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As was already reported earlier [1], miliacin (I), mp 282-283°C, was isolated from pulverized millet seeds of the strains Saratovskii 853 and Podolyanskii 24/273 by extraction with ether, and to it was assigned the structure of a pregnane derivatives on the basis of qualitative reactions, UV, IR, and NMR spectral data. The empirical formula $C_{23}H_{38}O$, resulting from elemental analysis data, was assigned to the compound.

UDC 541.6+547.599.2+547.9

EXPERIMENTAL

Our investigation of (I) showed that miliacin has mp 285-286° (from ethyl acetate), $[\alpha]_D^{25} + 16^\circ$ (C1, CHCl₃) and gives a positive reaction with $C(NO_2)_4$. On the basis of mass spectral data, (I) has a mol. wt. of 440, which also agrees with the results of elemental analysis. Found: C 84.54, 84.76; H 12.08, 12.29% $C_{31}H_{52}O$. Calculated: C 84.48; H 11.89%; mol. wt. 440.73. It also follows from the mass spectrum that (I) has the structure of a pentacyclic triterpenoid alcohol, since the main peaks (at m/e 440, 408, 204, 189, 177) correspond to fragmentation of Δ^{18} -oleaenes [2] (for Δ^{12} -oleanenes, a peak at m/e 218 is characteristic and for Δ^{13} (18)-derivatives, at m/e 205. Examination of the NMR spectrum of (I) also demonstrated the presence of one double bond (the signal of the vinyl proton at 4.82 p.p.m.).

Miliacin is not hydrogenated in the presence of $30\% \text{ Pd/CaCO}_3$ in ethyl acetate, is not dimethylated with $C_5H_5N \cdot \text{HCl}$ at 210°, and is stable upon pyrolysis (heating in a sealed ampule 330° , 3 h), but upon treatment of (I) (0.23 g) with acetic anhydride (15 ml) and paratoluenesulfonic acid (0.046 g) (boiling 20 min) or upon reaction of 0.02 g of (I) with BF₃ etherate (10 ml) in (CH₃CO)₂O (1.5 ml, 20°, 48 h), a C₃OH₄₈ hydrocarbon is obtained in a yield of 62% [3], mp 126-127° (from acetone), $[\alpha]_D^{25} + 58.4°$ (C1, CHCl₃). This hydrocarbon, to which structure (II) is assigned, gives a positive reaction with C(NO₂)₄ and is not hydrogenated in the presence of 30% Pd/CaCO₃ in ethyl acetate or with PtO₂ in CH₃COOH at 100° (80 atm).

The structure of (II) was confirmed by the IR spectrum (absence of a band at 1110 cm⁻¹ corresponding to the -OCH₃ group) and the NMR spectrum (presence of a vinyl proton at C_{18} of 4.82 p.p.m. and the total absence of signals in the region 2.68-1.59 p.p.m., characteristic for the methyls of an isopropylidene group).



On the basis of the obtained data, miliacin is 3β -methoxygermanicene (3β -methoxy- Δ^{18} -oleanene), and (II) is 8,10,14-trimethyl- Δ^{3} (5),8-neooleanadiene. This coincides with data of [4], in which a compound was also isolated (from Japanese varieties of millet) having mp 283°, to which the structure of 3β -methoxygermanicene was assigned on the basis of UV, IR spectra and a series of chemical transformations.

(I) in a maximum soluble dose (in alcohol) does not suppress the growth of <u>Staph.</u> <u>aureus</u> <u>209P</u>, <u>E.</u> Coli, and Candida albicans.

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CONCLUSIONS

On the basis of mass and NMR spectral data and a series of chemical transformations, the structure of 3β -methoxygermanicene (3β -methoxy- Δ ¹⁸-oleanene) has been assigned to miliacin.

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