ALKALOIDS OF *Rhinopetalum bucharicum*

THE STRUCTURE OF RHINOLINE

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From the epigeal part of the plant *Rhinopetalum bucharicum* (Rgl.) Losinsk. (family Liliaceae) [1], collected on April 1, 1977, in the Darvaza range of the Pamir-Alai in the flowering period we have isolated 0.2% of combined alkaloids by chloroform extraction.

By separating the combined alkaloids on a column of silica gel we isolated solanidine [2, 3], the new alkaloid rhinoline, with mp 255-257°C, $[\alpha]_D$ −53.2° (c 1.94; ethanol), $C_{34}H_{57}NO_7$ (I), and a base with mp 301-302°C. The IR spectrum of rhinoline shows absorption bands at (cm^{-1}) 3500-3120 (hydroxy groups), 2965-2830, 1470-1450 ($-CH_3$; $-CH_2-$), 2800 ($N-CH_3$), 1650 (C=CH), 1100-1000 (broad absorption band characteristic for glycoalkaloids [4, 5]). With acetic anhydride in pyridine, rhinoline formed pentaacetylrhinoline (II). The hydrolysis of rhinoline with hydrochloric acid in the presence of ethanol gave an aglycone with mp 199-201°C, $[\alpha]_D$ −52.9° (c 1.70; ethanol) with the composition $C_{28}H_{47}NO_2$, which we have called rhinolidine (III), and D-glucose [5]. The IR spectrum of (III) has absorption bands at (cm^{-1}) 3450-3140, 1050 (hydroxy group), and 2797 ($N-CH_3$).

The acetylation of (III) formed an O,O'-diacetyl derivative (IV), M^+ 513, the IR spectrum of which lacked the absorption band of an OH group but showed absorption bands of an ester carbonyl at 1738 and 1250 cm^{-1}.

The mass spectrum of (III) has the main peaks of ions with m/e 112 (100%), 113, 124, 125, 137, 149, 154, 164, 168, 179, 386, 400 $(M-29)^+$, 401, 402, 414 $(M-15)^+$, 429 $(M)^+$, which are characteristic for typical steroid alkaloids of the edpetilidine series [6, 7]. The NMR spectra of (I), (III), and (IV) are given below (chemical shifts δ, ppm; s — singlet; d — doublet; m — multiplet):

Substance	$19-CH_3$, s	$18-CH_3$, s	$21-CH_3$, d	$COOCH_3$, s	$N-CH_3$, s	$C\underline{H}-OH$, m	$\underline{H}COCOCH_3$, m	(C=CH), m
I	0.98	0.90	1.02		2.25			5.32
III	0.97	0.90	1.03		2,22	4.43; 3,62		5.30
IV	0.97	0,81	1.02	1,87; 1,89	2,21		5.05; 4,55	5.30

The results of a consideration of the IR, NMR, and mass spectra permits the suggestion for (II) of the heterocyclic skeleton of edpetilidine [6, 7].

The formation of a sparingly soluble digitonide of rhinolidine with digitonine, and also the presence of an absorption band at 1050 cm^{-1} in the IR spectrum of rhinolidine shows the presence of a Δ^5-3β-OH group in (III) [8-10].

The difference of 0.09 ppm in the chemical shifts of the protons of the $18-CH_3$ group between (III) and (IV) shows that the second OH group may be present at C_{12} or C_{15} [11]. In diacetylrhinolidine, the signal of the proton geminal to the acetoxy group resonates at 5.05 ppm, and in rhinolidine the signal of this proton is shifted upfield by 0.62 ppm. Such a displacement and difference in the chemical shifts in the spectra of (III) and (IV) indicates that the second OH group in rhinolidine is located at C_{15} and has the β-axial orientation [11, 12]. According to the chemical shifts of the C-19 CH_3 and C-18 CH_3 groups, rings B/C and C/D in rhinolidine are trans-linked [11].

Thus, rhinolidine has the most probable structure and partial configuration (III)

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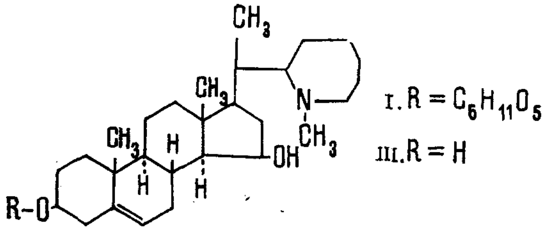

The results of a determination of the difference in molecular rotations between rhinoline and rhinolidine according to Klyne's rule [13] showed that in the rhinoline molecule the glucose is attached to the rhinolidine by a β-glycosidic bond.

On the basis of these facts, for rhinoline we can suggest the most probable structure and configuration as rhinolidine 3β-D-glucopyranoside (I).

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ALKALOIDS OF *Korolkowia sewerzowii*

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Sevcorine, korseveriline, korseveridine, korseveridinine, severine, and a base with mp 145-147°C have been isolated previously from the epigeal part of *Korolkowia sewerzowii* Rgl. collected in the Katrantau (KirgSSR) [1-3]. Continuing the separation of the mother liquor from the combined ether-soluble material according to basic strength, by chromatography on a column of silica gel from chloroform eluates we isolated korsidine [4].

The mother liquor from korseveriline [2] was chromatographed on a column of alumina with elution by chloroform and chloroform–methanol (10:0.5). From the chloroform–methanolic eluates we isolated an alkaloid with mp 212-214°C (acetone), identical with sevedine [5]. The mother liquor from korseveridine [2] was separated on a column of silica gel. The initial chloroform eluates yielded a base with mp 320-322°C (methanol), identical with korseverinine [6, 7].

The mother liquor from the base with mp 145-147°C and severine [3] was chromatographed on alumina. From the chloroform eluates we obtained a base with mp 241-243°C (acetone) having the composition $C_{28}H_{47}NO_2$ (I). The IR spectrum of (I) had ν_{max} (cm^{-1}) 3400, 3125 (OH), 2795 ($N-CH_3$, 1670 (C=C), and in the mass spectrum the main peaks were those of ions with m/e 112 (110%), 125, 138, 150, 164, 178, 358, 400 $(M-29)^+$, 411 $(M-15)$, 429 (M^+), which

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