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(*E*)-(20*S*,25*S*)-20,23-Diacetyl-5β-furost-22-ene-3β,26-diyl diacetate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.116
Data-to-parameter ratio = 9.6

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

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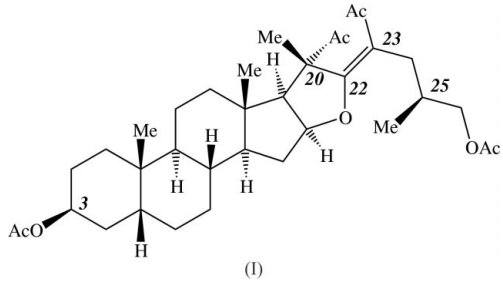
The crystal structure of the title compound, $C_{35}H_{52}O_7$, obtained by the Lewis-acid-catalysed acetolysis of sarsasapogenin, confirms that the configuration around the double bond of the side chain is *E* and that of the chiral C atom α to this double bond is *S*. This geometry is in agreement with NMR data.

Comment

Sapogenins are aglycones of saponins, which are present in a great variety of plants. Sarsasapogenin, a well known member of this class of compounds, is a potentially useful starting material for the partial synthesis of biologically important steroids (Marker, 1940). Acetolysis of sapogenins is of interest, since it allows access to a variety of derivatives resulting from the cleavage of the terminal *F* ring, followed by modification of the side chain. However, these reactions generally follow complicated pathways, through mechanisms that are not well understood, and give complex mixtures of products. A full characterization of these products, mainly using sophisticated NMR techniques, remains a challenge. For instance, several authors have claimed that the reactions of sapogenins of the 25*R* series with Ac_2O, in the presence of BF_3 or $AlCl_3$, afford 23-acetylfurost-22-enes (Cameron *et al.*, 1955; Zderick *et al.*, 1962; Uhle, 1965; Tian *et al.*, 1994). However, recent evidence has pointed to a re-interpretation of these results (Sandoval-Ramírez *et al.*, 1999). Clearly, in these cases, X-ray studies are essential to resolve the controversy.

In the case of the $BF_3\cdots Et_2O$-catalysed acetolysis of sarsasapogenin (25*S*-series), the reaction yields at least four products (Sandoval-Ramírez, Meza-Reyes, del Río *et al.*, 2003), one of which was characterized crystallographically, *viz*. (25*S*)-23-acetyl-5β-furost-22-ene-3β,26-diyl diacetate (Sandoval-Ramírez, Meza-Reyes, Montiel-Smith *et al.*, 2003), allowing confirmation of the *E* configuration of the double bond at C22═C23. We report here the structure of the title compound, (I), obtained from the same reaction, which differs in the substituents at C20: a methyl and an acetyl group.



(I)

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Compound (I) displays the expected *A*–*E* steroidal framework bonded to the side chain through a C22═C23 double bond (Fig. 1 and Table 1). The *E* configuration of the double bond in the solid state is also observed in solution, as shown by the high value for the molar absorptivity ε in the UV spectrum of (I) (see *Experimental*). The six-membered *A*, *B* and *C* rings adopt the expected chair conformation, while the five-membered *D* and *E* rings are twisted about C13—C14 and C16—C17, respectively. It is worth noting that the conformation of ring *E* depends on the substitution at C20. If the functional group at C20 is a methyl group, the molecule adopts an envelope conformation with C17 out of the plane (Sandoval-Ramírez, Meza-Reyes, Montiel-Smith *et al.*, 2003). In contrast, (I), where C20 is substituted by methyl and acetyl groups, exhibits a twisted conformation. The steric requirement of the acetyl group probably accounts for this distortion. On the other hand, the steric hindrance between the acetyl groups at C20 and C23 is minimized by the *s-cis* conformation adopted by the α,β-unsaturated system C22═C23—C23′(═O23″).

In this type of reaction, the absolute configuration at C20 should be examined carefully, since it is known that in nature the methyl group at C20 is placed on the α steroidal side, because of its steric hindrance. In the case where there are two groups at C20, it should be expected that the bulkier group will be placed α, as found in this study. The stereochemistry at C20 in (I) may be determined unambiguously by a NOESY (nuclear Overhauser effect spectroscopy) experiment, which established through-space interactions, for example that between the C18 methyl protons and those at C21. These results are confirmed by the present X-ray study, which establishes that the configuration at C20 is *S*. The C—CH_3 torsion angles were optimized for all methyl groups, allowing a degree of reliability for H-atom positions. For the methyl groups bonded to C18 and C20, the shortest observed H···H intramolecular contact is 2.24 Å, between H18*A* and H21*B*. This separation is shorter than the sum of the van der Waals radii, (2.40 Å; Bondi, 1964), and is likely to correspond to the interaction detected in the NOESY experiment.

