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STRUCTURE OF SEVELINE

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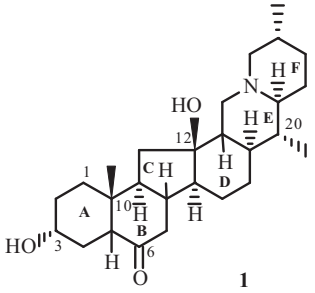
UDC 547.945+547.79+548.737

Separation of total alkaloids from the aerial part of *Korolkowia sewerzowii* (Liliaceae) over a column of silica gel isolated a base with mp 269–271°C (acetone) that was identical to the steroidal alkaloid seveline (according to TLC and IR spectroscopy), for which the most probable structure was proposed earlier as 3α,20β-dihydroxysevanin-6-one [1]. However, the methods used earlier [1] could not unambiguously resolve the question of the location of all substituents of **1**.



1

For this reason, we performed an x-ray crystal structure analysis (XSA) of **1**. Single crystals of **1** were transparent, elongated prisms with $a = 7.5657(2)$, $b = 10.7187(2)$, $c = 15.3648(3)$ Å, $\beta = 101.593(2)°$, V = 1220.58(5) Å^3, ρ_{calc} = 1.169 g/cm^3, space group $P2_1$, $Z = 2$. Unit-cell constants were determined and refined on a CCD Xcalibur Ruby diffractometer (Oxford Diffraction) using Cu K_α-radiation (300 K, graphite monochromator). A three-dimensional data set of reflections was collected on the same diffractometer. Absorption corrections were made semi-empirically using the SADABS program [2].

The structure was solved by direct methods using the SHELXS-97 program set. The structure was refined using the SHELXL-97 program [3]. All nonhydrogen atoms were refined by anisotropic full-matrix least-squares methods (over F^2). Positions of H atoms were found geometrically and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$ where n = 1.5 for methyls and n = 1.2 for others and U_{eq} is the equivalent isotropic thermal parameter of the corresponding C atoms. Hydroxyl H atoms were found in a difference electron-density synthesis. The final agreement factors (R) were 0.0447 for 2906 reflections [$I > 2\sigma(I)$] (wR2 = 0.1112) and 0.0621 over all 3724 reflections (wR2 = 0.1217). Data for the XSA were deposited in the Cambridge Crystallographic Data Centre (CCDC 766531).

The XSA resolved the previously proposed structure and determined that seveline has the structure and configuration 3α,12β-dihydroxysevanin-6-one (**1**). The third hydroxyl was found to be located on C-12 with the β-axial orientation. Figure 1 shows the molecular structure of **1** from the XSA. As expected, rings A/B-B/C-C/D-D/E-E/F are *trans*-fused. The location and configuration of all other substituents in the C skeleton were confirmed as a methyl on C-10, a β-hydroxyl on C-12, and an α-axial hydroxyl on C-3. The methyls on C-20 and C-25 have the α-equatorial orientation. According to the given structure and Flack 0.0 value (3), the configurations of the steroid chiral centers are 3*R*, 5*S*, 8*R*, 9*S*, 10*R*, 11*S*, 12*R*, 16*R*, 17*S*, 20*R*, 22*S*, and 25*R*. The six-membered rings A, B, E, and F in **1** have practically ideal chair conformations. Ring D is a slightly distorted boat because of the β-orientation of the C-12 hydroxyl. Five-membered ring C adopts a twist conformation with C_2 symmetry (axis passing through C-13 and the middle of the C-8–C-11 bond).

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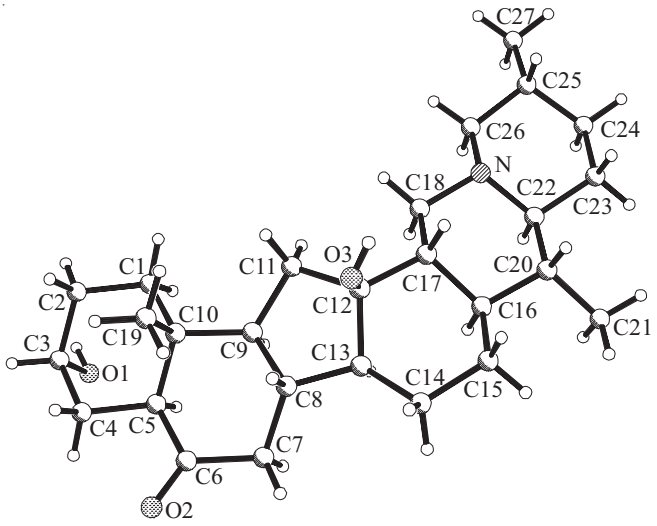

Fig. 1. Molecular structure and atomic numbering in **1**.

An intermolecular H-bond between the C-3 hydroxyl and the carbonyl forms a chain along the crystallographic *a* axis. The parameters of this bond are: O1…O2 2.773(2), O1–H…O2 1.89(3) Å ; angle O1–H…O2 173(3)°. Another intermolecular H-bond between different hydroxyls forms a chain along the 2_1 screw axis (along *b*): O3…O1 2.941(3), O3–H…O1 2.21(4) Å ; angle O3—H…O1 168(3)°. Thus, intermolecular H-bonds in the crystal form a two-dimensional network situated in the *ab* plane.

Seveline is the first steroidal alkaloid containing a C-12 β-axial hydroxyl.

ACKNOWLEDGMENT

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