STRUCTURE OF KORSELIMINE

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

UDC 547.944/945

The new base korselidine with mp 272-274°C (methanol), $[\alpha]_D$–75°, $C_{27}H_{43}NO_2$ (I), (ethanol), composition $C_{27}H_{43}NO_2$, has been isolated from the total alkaloids of the epigeal part of Korolkowia sewerzowii Regel. As a result of the study of the chemical properties of the alkaloid itself and of its products of its transformation, the structure and partial configuration of korselamine have been established as (1α,3β,-dihydroxy-$\Delta^{8,14}$)-cevanene.

A base with mp 272-274°C, $[\alpha]_D$–75°, $C_{27}H_{43}NO_2$ (I), has previously been isolated from the epigeal part of Korolkowia sewerzowii Regel.; this has proved to be new and we have called it korselimine [1].

The IR spectrum of (I) showed absorption bands at (cm^{-1}) 3350 (OH), 2960-2830 and 1450 ($-CH_3$; $-CH_2-$), and 2750 (trans-quinolizidine). In the PMR spectrum of (I) there was no signal from an olefinic proton, but in dilute sulfuric acid solution korselimine instantaneously decolorized a solution of potassium permanganate, which showed the presence of a double bond. The double bond in (I), like that in korseveridine, was not hydrogenated in acetic acid in the presence of platinum black [2]. The PMR spectrum of (I) contained the following signals (ppm): singlet at 0.58 (19-CH_3) and doublets 0.80 (21-CH_3) and 0.84 (27-CH_3). In the mass spectrum of (I), peaks of ions were observed with m/z 98, 111, 112, 124, 149, 150, 164, 178, 179, 272, 300, 356, 357, 384, 396, 398, 412, 413 M^+ (100%), which are characteristic for C-nor-D-homosteroid alkaloids of the cevine group [3].

When korselimine was acetylated with acetic anhydride in pyridine, diacetylkorselimine (II) was obtained, the IR spectrum of which lacked absorption in the region of hydroxy groups and showed absorption bands at 1740 and 1245 cm^{-1} (ester groups). The PMR spectrum of (II) contained the following signals (ppm): singlet at 0.66 (19-CH_3), doublets at 0.82 (21-CH_3) and 0.86 (27-CH_3), and signals from two methyls of acetyl groups (1.97 and 2.00 ppm) and from protons geminal to acetoxy groups at 4.50 and 5.02 ppm.

The action of chromium trioxide on korselimine formed the diketone korseliminedione (III). Its PMR spectrum contained a singlet at 1.19 ppm from 19-CH_3 and an unresolved signal at 0.82 ppm from the protons of the 21-CH_3 and 27-CH_3 groups.

The absence from the PMR spectra of (I-III) of the signal of an olefinic proton and also the presence in the mass spectra of korselimine and the products of its transformation of peaks with m/z 111, 112, 124, 149, and 178 permitted the assumption that in korselamine the double bond was present either between C_8 and C_9 or between C_8 and C_{14}. However, the double bond could not be between C_8 and C_9 since in this case in the PMR spectra of (I) and (II) the signal from 19-CH_3 should be observed at about 1 ppm, as in korsinine [4, 5]. In our case, this signal was present at 0.58 and 0.66 ppm, respectively [6]. Consequently, the double bond in korselimine was located between C_8 and C_{14} as in the alkaloids korseveridine and korseveridinine [2, 7].

In the PMR spectrum of (III), the signals of the protons of the 19-CH_3 group were observed in weaker field than for korselimine. This indicated that in (I) both hydroxy groups were attached to carbon atoms of rings A, B, and C. Korselimine was not oxidized by periodic acid, which showed the absence of vicinal hydroxyls. A hydroxy group in korselimine could not be present at C_{11} or C_7, since the IR spectrum of (III) showed no absorption band of a carbonyl group in a 5-membered ring and (III) did not possess the properties of an α,β-unsaturated ketone. The difference in the chemical shifts of the protons of the 19-CH_3 group in the passage from (I) to (III) (0.61 ppm) also eliminated the possibility of the

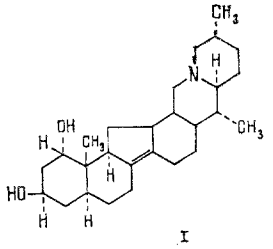
---

Institute of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 44-46, January-February, 1989. Original article submitted June 30, 1988.

0009-3130/89/2501-0037 $12.50

location of the OH groups at C_2, C_4, or C_6. According to the facts given above, the hydroxy groups in korselimine had to be located at C_1 and C_3. Multiplets from protons geminal to acetoxy groups at 4.50 and 5.02 ppm in the PMR spectrum of (II) showed that one hydroxy group in korselimine was oriented axially and the other equatorially. According to the CS of the 19-CH_3 protons, rings A/B were trans-linked. The resonance of the protons of the 19-CH_3 group at 0.58 and 0.66 ppm in (I) and (II) showed that the hydroxy group at C_3 had the β-equatorial and that at C_1 the α-axial orientation [5, 6, 8]. From the CS values it followed that the 21-CH_3 and 27-CH_3 groups were oriented equatorially in the α positions [3, 9].

On the basis of the facts presented above, korselimine has the structure and partial configuration of 1α,3β-dihydroxy-$\Delta^{8(14)}$-cevanene (I).



I

EXPERIMENTAL

Thin-layer chromatography (TLC) was carried out in a fixed layer of alumina (90 μm). The chloroform–methanol (20:1) system was used. IR spectra were taken on a UR-20 spectrometer in KBr, PMR spectra on a JNM-4H-100/100 MHz instrument (for substance (I) in CD_3OD, and for (II) and (III) in $CDCl_3$) with HMDS as internal standard (values given in the δ-scale), and mass spectra on a MKh-1310 instrument.

