Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Arjunglucoside I chloromethane 0.25-solvate monohydrate

Masood Parvez,[a]* Atta-ur-Rahman,[b] M. Iqbal Choudhary,[b] Seema Zareen,[b] Nadeem M. Akhtar,[b] Shahida Shujaat[b] and F. N. Ngounou[c]

[a]Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, [b]HEJ Research Institute of Chemistry, University of Karachi, Karachi 75270, Pakistan, and [c]Department of Organic Chemistry, University of Yaounde 1, PO Box 812, Yaounde, Cameroon

Correspondence e-mail: parvez@ucalgary.ca

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.115
Data-to-parameter ratio = 9.4

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

Received 14 October 2004
Accepted 20 October 2004
Online 30 October 2004

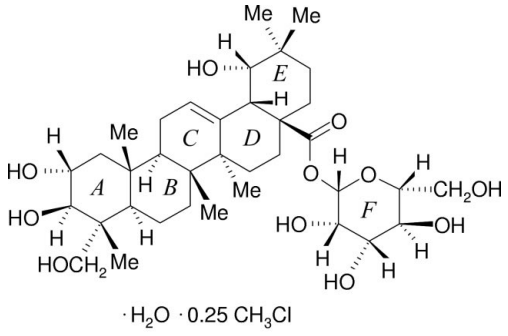
The crystal structure of the title compound (systematic name: β-D-glucopyranosyl 2α,3β,19α,23-tetrahydroxyolean-12-en-28-oate chloromethane 0.25-solvate monohydrate), $C_{36}H_{58}O_{11}\cdot 0.25CH_3Cl\cdot H_2O$, contains a triterpenyl moiety esterified with a glucopyranosyl unit, a disordered molecule of chloromethane solvent with a partial site occupancy located about a twofold axis and a water molecule of hydration. Three rings of the triterpenyl moiety adopt classical chair conformations, while one ring exhibits an envelope conformation and one has a flattened chair conformation. The glucopyranosyl ring also adopts a chair conformation. The structure is stabilized by extensive intermolecular hydrogen bonds as well as an intramolecular interaction.

Comment

The genus *Terminalia* (*Combretaceae*) comprises 135 species that are distributed in the tropical parts of the world (Nasir & Ali, 1978). Various species of this genus are used for cardiac effects, anti-atherogenic and hypolipidemic actions, hepatoprotection, and as antimicrobials (Dermarderosian, 2002). *T. glaucescens* is prescribed as an antidysenteric antimicrobial agent and is also useful in the last phase of AIDS (Koudou *et al.*, 1995). The extract of this plant showed a wide spectrum of antibacterial activity against periodontopathic bacteria (Sote & Wilson, 1995). The ethanolic decoction of this plant exhibited antiplasmodial (Mustofa *et al.*, 2000) and aldose reductase inhibition activities (Terashima *et al.*, 1990). It has also been reported as an important drug in folk medicine (Ekong & Idemudia, 1967). The *Terminalia* species are known to contain several triterpenes, some of which have shown antifungal as well as antiviral activities (Dermarderosian, 2002). During our ongoing phytochemical investigations on this plant, we have isolated several constituents along with a saponin, arjunglucoside I, which has previously been reported from other species of *Terminalia* (Honda *et al.*, 1976; Nandy *et al.*, 1989). In this article, the structure of the monohydrate chloromethane 0.25-solvate, (I), is reported.

The structure of (I) consists mainly of a triterpenyl moiety esterified with a glucopyranosyl unit (Fig. 1). The asymmetric unit also contains a disordered molecule of chloroform solvent with a partial site occupancy located about a twofold axis and a water molecule of hydration. The molecular dimensions in (I) are as expected, with the following mean bond distances: C—C in the triterpenyl moiety is 1.541 (15) Å and in glucosanyl 1.523 (9) Å, Csp^2—Csp^2 1.527 (14) Å and O—Csp^3 1.430 (10) Å. The remaining bond distances are: O—Csp^2 1.345 (4) Å, C=O 1.216 (3) Å and C=C 1.329 (4) Å. The cyclohexyl rings *A*, *B* and *E* of the triterpenyl moiety adopt classical chair conformations, with puckering parameters

