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Methyl 2-methyl-6-methylthio-1,3-dioxo-4-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)amino]-2,3-dihydro-1*H*-pyrrolo[3,4-c]pyridine-7-carboxylate

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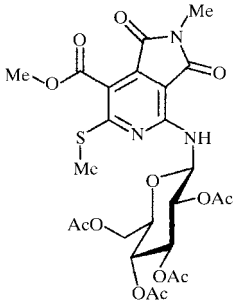
The title compound, $C_{25}H_{29}N_3O_{13}S$, has peripheral acetyl and carbomethoxy groups which show disorder. The absolute structure, although known from the starting materials, was confirmed by the analysis. There are no intermolecular hydrogen bonds. This structure is of importance because it elucidates the pathway for hetero-Diels–Alder reactions between dimethyl acetylenedicarboxylate and 6-amino-pyridin-4(3*H*)-one derivatives catalyzed by trifluoroacetic acid.

Comment

Examination of the structure of the title compound, (I), with *PLATON* (Spek, 2000) showed that there was a potential solvent-accessible void (168.3 Å^3) in the crystal lattice. This was dealt with as explained in the *Experimental* text below.



(I)

Experimental

Dimethyl acetylenedicarboxylate (0.57 g, 4 mmol) was added to a solution of 3-methyl-2-methythio-6-[(tetra-*O*-acetyl-β-D-glucopyranosyl)amino]-4(3*H*)- pyrimidin-4(3*H*)-one (1.00 g, 2.0 mmol) in 10 ml of acetonitrile containing a catalytic amount of trifluoroacetic acid (0.06 g, 0,5 mmol). The mixture was stirred in refluxing acetonitrile for 29 h. The solvent was evaporated under reduced pressure and the title compound was isolated by flash column chromatography on silica gel (toluene/acetone). Recrystallization from acetone produced yellow crystals (yield: 81%, m.p. 481–482 K). Analysis calculated for $C_{25}H_{29}N_3O_{13}S$: C 49.10, H 4.78, N 6.87, S 5.24%; found: C 48.79, H 5.02, N 6.47, S 4.75%.

Crystal data

$C_{25}H_{29}N_3O_{13}S$	D_x = 1.332 Mg m^{-3}
M_r = 611.57	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 4963 reflections
a = 10.1696 (9) Å	θ = 2.18–26.27°
b = 6.9695 (7) Å	μ = 0.173 mm^{-1}
c = 21.526 (2) Å	T = 150 (1) K
β = 92.036 (5)°	Plate, yellow
V = 1524.7 (3) Å^3	0.25 × 0.1 × 0.1 mm
Z = 2	

Data collection

KappaCCD diffractometer	2950 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	R_{int} = 0.064
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)	θ_{max} = 26.27°
T_{min} = 0.958, T_{max} = 0.983	$h = -12 \rightarrow 12$
10 860 measured reflections	$k = -6 \rightarrow 8$
4963 independent reflections	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.068	$(\Delta/\sigma)_{max}$ = 0.005
$wR(F^2)$ = 0.160	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
S = 0.965	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
4963 reflections	Absolute structure: Flack (1983), 2844 Friedel pairs
378 parameters	Flack parameter = −0.04 (15)
H-atom parameters constrained	

Molecule (I) crystallized in the monoclinic system; space group $P2_1$ was assumed from the systematic absences. H atoms were treated as riding atoms with C—H = 0.98–1.00 Å and N—H = 0.88 Å. The methyl H atoms were modelled as disordered groups with two positions rotated from each other by 60°. Each such H atom was given a site-occupancy factor of 0.5. The *hkl* data were modified using the *SQUEEZE* option of *PLATON* (Spek, 2000), since no electron density in the area of the void could be found with an electron density greater than 0.66 e Å^{-3} and no definitive solvent molecule could be found. The anisotropic displacement parameters of the peripheral atoms of the substituent acetyl groups show large movement at right angles to their connecting bonds, indicating that these atoms show a degree of dynamic disorder. In fact, the O atom of the carbomethoxy group attached to C4 of the nucleobase ring was shown from a difference Fourier map to have two possible sites. However, only one site was obtained for the attached methyl group. Refinement of the site occupancies for O resulted in a major and a minor component with occupancies of 0.71 and 0.29, respectively. These O atoms were refined isotropically. The position of the O atom of the minor component was restrained using the *DFIX* option of *SHELXL* to have connecting bond lengths similar to those of the major component. No attempt was made to include H atoms on the minor

components since the H atoms attached to methyl C atoms involved were already modelled as a disordered methyl group.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC, X-ray Crystallographic Service, University of Southampton, using an Enraf–Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2000). *PLATON*. Version of March 2000. University of Utrecht, The Netherlands.