ALKALOIDS OF *Rhinopetalum stenantherum.*

STRUCTURE OF STENANZIDINE

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Three new alkaloids have been isolated from the combined alkaloids of the epigeal part of *Rhinopetalum stenantherum*: stenanzidine, stenanzidinine, and stenanzamine.

From the epigeal part of *Rhinopetalum stenantherum* Regel, by separating the stenanzine mother liquor [1, 2], we have isolated three new bases — stenanzidine, stenanzidinine, and stenanzamine.

Stenanzidine, $C_{27}H_{45}NO_2$ (I), is a tertiary base. Its spectrum contains characteristic absorption frequencies at 3410, 1047, and 1075 cm^{-1} (OH) and at 2975-2865 and 1147 cm^{-1} ($-CH_3$, $-CH_2-$). The mass spectrum of (I) has the peak of ions with m/z 98, 111 (100%), 112, 124, 125, 138, 139, 140, 149, 150, 164, 166, 178, 179, 344, 358, 360, 372, 386, 388, $(M - 18)^+$, $(M - 17)^+$, $(M - 15)^+$, 415 M^+, which are characteristic for alkaloids of the cevine group. The PMR spectra contains a singlet at 1.00 ppm (3 H, 19-CH_3), two doublets at 1.13 and 1.19 ppm from secondary methyl groups, and multiplets at 3.30 and 3.77 ppm (2 H, H—C—OH) ($CDCl_3$ + CD_3OD).

In stenanzidine, the oxygen atoms are present in the form of secondary hydroxy groups as was confirmed by the preparation of diacetylstenanzidine (II). The IR spectrum of (II) showed absorption frequencies of 1740 and 1245 cm^{-1} (ester C=O), and it lacked the absorption of a hydroxy group. The PMR spectrum showed singlets at 0.94 ppm (3H, 19-CH_3), 1.95 ppm ($OCOCH_3$), 1.96 ppm (3 H, $OCOCH_3$), doublets at 1.10 and 1.16 ppm (two secondary methyl groups), and multiplets at 4.65 and 4.90 ppm (2 H, H—$COCOCH_3$) ($CDCl_3$).

The oxidation of stenanzidine with chromium trioxide gave a diketone — stenanzidinedione (III). The latter had λ_{max} 302 nm (log ε 3.97) in its UV spectrum, which is characteristic for nonconjugated carbonyl groups. The IR spectrum of (III) had absorption bands at 1717 cm^{-1} (carbonyl in a six-membered ring) and lacked the absorption band of hydroxy groups. The PMR spectrum of (III) showed a singlet from the 19-CH_3 group at 0.90 ppm and an unresolved doublet from two secondary methyl groups.

Thus, stenanzidine contains the cevanine skeleton [3, 4] in which there are two secondary and one tertiary methyl groups.

It can be seen from the mass spectra of (I-III) that when the hydroxy group in (I) was replaced by an acyl (II) or a keto (III) group, the peaks of ions with m/z 98, 111, 112, 124, 138, 139, 140, 149, 150, 164, 166, 178, and 179, which are formed from rings D, E, and F, remained unaffected. It follows from this that the secondary hydroxy groups in stenanzidine can be present only on the carbon atoms of rings A, B, and C.

From a comparison of the CSs of the signals from the 19-CH_3 protons of (I-III) with those of dihydroimperialine and severtzidine [5-7], it is possible to draw the conclusion that rings A/B and B/C are trans-linked and C/D cis-linked, as in the sevine molecule [3, 4]. Ring C is excluded for the hydroxy group because of the absence of the absorption of a carbonyl group in a five-membered ring in the IR spectrum of (III).

The IR spectra of (I) and (III) have absorption bands at 1077 and 1035 cm^{-1}, respectively, showing the presence of a β-oriented hydroxy group at C_3 in each case. This is confirmed by the presence of a multiplet at 4.65 ppm for $C_3\alpha$-H in the PMR spectrum of diacetylstenanzidine [5-9]. Stenanzidine is not oxidized by periodic acid, which shows the absence of vicinal hydroxyls and excludes the presence of the second hydroxyl at C_2 or C_4. The chemical shift of the proton of the 19-CH_3 group in the PMR spectrum of (III) is 10 Hz more upfield than that of stenanzidine. This excludes the presence of the hydroxy group at C_1 or

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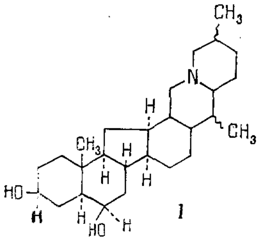
C_7 [10]. Consequently, the second hydroxy group is present in the C_6 position and has the β orientation. This is confirmed by a comparison of the CSs of the protons of the C-19 methyl groups in the PMR spectra of (I-III) with those for dihydroimperialine and severtzidine [5-7] and also by the presence in the PMR spectrum of diacetylstenanzidine of a multiplet at 4.90 ppm from $C_6\alpha$–H [8].

According to these facts, stenanzidine has the most probable structure and partial configuration of 3β,6β-dihydroxycevanine (I).



I

EXPERIMENTAL

For thin-layer chromatography (TLC) we used KSK silica gel (90 mμ), alumina (activity grade II), and the solvent systems chloroform–methanol (10:0.5) (1), (10:1.5) (2), and (20:1.5) (3), the revealing agent being Dragendorff's solution. UV spectra were taken on a Hitachi spectrophotometer, IR spectra on a UR-20 double-beam spectrophotometer (molded tablets with KBr), mass spectra on a MKh 1303 instrument, and PMR on a JNM-4H-100/100 MHz instrument with HMDS as internal standard (δ scale).

