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α-Onocerin chloroform hemisolvate

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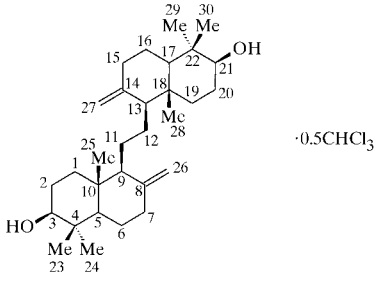
The triterpenoid natural product α-onocerin [8,14-secogammacera-8(26),14(27)-diene-3,21-diol], determined here as the chloroform hemisolvate, $C_{30}H_{50}O_2{\cdot}0.5CHCl_3$, consists of two independent symmetric *trans*-decalin C_{15} building blocks. Hydrogen bonds between the hydroxyl groups form an infinite two-dimensional network perpendicular to the *c* axis.

Comment

The roots of *Ononis spinosa* L. (Fabaceae) are used medicinally as a diuretic drug. Phytochemical identification, diagnosis of drug adulterations and the standardization of extracts are performed using pure α-onocerin as a reference compound. While isolated in 1855, its constitution was assigned using chemical methods only in 1955 (Barton & Overton, 1955, and references therein). However, only the structure of the related 8(26),14(27)-diketones have been studied by X-ray analysis so far (Tsuda *et al.*, 1983). We report here the first X-ray structure of a 3,21-onoceradiene-3,21-diol, (I). This is in continuation of the comprehensive spectral evaluation of α-onocerin focusing on NMR and MS spectral methods which was published recently (Pauli, 2000) and which supported the presence of two *trans*-decalin C_{15} building blocks symmetrically linked by a bimethylene bridge.



(I)

The structural investigation of (I) confirms the assumed geometry. The framework consists mainly of Csp^3-Csp^3 bonds [1.498 (6)–1.576 (5) Å], with only C11—C111 and C21—C211 [1.317 (7) and 1.329 (7) Å] being clearly Csp^2-Csp^2 bonds. Also, both bonds to the hydroxyl groups are in the expected range for a single C—O bond [1.445 (5) and 1.441 (5) Å]. Furthermore, the geometries of both *trans*-decalin C_{15} building blocks are quite similar and comparable with the same skeleton found in gummozine (Nasirov *et al.*, 1977) and 3-α-hydroxymanool hydrate (Kagawa *et al.*, 1993).

Hydrogen bonds between the hydroxyl groups form an infinite two-dimensional network perpendicular to the *c* axis (Table 1). Besides these, there are no further contacts closer than van der Waals distances.

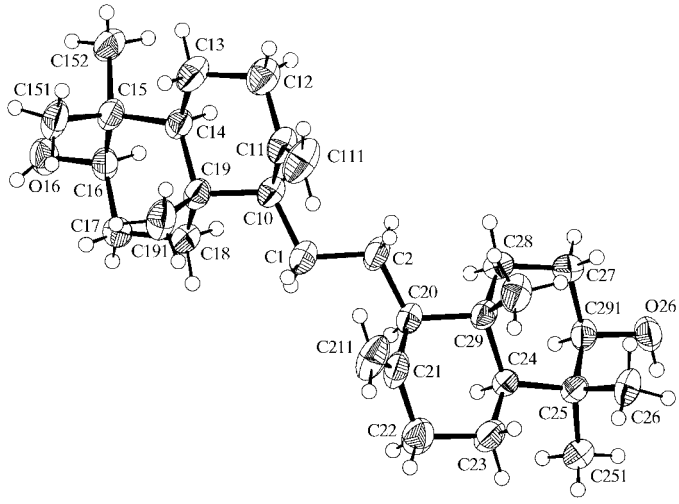


Figure 1
DIAMOND (50% probability) plot (Brandenburg, 1996) of the title compound with the atomic numbering scheme.

The recently published NMR spectroscopic evidence for a symmetric constitution of α-onocerin is now definitively corroborated by the crystallographic data. Therefore, it becomes clear that the C_{30} skeleton consists of two halves that are stereochemically identical. Compared with typical pentacyclic triterpene skeletons, such as oleanolic acid, however, this must be rated a very unusual feature with respect to the designated triterpenoid origin of α-onocerin which has not been supported by biogenetic studies so far. It must be mentioned that no diastereomeric analogues, *e.g.* isomers with inversion of one or more stereocentres, could be detected by NMR (Pauli, 2000). The biogenetic assignment may be challenged in three points: the necessity for fully stereospecific alterations such as (i) the hydrogenation of the 12,13 double bond and (ii) the hydroxylation of the C-21 position, and most importantly, (iii) an inversion of the decalin ring fusion being [*D*/*E*]*cis* in oleanolic acid. Therefore, the classification of α-onocerin as a dimeric sesquiterpene is equally justified at this point and should not be omitted. Concerning the numbering of the α-onocerin framework, which in the literature is again based on the assumption that it represents a triterpene, at this point, revision should be avoided unless the biosynthesis has been investigated.

