2. N. L. Mukhmed'yarova, M. K. Yusupov, M. G. Levkovich, Kh. A. Aslanov, A. S. Sadykov, Khim. Prir. Soedin., No. 354 (1976).
3. K. L. Stuart and M. P. Cava, Chem. Rev., 68, 321 (1968).
4. F. Shantavy, in: The Chemistry of Plant Substances [in Russian], Tashkent (1972), p. 7.
5. H. Hara, O. Hoshino, B. Umezawa, and I. Iitaka, Acta Cryst., B34, No. 12, 3825 (1978).
6. L. E. Sutton, Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 18, Chemical Society, London (1965).
7. A. R. Battersby, E. McDonald, M. H. J. Munro, and R. Ramage, Chem. Commun., 934 (1967).
8. Yu. V. Zefirov and P. M. Zorkii, Zh. Strukt. Khim., 15, 119 (1974).
9. V. I. Andrianov, Z. I. Safina, and B. L. Tarnopol'skii, Rentgen-75. An automated System of Programs for Interpreting Crystal Structures [in Russian], Chernogolovka (1975).

ACETYLSEVEDINE FROM *Korolkowia sewerzowii*

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UDC 547.944/945

The epigeal part of *Korolkowia sewerzowii* Regl. has yielded a new alkaloid — acetylsevedine with mp 189°C (with foaming), $[\alpha]_D$ $-36.6°$, $C_{29}H_{47}NO_4$. On the basis of the IR, PMR, and mass spectra of acetylsevedine, of the products of its transformation, and also a passage to the known alkaloid sevedine, the structure of 6β-acetoxy-3β, 14α-dihydroxycevanine has been established for acetylsevedine.

Continuing an investigation of the alkaloids of the epigeal part of *Korolkowia sewerzovii* Regl. collected in Fergana province [1], from the total ether-extracted bases we have isolated a new alkaloid with the composition $C_{29}H_{47}NO_4$ (I) with mp 189°C (foaming).

The spectral characteristics of the base (I) indicate the presence in it of hydroxy groups, two secondary and one tertiary methyl groups and an ester (acetoxy) group. The latter shows that this base belongs to the group of ester alkaloids.

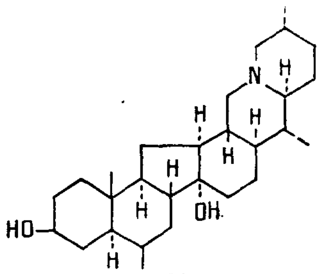
The results of a mass-spectrometric analysis showed the similarity of the structure of (I) to the alkaloid sevedine (their molecular weights differ by 42 units).

When (I) was saponified, an amino alcohol with the composition $C_{27}H_{45}NO_3$, mp 212-214°C, was obtained which proved to be identical with sevedine (mixed melting point, R_f, IR and mass spectra) [2]. Acetic acid was detected in the hydrolysate by paper chromatography.

The acetylation of (I) with acetic anhydride in pyridine led to the formation of a product identical with diacetylsevedine [2].

All the facts given above permit the statement that base (I) is a monoacetyl derivative of sevedine.

The acetic acid residue may be present at C_3 to C_6 in the acetylsevedine molecule.



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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 352-353, May-June, 1986. Original article submitted November 20, 1985.

In the PMR spectrum of diacetylsevedine the multiplet from the protons geminal to an acetoxy group at 4.68 ppm relates to C_3—αH, and one at 4.97 ppm to C_6—αH [2]. In acetylsevedine the proton geminal to the acetoxy group appears at 4.94 ppm. Consequently, the acetic acid residue in the acetylsevedine, molecule can be present only at C_6. This was confirmed by the fact that in the PMR spectrum of acetylsevedine the chemical shifts of the protons of the 19-CH_3 group shifted upfield by 4 Hz as compared with sevedine [2-4].

Thus, it may be concluded that acetylsevedine is 6β-acetoxy-3β,14α-dihydroxycevanine and has the structure (I).

EXPERIMENTAL

IR spectra (KBr) were taken on a UR-20 instrument; PMR spectra on a JNM-4H-100/100 Hz instrument (in $CDCl_3$) with HMDS as internal standard (the values are given in the δ scale); and mass spectra on an MKh-1310 instrument. For TLC we used KSK silica gel with the solvent system chloroform—ethanol (10:1).

Isolation of Acetylsevedine. The total ether-extracted alkaloids (60 g) were chromatographed on a column of KSK silica gel (250 mμ, 4 × 130 cm). The column was washed with benzene and with benzene—methanol (100:0.5; 100:1; 100:3; 10:1; 10:3; 10:5; 10:8; 1:1; and 1:2). With TLC monitoring, similar fractions were combined. When the benzene—methanol (100:3) eluates were rechromatographed on a column of silica gel [with chloroform—ethanol (10:0.5) as eluent], acetylsevedine with mp 189°C (foaming) (ether—acetone (5:1)), $[\alpha]_D$ −36.6° (c 1.202; ethanol), R_f 0.41, was isolated. Yield 0.220 g.

IR spectrum of (I): ν_{max}, cm^{-1}: 3400, 1030 (OH); 2940-2865, 1455 ($-CH_3$, $-CH_2-$); 1735, 1255 (ester C=O).

Mass spectrum of (I): m/z 98, 111 (100%), 112, 124, 125, 138, 139, 150, 162, 164, 166, 179, 384, 394, 402, 412, 416, 430, 431, 444, 445, 456, 458, 473 M^+.

PMR spectrum of (II): ppm: 0.90 (3 H, 19-CH_3); 1.99 (3 H, $OCOCH_3$); 4.94 (m, H, $\underline{H}C-OCOCH_3$), and poorly resolved triplets from the protons of two secondary methyl groups.

Saponification of Acetylsevedine. A solution of 67 mg of acetylsevedine in 2 ml of methanol was treated with 7 ml of 5% caustic potash in methanol. The mixture was kept in the water bath for 2 h, the solvent was dissolved off, the residue was diluted with water, and the reaction product was extracted with chloroform. This gave 62 mg of an amino alcohol with mp 212-214°C (acetone), M^+ 431, R_f 0.13, identical with sevedine. In the alkaline solution after the separation of the sevedine, acetic acid was detected by a method described previously [5], R_f 0.13.

Acetylation of Acetylsevedine. A mixture consisting of 10 ml of acetylsevedine, 0.15 ml of pyridine, and 0.5 ml of acetic anhydride was kept at room temperature for 3 days. After the pyridine had been driven off, the residue was dissolved in 5% sulfuric acid, the solution was made alkaline with ammonia, the alkaloids were extracted with chloroform, and the solvent was distilled off. This gave a product with R_f 0.8, M^+ 515, identical with diacetylsevedine.

SUMMARY

A new alkaloid — acetylsevedine has been isolated from the epigeal part of *Korolkowia sewerzowii* Regl., collected in the Fergana province.

It has been established that it has the structure of 6β-acetoxy-3β,14α-dihydroxycevanine.

LITERATURE CITED

1. V. V. Kul'kova, K. Samikov, R. Shakirov, S. Yu. Yunusov, Khim. Prir. Soedin., 72 (1983).
2. K. Samikov, R. Shakirov, S. Yu. Yunusov, Khim. Prir. Soedin., 673 (1977).
3. G. Fried, P. Grabowich, E. F. Sabo, and A. J. Cohen, Tetrahedron, 20, 2297 (1964).
4. P. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).
5. A. M. Khashimov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 779 (1971).