Isolation of the Alkaloids. The mother liquor from stenanzine was concentrated, dissolved in chloroform–methanol (10:0.1), and passed through a column of alumina, with elution by chloroform–methanol (10:0.1). The first 50 ml of eluate yielded stenanzine with mp 275-277°C (methanol–acetone (1:5), $[\alpha]_D - 17°$ (c 0.7; ethanol)), M^+ 415, R_f 0.3 (SiO_2, system 2).

The subsequent eluates yielded stenanzidinine with mp 215-217°C (acetone) $[\alpha]_D - 5°$ (c 0.7; chloroform), R_f 0.3 (Al_2O_3, system 1). From the combined stenanzidine and stenanzidinine mother liquors after rechromatography on a column of alumina, we obtained an amorphous base – stenanzamine, $[\alpha]_D - 22.3°$ (c 0.85; chloroform), R_f 0.50 (Al_2O_3, system 1).

O,O'-Diacetylstenanzidine. A mixture of 0.06 g of stenanzidine, 1 ml of pyridine, and 1 ml of acetic anhydride was kept at room temperature for 2 days. After the elimination of the pyridine, the residue was treated with 5% sulfuric acid. The acid solution was made alkaline with ammonia, and the alkaloids were extracted with chloroform. This gave diacetylstenanzidine with R_f 0.18 (SiO_2, system 3). The saponification of diacetylstenanzidine with methanolic caustic potash formed stenanzidine.

Mass spectrum: m/z 98, 111 (100%), 112, 124, 125, 138, 139, 140, 149, 150, 164, 166, 178, 179, 396, 429, 430, 431, $(M-60)^+$, $(M-59)^+$, $(M-43)^+$, $(M-42)^+$, 470, 471, $(M-15)^+$, 499 M^+.

Oxidation of Stenanzidine. A solution of 15 mg of chromium trioxide in 1 ml of 80% acetic acid was added to 0.03 g of stenanzidine in 1 ml of acetic acid. The mixture was heated in the water bath for 30 min, and then the solvent was distilled off, the residue was dissolved in water, the solution was made alkaline and extracted with chloroform. This gave a diketone – stenanzidinedione – with mp 174-176°C (acetone), R_f 0.76 (Al_2O_3, system 1).

Mass spectrum: m/z 98, 111 (100%), 112, 124, 125, 138, 139, 140, 149, 150, 164, 166, 178, 179, 340, 341, 342, 354, 368, 370, 382, 383, 384, 396, 411 M^+.

CONCLUSION

1. Three new alkaloids have been isolated from the combined alkaloids of the epigeal part of *Rhinopetalum stenantherum*: stenanzidine, stenanzidinine, and stenanzamine.

2. On the basis of the chemical and physical characteristics of the alkaloid itself and the products of its transformation, the most probable structure and partial configuration of 3β,6β-dihydroxysevanine have been established for stenanzidine.

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THE NMR INVESTIGATION OF ALKALOIDS.

VII. ^{13}C NMR SPECTRA AND STRUCTURE OF "KOPSANONE" AND KOPSINILAM

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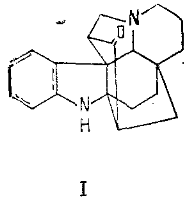
On the basis of a study of the ^{13}C NMR spectra of a base from *Vinca erecta* previously regarded as "kopsanone," and the known alkaloid kopsinilam, it has been shown that the former is 5,22-dioxokopsane.

A base with mp 284-285°C, $[\alpha]^{20}_{D}$ + 98.6° (c 0.18; chloroform), R_f 0.4 [5], has previously been isolated from the plant *Vinca erecta* Regel et Schmalh., for which, on the basis of its composition and an analysis of its UV, IR, and mass spectra, the structure of "kopsanone" (I) was proposed [1]. However, the later purification of this base led to a rise in the melting point to 304-305°C. In addition, the mass spectrum, the composition, and the presence in its IR spectrum of two bands corresponding to the stretching vibrations of a ketonic C=O group in a five-membered ring at 1750 cm^{-1} and of a lactam at 1670 cm^{-1} showed that this base was not "kopsanone" but 5,22-dioxokopsane (II) (kopsanone lactam) isolated previously from the plants *Pleiocarpa mutica* Benth. [2] and *Alstonia venenata* R. Br. [3], and synthesized from kopsanone [4].

In order to investigate the structure further, we have studied the ^{13}C NMR spectrum both of the base 5,22-dioxokopsane under investigation and of the known alkaloid kopsinilam (III) [5, 6].



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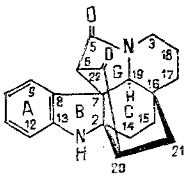

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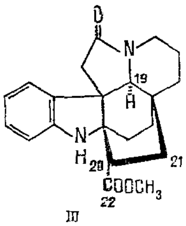

III

The assignment of the signals of the carbon atoms was made on the basis of an experiment with complete and incomplete decoupling of C–H interactions taking α-, β-, and γ- contributions into account [12], and also by a comparison with literature figures for the ^{13}C CSs of substances having similar structures [7-9]. The results are given in Table 1 and in Fig. 1.

In the spectrum of (II) eight signals of sp^2 carbon atoms appear in the 110-205 ppm region — six signals from an aromatic ring and two signals of carbonyl carbons (ketonic and lactamic). The signals of the sp^3 carbons resonate in the 70-19.5 ppm region, two of them

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