Experimental

The title compound, (I), was prepared as previously reported (Sandoval-Ramírez, Meza-Reyes, del Río *et al.*, 2003; Sandoval-Ramírez, Meza-Reyes, Montiel-Smith *et al.*, 2003). Suitable single crystals of (I) were obtained from an MeOH solution. Spectroscopic data are in full agreement with the crystal structure. Data related to the double bond: IR, ν_{max}(C═C) = 1607 cm^{-1}; UV, λ_{max} (ε): 282 nm (14400 l mol^{-1} cm^{-1}).

Crystal data

$C_{35}H_{52}O_7$
M_r = 584.77
Triclinic, *P*1
a = 7.6789 (9) Å
b = 10.2222 (11) Å
c = 11.3519 (13) Å
α = 102.368 (9)°
β = 103.812 (10)°
γ = 101.113 (9)°
V = 816.81 (16) Å^3
Z = 1
D_x = 1.189 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 65 reflections
θ = 4.7–13.4°
μ = 0.08 mm^{-1}
T = 296 (1) K
Plate, colorless
0.60 × 0.60 × 0.20 mm

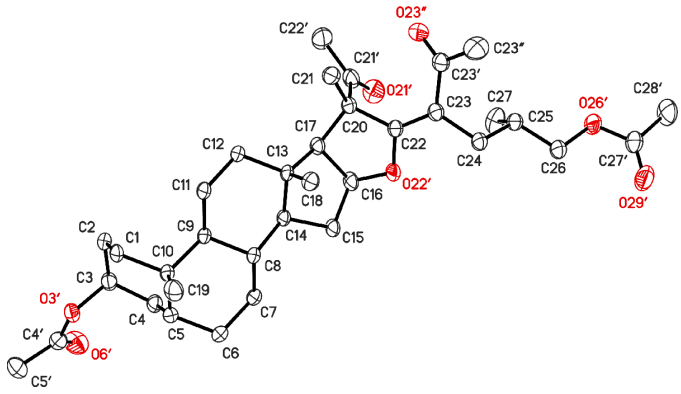

Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. For clarity, H atoms have been omitted.

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
5573 measured reflections
3710 independent reflections
3430 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.5°
$h = -9 \rightarrow 3$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
every 97 reflections
intensity decay: 10.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
S = 0.97
3710 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.0696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.022 (6)

Table 1
Selected geometric parameters (Å, °).

C3—O3′	1.469 (3)	C22—C23	1.340 (3)
O3′—C4′	1.339 (4)	C22—O22′	1.360 (3)
C4′—O6′	1.204 (4)	C23′—O2″	1.218 (3)
C4′—C5′	1.485 (5)	C23′—C23″	1.508 (4)
C16—O22′	1.443 (3)	C26—O26′	1.453 (3)
C20—C21	1.541 (3)	O26′—C27′	1.327 (3)
C20—C21′	1.548 (3)	C27′—O29′	1.199 (4)
C21′—O21′	1.209 (4)	C27′—C28′	1.494 (5)
C21′—C22′	1.506 (4)		
C22—C20—C21′—O21′	30.8 (3)	O22′—C22—C23—C24	1.3 (3)
C21′—C20—C22—C23	81.0 (3)	C20—C22—C23—C24	−178.6 (2)
O22′—C22—C23—C23′	176.8 (2)	C22—C23—C23′—O2″	−33.0 (3)
C20—C22—C23—C23′	−3.2 (3)		

Friedel pairs (1863 pairs) were merged in the last least-squares cycles. The absolute configuration of (I) was assigned on the basis of an unchanged configuration of chiral C atoms during the synthetic process; the starting material, sarsasapogenin, was previously reported with an *S*-C10 configuration (Agrawal *et al.*, 1997) and this configuration is reflected in chemical displacements in NMR spectroscopy for C19: δ = 0.97 for ^{1}H-NMR and δ = 23.92 p.p.m. for ^{13}C NMR. For (I), spectroscopic data indicate that this chiral center is unchanged: δ = 0.97 for ^{1}H-NMR and δ = 23.56 p.p.m. for ^{13}C NMR (Sandoval-Ramírez, Meza-Reyes, del Río *et al.*, 2003).

H atoms were placed at idealized positions and were treated as riding atoms, with C—H distances constrained to 0.96 Å (methyl groups), 0.97 Å (methylene CH_2) or 0.98 Å (methine CH). U_{iso}(H) parameters were set to 1.5U_{eq}(parent C) for methyl groups or

$1.2U_{eq}$(parent C) for methylene and methine groups. In the final least-squares cycles, torsion angles for $C-CH_3$ groups were allowed to refine, maintaining a tetrahedral geometry for CH_3 groups.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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