STRUCTURE OF STENANZIDININE

K. Samikov, R. Shakirov,
and S. Yu. Yunusov

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On the basis of the results of a study of the chemical and physical characteristics of the alkaloid itself and of the products of its transformation, the most probable structure and partial configuration of stenanzidinine have been established as 3β,6α-dihydroxycevanine.

The new alkaloid stenanzidinine, $C_{27}H_{45}NO_2$ (I) was isolated some time ago from the epigeal part of *Rhinopetalum stenantherum* Regel [1, 2]. The IR spectrum of the base contains absorption bands at (cm^{-1}) 3450 (OH), 2980-2818, 1470, 1454 ($-CH_3$; $-CH_2-$), 2777 (trans-quinolizidine). The mass-spectrometric fragmentation of stenanzidinine takes place in a similar manner to that of petilidine: peaks of ions are recorded with m/z 98, 111, 112, 124, 125, 139, 149, 164, 358, $(M-56)^+$, $(M-29)^+$, $(M-28)^+$, $(M-17)^+$, $(M-15)^+$, 415 M^+ [3].

With acetic anhydride in pyridine, (I) formed diacetylstenanzidinine (II). The IR spectrum of (II) contained absorption bands at 1743 and 1247 cm^{-1} (ester C=O) and lacked the absorption band of hydroxy groups. The oxidation of stenanzidinine with chromium trioxide gave a diketone — stenanzidininedione (III).

The IR spectrum of (III) showed an absorption band at 1713 cm^{-1} (carbonyl in a six-membered ring). Consequently, both hydroxy groups of (I) have a secondary nature. Details of the PMR spectra of (I) and (II) are given below (s — singlet; d — doublet; m — multiplet) (δ, ppm):

Substance	19-CH_3, s	21-CH_3, d	27-CH_3, d	6H,$OCOCH_3$, s	2H,H—$COCOCH_4$,m
I	0,73	0.83	0,83		
II	0,82	0.82	0,82	1,95	4,59

To judge from the mass and PMR spectra of (I) and (II), stananzidinine has the heterocyclic skeleton of cevanine [3]. The positions of the secondary hydroxy groups were determined by comparing the CS values for the 19-CH_3 group of (I) and (II) with the CS values of the 19-CH_3 in the spectra of petilidine (IV) and of diacetylpetilidine (V) [3]. The values of the 19-CH_3 signals in the PMR spectra of (I) and (II), on the one hand, and (IV) and (V), on the other hand, are close. This shows the positions of the hydroxy groups at C_3 and C_6 and the trans-linkage of rings A/B and B/C. In the PMR spectrum of diacetylstenanzidinine the protons geminal to the acetyl groups resonate at 4.59 ppm, which corresponds to the 3β,6α-equatorial orientation of the hydroxy groups at (I) [5].

In the PMR spectra of (I) and (II), the CSs from the C-21 and C-27 methyl groups are present in strong fields, which is due to their α orientation [6]. The absorption band of a trans-quinolizidine system shows the trans-linkage of rings E/F. A comparison of the IR and mass spectra of stenanzidinine and of petilidine showed that they are close. In the PMR spectrum of (I), the signal from the 21-CH_3 and 27-CH_3 groups is shifted downfield by 6 Hz as compared with that of petilidine. Stenanzidinine differs from petilidine in its R_f values, melting point, and specific rotation. A mixture of stenanzidinine and petilidine melted at 203-205°C. Thus, stenanzidinine is an isomer of petilidine which may differ from it by the linkage of rings C/D or D/E.

According to the facts presented above, stenanzidine has the structure and partial configuration of (I).

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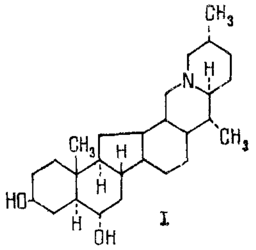

I

EXPERIMENTAL

For thin-layer chromatography (TLC) we used KSK silica gel (90 mμ) and alumina (activity grade II) and chloroform–methanol solvent systems: 1) (10:0.5); 2) (10:0.7). The IR spectra were taken on a UR-20 double-beam spectrophotometer (molded tablets with KBr) the mass spectra on a MKh-1310 instrument, and the PMR spectra on a JNM-4H-100/MHz instrument in deuterochloroform with HMDS as internal standard (δ scale).

Stenanzidinine has mp 215-217°C (acetone, $[\alpha]_D$ +5° (c 0.8; chloroform), R_f 0.35 (Al_2O_3, system 1) [1, 2].

Diacetylstenanzidinine. The acetylation of 0.05 g of stenanzidinine was performed with 1 ml of pyridine and 1 ml of acetic anhydride as for the acetylation of petilidine [3]. Amorphous diacetylstenanzidinine was obtained with R_f 0.45 (SiO_2, system 2).

Mass spectrum: m/z 98, 111, 112, 124, 125, 138, 139, 140, 149, 150, 162, 164, 166, 178, 190, $(M - 60)^+$, $(M - 59)^+$, $(M - 43)^+$, $(M - 42)^+$, $(M - 15)^+$, 499 M^+.

Stenanzidinindione. A solution of 0.07 g of chromium trioxide in 2 ml of 80% acetic acid was added to a solution of 0.13 g of the base in 2 ml of acetic acid. The mixture was heated on the water bath for 1 h, the solvent was evaporated off in vacuum, the residue was dissolved in water, and the solution was made alkaline with ammonia and was extracted with chloroform. This yielded the diketone stenanzidinindione with mp 173-174°C (acetone), R_f 0.80 (Al_2O_3, system 1).

Mass spectrum: m/z 98, 111, 112, 124, 125, 138, 139, 149, 150, 164, 178, 354, 355, 382, 383, 396, 411 M^+.

SUMMARY

On the basis of the results of a study of the chemical and physical properties of the alkaloid and the products of its transformation, a most probable structure and partial configuration has been established for stenanzidinine.

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