Korselimine – mp 272-274°C (methanol) $[\alpha]_D$–75° (c 0.12; ethanol), $C_{27}H_{43}NO_2$. The isolation of the alkaloids was described in [1].

Diacetylkorselimine. A mixture of 55 mg of korselimine, 1 ml of pyridine, and 1 ml of acetic anhydride was kept at room temperature for two days. After the solvent had been driven off, the residue was dissolved in 5% sulfuric acid; this solution was made alkaline with ammonia and the reaction product was extracted with chloroform. After the chloroform had been distilled off, amorphous diacetylkorselimine was obtained with R_f 0.75.

Mass spectrum, m/z: 98, 111, 112, 124, 149, 150, 164, 178, 179, 377, 437, 454, 455, 468, 482, 496, 497 M^+.

Korseliminedione. A solution of 50 mg of korselimine in 1 ml of pyridine was treated with 30 mg of chromium trioxide and one drop of water in 1 ml of pyridine. The reaction mixture was kept at room temperature for three days. The solvent was driven off in vacuum, the residue was dissolved in 5% sulfuric acid, and the solution was made alkaline with ammonia and was extracted with chloroform. The solvent was distilled off and the residue was chromatographed on a column of alumina with elution by chloroform. This gave 27 mg of korseliminedione with R_f 0.65.

IR spectrum: 1715 cm^{-1} (C=O).

Mass spectrum, m/z: 98, 111 (100%), 112, 124, 149, 150, 164, 178, 179, 354, 355, 367, 380, 382, 392, 394, 409 M^+.

SUMMARY

On the basis of the results of a study of the IR, PMR, and mass spectra of korselimine and the products of its transformation it has been established that korselimine has the structure and partial configuration of 1α,3β-dihydroxy-$\Delta^{8,(14)}$-cevanene.

LITERATURE CITED

1. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 34 (1989). [In this issue.]
2. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prir. Soedin., 101 (1968).

3. R. Shakirov and S. Yu. Yunusov, Khim. Prir. Soedin., 3 (1980).
4. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, Khim. Prir. Soedin., 61 (1969).
5. R. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).
6. S. Ito, Y. Fukazawa, and M. Miyasshita, Tetrahedron Lett., 36, 3161 (1976).
7. D. U. Abdullaeva, K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 796 (1976).
8. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, Khim. Prir. Soedin., 61 (1969).
9. T. M. Moynehen, K. Schofield, R. A. V. Jones, and A. R. Katritzky, J. Chem. Soc., 2637 (1962).

COMPONENTS OF Haplophyllum ramosissimum

I. A. Bessonova, D. Kurbanov, and S. Yu. Yunusov

UDC 547.944/945

Plants of the genus Haplophyllum have long been used in folk medicine for toothache, stomach and skin diseases, and in the treatment of some forms of cancer [1-3]. The extracts of some species of Haplophyllum exhibit cytotoxic activity [4]. Alkaloids isolated from plants of this genus possess a broad spectrum of pharmacological action [5]. All this indicates the promising nature of the study of Haplophyllum species.

The alkaloids skimmianine, dictamnine, and evoxine, and a substance with mp 145-146°C containing no nitrogen atoms [7] have been isolated previously from the plant Haplophyllum ramosissimum Vved., which belongs to the Oligoon section [6].

We have investigated the chemical composition of the epigeal part of this plant growing on the Ustyurt plateau. The dry comminuted raw material (3 kg) was extracted with methanol. The evaporated methanolic extract was treated with chloroform. The chloroform solution was shaken with 5% sulfuric acid. The total alkaloids (0.15% on the weight of the dry epigeal part) were obtained from the acid solution in the usual way and their chromatography on silica gel gave robustine (0.05 g), mp 148-149°C (ethanol), dictamnine (0.1 g), mp 132-133°C (acetone), skimmianine (0.18 g), mp 175-176°C (methanol), haplopine (0.12 g), mp 203-204°C (methanol), evodine (0.87 g), mp 152-153°C (acetone), methylevoxine (0.5 g), mp 105-106°C (ether), and evoxine (2.16 g), mp 154-155°C (methanol). The repeated crystallization of the methylevoxine from ether raised its melting point by 20°C [8]. All the substances were identified with authentic samples isolated from other plants of the Haplophyllum genus [9].

The neutral fraction remaining after the chloroform treatment of the acid solution, when chromatographed on silica gel, yielded two substances: $C_{10}H_8O_4$ (I), mp 204-205°C (acetone), and $C_{11}H_{10}O_4$ (II), mp 143-145°C (water). Both components gave the blue fluorescence in UV light that is characteristic for coumarins. The results of a study of their IR, UV, and mass spectra enabled substance (I) to be identified as 7-hydroxy-6-methoxycoumarine (scopoletin) and substance (II) as 6,7-dimethoxycoumarin (scoparone) [10]. The PMR spectrum of (II) was identical with that described for scoparone in [11].

Chromatography on silica gel of the polar fraction obtained after the treatment of the methanolic extract with chloroform gave a substance with the composition $C_{12}H_{22}O_{11}$, mp 190-191°C, $[\alpha]_D^{28}$ + 65.2° (c 1.05; water) which was found to be identical with an authentical sample of sucrose according to a mixed melting point and its IR spectrum.

LITERATURE CITED

1. Yu. D. Sadykov and M. Khodzhimatov, Rast. Res., 24, No. 1, 77 (1988).

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 46-47, January-February, 1989. Original article submitted May 6, 1988.

0009-3130/89/2501-0039 $12.50