Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

6-(Acetoxymethyl)-5-chloro-2-[(2*R*,3*R*,4*R*,5*S*)-3,4-diacetoxy-2,5-bis(chloromethyl)-2,3,4,5-tetrahydrofuran-2-yloxy]-3,4,5,6-tetrahydro-2*H*-pyran-3,4-diyl diacetate toluene solvate

Hui-Liang Wen,[a,b] Zhi-Jie Fang,[a]* Zi-Sheng Wu[c] and Ming-Yong Xie[b]

[a]School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, [b]Key Laboratory of Food Science of the Ministry of Education, Nanchang University, Nanchang 330047, People's Republic of China, and [c]Department of Chemistry, Nanchang University, Nanchang 330047, People's Republic of China

Correspondence e-mail: hlwen@sohu.com

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.010 Å
R factor = 0.063
wR factor = 0.153
Data-to-parameter ratio = 17.0

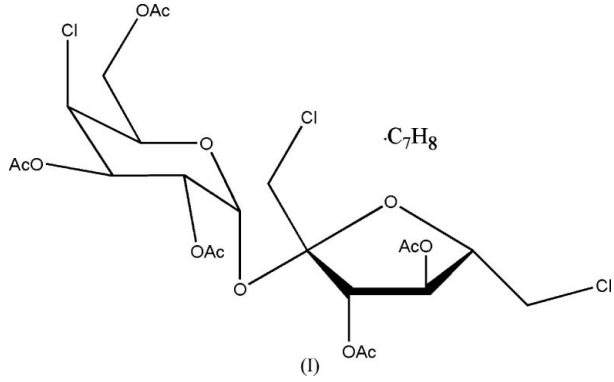
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 23 January 2006
Accepted 20 February 2006

In sugar molecule of the title compound, $C_{22}H_{29}Cl_3O_{13}\cdot C_7H_8$, the pyranose ring adopts the expected chair conformation. The acetoxymethyl and two acetoxy substituents are in the equatorial positions of this ring. In the crystal structure, there is a single weak C—H···O intermolecular interaction (H···O = 2.46 Å), which links molecules into chains in the *a*-axis direxion.

Comment

4,1′,6′-Trichloro-4,1′,6′-trideoxygalactosucrose (TGS), one of a series of chlorodeoxy derivatives of sucrose synthesized by Hough and his colleagues (Hough *et al.*, 1978; Hough *et al.*, 1979*a*), was found to be much sweeter than saccharin but without the unpleasant after-taste of saccharin (Kanters *et al.*, 1988). In fact TGS is six hundred times sweeter than sucrose (Hough *et al.*, 1979*b*). TGS is the only functional glycogen produced by sucrose and the newest and fifth most powerful edulcorant. At present, most synthetic routes for TGS include the hologroup protected method (Zheng *et al.*, 2002), the monoesterification method and the chemico-enzymatic method, of which the hologroup protected method has the advantages of easy separation, few auxiliary reactions and easy control.



(I)

6-(Acetoxymethyl)-5-chloro-2-[(2*R*,3*R*,4*R*,5*S*)-3,4-diacetoxy-2,5-bis(chloromethyl)-2,3,4,5-tetrahydrofuran-2-yloxy]-3,4,5,6-tetrahydro-2*H*-pyran-3,4-diyl diacetate (TOSPA) is an important intermediate in the synthesis of TGS. The purity of TOSPA plays a crucial role in the crystallization of TGS. We used toluene to crystallize TOSPA, which effectively enhances its purity and hence decreases the level of impurities in the deacetylation process, thereby increasing the purity of TGS.

In the molecular structure of the title compound (Fig. 1), all bond lengths and angles are normal and the pyranose ring adopts the expected chair conformation (Krishnakumar *et al.*,

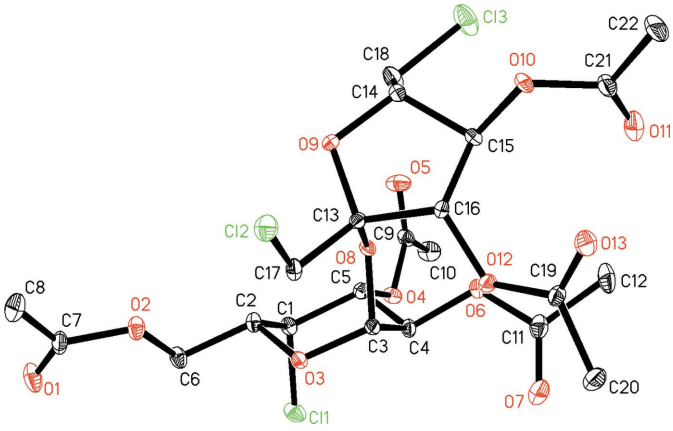


Figure 1
The molecular structure of TOSPA, showing 10% probability displacement ellipsoids. The toluene solvent molecule has been omitted for clarity.