(Cremer & Pople, 1975) Q = 0.558 (3), 0.566 (3) and 0.532 (3) Å, θ = 0.0 (3), 10.4 (3) and 170.4 (3)°, and φ = 315 (9), 19.8 (18) and 37 (2)°, respectively. The cyclohexenyl ring *C* exhibits a C8-envelope conformation, with C8 0.800 (4) Å out of the plane formed by the remaining ring atoms [maximum deviation 0.039 (2) Å for C11]. Ring *D* has a rather flattened chair conformation that is influenced by its fusion with cyclohexenyl ring *C,* with atoms C13 and C16 0.283 (4) and 0.710 (4) Å, respectively, above and below the plane formed by the remaining ring atoms. The puckering parameters for rings *C* and *D* are: Q = 0.591 (3) and 0.505 (3) Å, θ = 54.1 (3) and 147.7 (3)° and φ = 350.6 (4) and 12.9 (7)°, respectively. The *gluco*pyranosyl ring, *F*, also adopts a chair conformation with puckering parameters Q = 0.575 (3) Å, θ = 8.2 (3)° and φ = 305.4 (19)°. A search of the Cambridge Structural Database revealed only one structure, asiaticoside dihydrate dioxane solvate (refcode FUNXAN; CSD Version 5.25, 2003 release; Allen, 2002), that is closely related to the structure of (I).



(I)

The structure of (I) is stabilized by strong intermolecular hydrogen bonds between hydroxyl groups [O—H···O, with H···O and O···O distances in the ranges 1.79–2.15 and 2.602 (3)–2.901 (3) Å, respectively] and carbonyl O5 and hydroxyl H atoms [O—H···O, with H···O = 2.12 and 2.13 Å, and O···O5 = 2.900 (3) and 2.914 (3) Å]. H atoms of water are also involved in interactions with a hydroxyl group [H···O = 2.13 Å and O···O = 2.900 (5) Å] and Cl1 atom of chloromethane of solvation [H···Cl = 2.24 Å and O···Cl = 3.056 (13) Å]. The structure also exhibits a strong intramolecular interaction, O1—H1···O2 [H···O = 2.35 Å and O···O = 2.772 (3) Å]. Details of hydrogen-bonding geometries have been provided in Table 2.

Compound (I) showed significant β-glucuronidase inhibitory activity with IC_{50} value 80.1 μM as compared to the standard glucosaccharo-1,4-lactone with IC_{50} = 1.8 μM.

Experimental

Air-dried stem barks (7.5 kg) of *T. Glaucescens* collected from Mount Bankolo near Yaounde, Cameroon, were cut into pieces, dried, pulverized and soaked in a mixture of CH_3OH and CH_2Cl_2 (1:1) at room temperature for 24 h. The extract (611.5 g) was suspended in water (distilled) and defatted with petroleum ether. The defatted extract was further extracted by petroleum ether/chloroform, ethyl acetate and *n*-butanol. The ethyl acetate extract (58.7 g) was repeatedly chromatographed on silica gel using various polarities of solvent mixtures of hexane, chloroform and methanol. Preparative thin-layer chromatography was carried out on precoated plates (DC–Alufolien 60 F_{254} from Merck) and using ceric sulfate as spraying reagent. A fraction obtained on elution with CH_3Cl/CH_3OH (90:10) contained (I), which was then recrystallized from CH_3Cl/CH_3OH (3:1).