Experimental

The title compound was obtained from the dried roots of *Ononis spinosa* (sample No. 9200280, PhytoLab, Vestenbergsgreuth) upon Soxhlet extraction with petrol ether, cleaning-up with active charcoal, *in vacuo* precipitation, and repeated crystallization from petrol ether, CH_2Cl_2/EtOAc (1:1), and $CHCl_3$ in a final yield of 0.05%. Colourless crystals were obtained from $CHCl_3$. Calculated mass for $C_{30}H_{50}O_2$: 442.7. Mass spectrum (El; *m*/*z*): 442 (M^+), 427 ($[M-CH_3]^+$), 409 ($[M-CH_3-H_2O]^+$), 391 ($[M-CH_3-2H_2O]^+$), 381 ($[M-CH_3-CO-H_2O]^+$). ^{1}H NMR ($CDCl_3$): δ, 1.572 (*qddd*, 1[19]*A* = eq), 0.952 (*ddd*, 1[19]*B* = ax), 1.552 (*dddd*, 2[20]*A* = eq), 1.441 (*dddd*, 2[20]*B* = ax), 3.090 (*dd*, 3[21]α), 0.946 (*dd*, 5[17]ax), 1.604 ([*d*]*dddd*, 6[16]*A* = eq), 1.239 (*dddd*, 6[16]*B* = ax), 2.268 (*ddd*, 7[15]*A* = eq), 1.839 (*dddddt*, 7[15]*B* = ax), 1.369 (*m*, 9[13]), 1.369 (*m*[*dddd*], 11[12]*A*), 1.055 (*m*[*dddd*], 11[12]*B*), 0.845 (*s*, 23[30]), 0.616 (*s*, 24[29]), 0.505 (*br s*/*d*, 25[28]), 4.695 (*dd*, 26[27]*A*), 4.442 (*ddd*, 26[27]*B*). ^{13}C NMR ($CDCl_3$): 36.84 (1[19]), 27.27 (2[20]), 78.43 (3[21]), 38.84 (4[22]), 54.50 (5[17]), 23.81 (6[16]), 38.03 (7[15]), 148.28 (8[14]), 57.28 (9[13]), 39.00 (10[18]), 22.30 (11[12]), 27.91 (23[30]), 15.09 (24[29]), 14.21 (25[28]), 106.35 (26[27]).

Crystal data

$C_{30}H_{50}O_2\cdot0.5CHCl_3$
M_r = 502.38
Orthorhombic, $P2_12_12_1$
a = 7.470 (1) Å
b = 14.681 (2) Å
c = 27.079 (4) Å
V = 2969.7 (7) Å^3
Z = 4
D_x = 1.124 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 22.46–46.14°
μ = 1.716 mm^{-1}
T = 223 (2) K
Block, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (Fair, 1990)
T_{min} = 0.627, T_{max} = 0.783
3450 measured reflections
3450 independent reflections
2318 reflections with $I > 2\sigma(I)$
θ_{max} = 74.29°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 33$
3 standard reflections
every 250 reflections
frequency: 120 min
intensity decay: 6.7%

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

D—H···A	D—H	H···A	D···A	D—H···A
O16—H16A···O26^{i}	0.83	2.04	2.822 (5)	157
O26—H26A···O16^{ii}	0.83	2.17	2.817 (5)	135

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.076
$wR(F^2)$ = 0.228
S = 0.991
3450 reflections
313 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1687P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.05 (19)

The asymmetric unit contains half a disordered molecule of chloroform as a residual solvent. This disorder decreases the quality of the whole investigation. The Flack parameter of −0.05 (19) favours the reported absolute configuration, but due to the disorder problem and the fact that a large fraction of Friedel-related reflections have not been measured, this detail should not be overrated. The occupancy of the disordered chloroform was first refined and then fixed with a site-occupancy factor of 0.5. Refinement with anisotropic displacement parameters and/or restraints did not improve the model; therefore, these four atoms are only refined isotropically.

Data collection: *EXPRESS* (Nonius, 1994); cell refinement: *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1405). Services for accessing these data are described at the back of the journal.

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