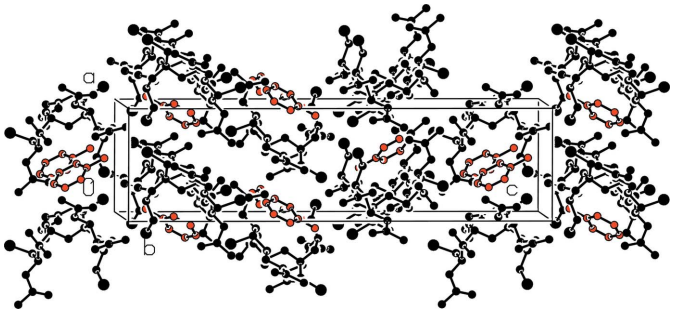


Figure 2
A packing diagram (Spek, 2003) of the title compound. The toluene solvate molecules are shown in red. H atoms have been omitted.

1996). The acetoxymethyl substituent on atom C2 and the acetoxy substituents on C4 and C5 are in the equatorial positions of this ring. In the crystal structure, a single weak C—H···O intermolecular interaction [H···O = 2.46 Å] links TOSPA molecules into chains in the *a* axis direxion (Table 1), while the closest H···O contact between the toluene solvent and the TOSPA molecule is 2.83 Å [C29—H29···O11(x, $y-1$, z)].

Experimental

TOSPA was prepared according to a literature method (O'Brien *et al.*, 1988; Tully *et al.*, 1989; Homer *et al.*, 1990; Jenner *et al.*, 1982). To a stirred solution of 2,3,6,3′,4′-penta-*O*-acetylsucrose (2.00 g) in *N*,*N*-dimethylformamide (1 ml) and 1,1,2-trichloroethane (15 ml), was added, below 314 K, $SOCl_2$ (6 ml) diluted with 1,1,2-trichloroethane (15 ml). The reaction mixture was stirred for 3 h at 388 K. The resulting solution was washed successively with 10% HCl, water and 10% $NaHCO_3$ to neutrality. The organic phase was dried, concentrated to an oil and crystallized from toluene (5 ml) to give 1.76 g light-yellow powder (TOSPA). Yield 80%, m.p. 373–374 K. Anal. Calcd for $C_{22}H_{29}Cl_3O_{13}$ (TOSPA, 607.9): C, 43.43; H, 4.77%. Found: C, 43.53; H, 4.88%. The crystal used for the data collection was obtained by slow evaporation of a saturated toluene solution of TOSPA (m.p. 358–359 K). Analysis calculated for $C_{29}H_{37}Cl_3O_{13}$ (TOSPA·C_5H_8), 699.9: C 49.72, H 5.29%; found: C 49.78, H 5.41%.

Crystal data

$C_{22}H_{29}Cl_3O_{13}\cdot C_7H_8$
M_r = 699.94
Orthorhombic, $P2_12_12_1$
a = 8.3693 (13) Å
b = 13.072 (2) Å
c = 31.603 (5) Å
V = 3457.4 (9) Å^3
Z = 4
D_x = 1.345 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4347 reflections
θ = 2.5–26.1°
μ = 0.33 mm^{-1}
T = 294 (2) K
Prism, colorless
0.22 × 0.16 × 0.12 mm

Data collection

Bruker SMART-CCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.756, T_{max} = 0.960
18609 measured reflections
7000 independent reflections
3951 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 26.3°
$h = -9 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -39 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.153
S = 1.09
7000 reflections
411 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 3.6447P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983) 3019 Friedel pairs
Flack parameter: 0.00 (10)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C22—H22A···O13^{i}	0.96	2.46	3.252 (10)	140

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$.

All H atoms were included in calculated positions and refined as riding (C—H = 0.93 − 0.98 Å), with U_{iso}(H) = 1.5U_{eq}(C) for methyl and 1.2U_{eq}(C) for the rest.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

This work is supported by the Key Laboratory Open Foundation of Food Science of the Ministry of Education, Nanchang University (NCU200407), and the authors thank Processor Lin Pei Jin at Beijing Normal University for his help.

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