K
Block, colourless
0.60 × 0.40 × 0.35 mm

Data collection

Nonius KappaCCD diffractometer
323 frames *via* ω-rotation ($\Delta\omega = 1°$) with 3 sets at different κ-angles and two times 10 s per frame
Absorption correction: none
15324 measured reflections
10443 independent reflections

5566 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.078$
$S = 0.84$
10443 reflections
747 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983); 3632 Friedel pairs
Flack parameter = −0.05 (4)

H atoms were placed in calculated positions with $U_{\rm iso}$ constrained to be 1.5 times $U_{\rm eq}$ of the carrier atom for the methyl-H and 1.2 times $U_{\rm eq}$ for the remaining H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995) and *PLATON* (Spek, 2001).

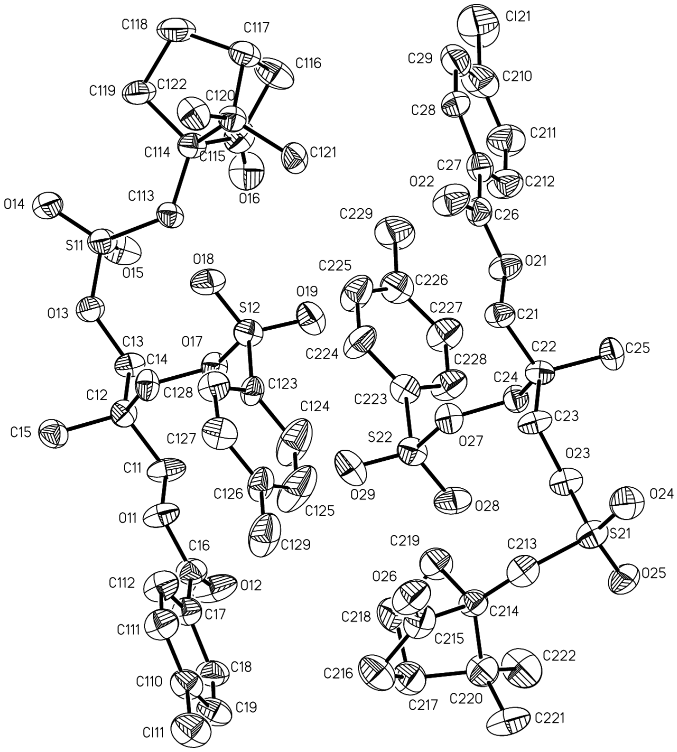


Figure 1
View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted.

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