Crystal data

$C_{36}H_{58}O_{11}\cdot 0.25CH_3Cl\cdot H_2O$	D_x = 1.284 Mg m^{-3}
M_r = 697.46	Mo $K\alpha$ radiation
Monoclinic, *C*2	Cell parameters from 7564 reflections
a = 30.241 (9) Å	θ = 3.8–27.4°
b = 7.441 (2) Å	μ = 0.11 mm^{-1}
c = 16.290 (7) Å	T = 293 (2) K
β = 100.103 (12)°	Block, colorless
V = 3609 (2) Å^3	0.22 × 0.15 × 0.08 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	3817 reflections with $I > 2\sigma(I)$
ω and φ scans	R_{int} = 0.024
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)	θ_{max} = 27.4°
T_{min} = 0.976, T_{max} = 0.991	$h = -38 \rightarrow 38$
7564 measured reflections	$k = -9 \rightarrow 9$
4380 independent reflections	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 2.40P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$(\Delta/\sigma)_{max}$ = 0.002
$wR(F^2)$ = 0.115	$\Delta\rho_{max}$ = 0.38 e Å^{-3}
S = 0.98	$\Delta\rho_{min}$ = −0.38 e Å^{-3}
4380 reflections	
467 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.444 (3)	O1′—C1′	1.410 (3)
O2—C3	1.437 (3)	O1′—C5′	1.444 (3)
O3—C23	1.432 (4)	O2′—C2′	1.423 (3)
O4—C19	1.432 (4)	O3′—C3′	1.437 (3)
O5—C28	1.216 (3)	O4′—C4′	1.424 (3)
O6—C28	1.345 (3)	O6′—C6′	1.431 (3)
O6—C1′	1.429 (3)		
C28—O6—C1′	120.7 (2)	C1′—O1′—C5′	111.7 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.82	2.15	2.901 (3)	152
O1—H1···O2	0.82	2.35	2.772 (3)	113
O2—H2···O6^{ii}	0.82	1.97	2.781 (3)	171
O3—H3···O1^{iii}	0.82	1.79	2.602 (3)	170
O4—H4···Cl1^{iv}	0.82	2.06	2.848 (7)	161
O2′—H2′···O5^{iii}	0.82	2.12	2.914 (3)	163
O3′—H3′···O5^{iii}	0.82	2.13	2.900 (3)	157
O4′—H4′···O6′^{v}	0.82	2.02	2.827 (3)	169
O6′—H6′···O3′^{vi}	0.82	1.94	2.758 (3)	174
O12—H12A···Cl1^{vii}	0.82	2.24	3.056 (12)	171
O12—H12B···O3^{vii}	0.82	2.20	2.891 (5)	142

Symmetry codes: (i) $x, 1+y, z-1$; (ii) $x, y, z-1$; (iii) $x, y-1, z$; (iv) $1-x, 1+y, 1-z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (vi) $x, 1+y, z$; (vii) $1-x, y, 1-z$.

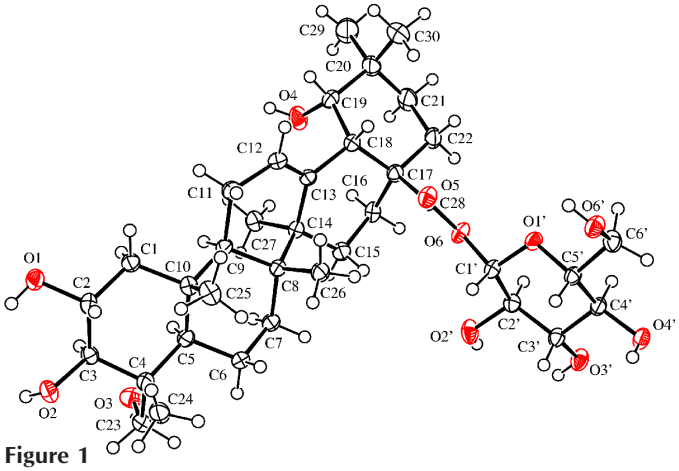


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), with displacement ellipsoids plotted at the 50% probability level. The solvent molecules have been omitted.

A disordered molecule of chloromethane with site occupancy of 0.25 was located about a twofold axis; its C atom was allowed an isotropic displacement parameter during refinement. H atoms were included in the refinement at geometrically idealized positions, with O—H = 0.82 Å and C—H = 0.96–0.99 Å, and U_{iso} = 1.5 (methyl and hydroxyl) and 1.2 (others) times U_{eq} of the atoms to which they were bonded. The final difference map was free of any chemically significant features. The absolute configuration could not be determined in the absence of any significant anomalous scattering other than that of disordered an partially occupied Cl; Friedel pairs were merged.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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