

TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS. LXXII. X-RAY CRYSTAL STRUCTURE OF CYCLOORBICOSIDE D

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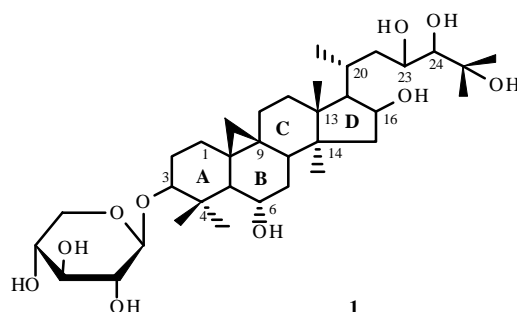
UDC 548.737+547.918:547.926

The structure of the new cycloartane glycoside cycloorbicoside D (**1**), which was isolated from *Astragalus orbiculatus* Ledeb. (Leguminosae), was determined based on chemical transformations and spectral data as 23 ξ ,24 ξ -cycloartan-3 β ,6 α ,16 β ,23,24,25-hexaol 3-*O*- β -D-xylopyranoside [1]. The methods used previously [1] were not capable of resolving the issue of the stereochemistry of asymmetric C-23 and C-24 in the glycoside. The present communication addresses this problem.

Figure 1 shows the molecular structure of **1** that was established by an x-ray crystal structure (XCS). Glycoside **1** contains six-membered rings A and C with practically ideal chair conformations (four atoms of the ring lie in a plane within ± 0.015 Å). Ring B has the twist-boat conformation due to the presence of β -orientated 9,19-cyclopropane. Five-membered ring D takes the conformation of an envelope. As expected, the ring fusions are A/B *trans*, B/C *cis*, and C/D *trans*. The location and configuration of all substituents were confirmed. The conformation of the side chain favors the formation of intramolecular H-bonds (IHB) between the C-23 and C-25 hydroxyls (O23—O25 distance 2.60 Å).

Taking into account the (3*S*,5*S*,6*S*,8*R*,13*R*,14*S*,16*S*,17*S*,20*R*) stereochemistry for **1**, the molecular structure indicates that asymmetric C-23 and C-24 have the 23*R*,24*R* configurations.

Thus, **1** has the structure 23*R*,24*R*-cycloartan-3 β ,6 α ,16 β ,23,24,25-hexaol 3-*O*- β -D-xylopyranoside.



Single crystals of **1** were the dihydrate (C₃₅H₆₀O₁₀·2H₂O). The packing and intermolecular contacts in the crystal revealed O...H—O H-bonds between the hydroxyls and the waters of crystallization that formed a three-dimensional framework of weak interactions.

Compound **1** was recrystallized from CHCl₃:CH₃OH:H₂O (70:23:4) at 19°C, mp 266–267°C. Single crystals of **1** were transparent elongated prisms: *a* = 13.366(3), *b* = 6.074(1), *c* = 22.663(5) Å, β = 104.26(3)°, *V* = 1783.2(6) Å³, ρ_{calc} = 1.261 g/cm³, space group *P*2₁, *Z* = 2. Unit cell constants and intensities of reflections were measured on a STOE Stadi-4 four-circle diffractometer ($\theta/2\theta$ -scanning) using Mo K α -radiation (graphite monochromator). Absorption corrections were not applied.

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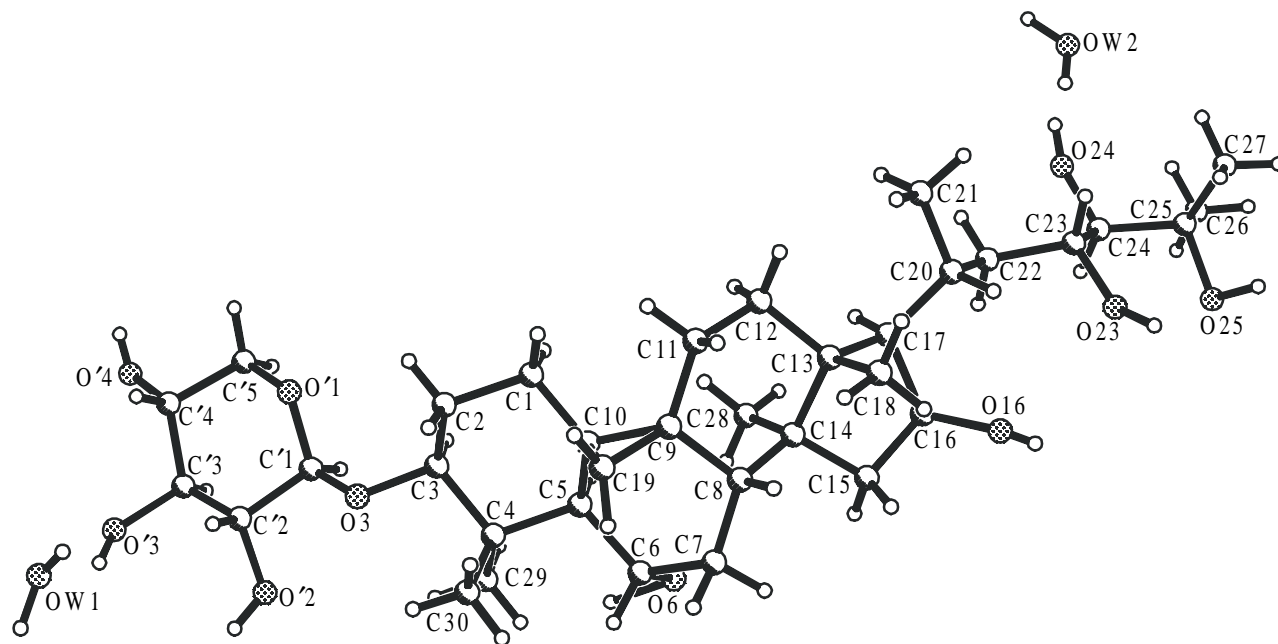


Fig. 1. Molecular structure and atomic numbering for cycloorbicoside D (water of crystallization also shown).

The structure was solved by direct methods using the SHELXS-97 programs. The structure was refined using the SHELXL-97 program. All nonhydrogen atoms were refined using anisotropic full-matrix least-squares methods (over F^2). The positions of H atoms were found geometrically and refined with fixed isotropic thermal parameters $U_{\text{iso}} = nU_{\text{eq}}$, where $n = 1.5$ for methyls and 1.2 for others and U_{eq} is the equivalent isotropic parameter of the corresponding C atom. Hydrogen atoms of hydroxyls and the water of crystallization were found in a difference electron-density synthesis. The final agreement factors (R) were 0.0860 for 2203 reflections [$I > 2\sigma(I)$] ($wR2 = 0.1766$) and 0.1159 for all 3031 reflections ($wR2 = 0.1950$).

The data from the XCS were deposited in the Cambridge Crystallographic Data Centre (CCDC 604459).

REFERENCES

1. R. P. Mamedova, M. A. Agzamova, and M. I. Isaev, *Khim. Prir. Soedin.*, 345 (2005).