Compound (III), mp 247-253°C, $[\alpha]_D^{22}$ −5.9 ± 2° (c 1.0; chloroform–methanol). The elementary analysis corresponded to the figures calculated for the composition $C_{41}H_{64}O_{13}$. Since the initial digitoxin had the same composition, we assume that (III) was isodigitoxin, i.e., 14β,21-epoxycardenolide. An independent isomerization of digitoxin with the aid of KOH led to an identical compound.

Thus, the saponification of acylcardenolides by ammonia is accompanied by the formation of by-products – 14β,21-epoxycardenolides and their lactam analogues. Both these types of cardiotonic derivatives have low activities [1, 2]. We consider that the method of deacetylating cardiac glycosides with ammonia is unsuitable in industrial practice since it greatly complicated the purification of the desired substances and lowers the yield.

LITERATURE CITED

1. C. Douglas, W. L. Duax, J. A. Munoz, and M. E. Wolff, J. Am. Chem. Soc., 98, 6308 (1976).
2. R. Megges, H.-J. Portius, and K. Repke, Eleventh International Symposium on the Chemistry of Natural Products, Bulgarian Academy of Sciences, Sofia (1978).

ALKALOIDS OF *Veratrum lobelianum*.

X. STRUCTURE OF VERDINE

I. Nakhatov, R. Shakirov, and S. Yu. Yunusov

UDC 944/945

Continuing the separation of the total alkaloids of the epigeal part of *Veratrum lobelianum* Bernh., collected in the Caucasus, Alma-Ata province, according to their basicities and also by column chromatography, we have isolated veralodine, germinaline, jervine, veratroylzygadenine, germbudine, veralosine, veralomine, [1-3], and the new alkaloid verdine with mp 218-220°C, $C_{27}H_{41}NO_5$ (I) [4].

The IR spectrum of (I) contained absorption bands at (cm^{-1}) 3400 (OH), 1710, and 1630 (CO–C=C–).

The UV spectrum [λ_{max} 252 nm (log ε 4.07)] was characteristic for an α,β-unsaturated ketone [5]. The mass-spectrometric fragmentation of verdine (I) took place in a similar manner to that of the alkaloids of the jervine group [6] (m/z: 97, 110 (100%), 112, 113, 124, 125, 328, 346, 426, 430, 441, 444, 459, M^+).

The PMR spectrum contained signals of the 19-CH_3, 18-CH_3, 21-CH_3, and 27-CH_3 methyl groups (Table 1).

The acetylation of (I) formed O,O',O'',N-tetraacetylverdine (II) [M^+ 627, ν_{max}, cm^{-1}, 1710, 1635 (CO–C=C–), 1635 (N–Ac), 1740, 1245 (O–Ac)]. The saponification of (II) led to O,N-diacetylverdine (III) [M^+ 543; ν_{max}, cm^{-1}: 3450 (OH), 1710, 1635 (CO–C=C–), 1740, 1250 (O–Ac), 1635 (N–Ac)] and N-acetylverdine (IV) [M^+ 501; ν_{max}, cm^{-1}: 3420 (OH), 1710, 1630 (CO–C=C–), 1630 (N–Ac)].

The reduction of (I) by Adams' method and with palladium on carbon gave isomeric dihydroverdines with M^+ 461 the IR spectra of which lacked the absorption band of a –C=C– bond but contained the absorption band of a carbonyl group in a five-membered ring (1730 cm^{-1}). The Huang-Minlon reduction of (I) gave deoxodihydroverdine with M^+ 445, the IR spectrum of which lacked the absorption band of a carbonyl group. Details of the PMR spectra of compounds (I-III) are given in Table 1.

In the PMR spectra of compounds (I-III), the signals from the protons of the 18-CH_3 groups are observed in the weak field at 2.17-2.27 ppm. Consequently, the double bond in (I) is located at C_{12}-C_{13}, as in jervine [7].

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 395-396, May-June, 1984. Original article submitted October 27, 1983.

0009-3130/84/2003-0375$08.50

TABLE 1. Chemical Shifts of the Protons (δ, ppm)

Substance	19-CH_3, s	18-CH_3, s	21-CH_3, d	27-CH_3, d	O–$COCH_3$, s	CH–$OCOCH_3$, m
I (in C_5D_5N)	1,31	2,23	0,70	0,93		
II (in C_5D_5N)	0,96	2,27	0,78	0,89	1,89; 1,91; 1,95; 1,98 (N–Ac)	6,36 (H) 5,09 (2H)
II (in $CDCl_3$)	0,94	2,19	0,90	0,99	1,97; 2,00; 2,03; 2,06 (N–Ac)	6,03 (H) 5,02 (2H)
III (in $CDCl_3$)	0,87	2,17	0,83	1,00	2,01; 2,06 (N–Ac)	5,96 (H)

s – singlet; d – doublet; m – multiplet.

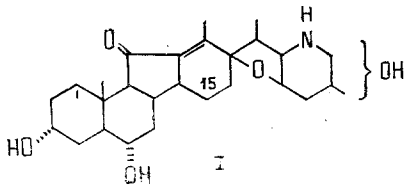
According to the facts presented above, verdine contains the heterocyclic skeleton of jervanine and three secondary hydroxy groups, a carbonyl group, and a double bond. Verdine contains no vicinal hydroxy groups, since it is not oxidized by periodic acid.

In the PMR spectra of the acetyl derivatives of verdine (in $CDCl_3$), the signal from one proton geminal to an acetoxy group appears at 6.03 ppm [(in (II)) or 5.96 ppm (in (III)], and those of two protons geminal to acetoxy groups at 5.02 ppm [in (II)] (see Table 1).

Consequently, the downfield shift of a proton geminal to an acetoxy group is apparently due to the influence either of an carbonyl group or of a 17,23-oxido group. Then one of the three hydroxy groups must be located either at C_1 or at C_{15} in the axial orientation.

The difference of 0.07 ppm in the chemical shifts of the protons of the 19-CH_3 groups of (II) and (III) showed that the two hydroxy groups are present at C_3 and C_6, each in the α-equatorial orientation [8].

Thus, verdine has the structure (I).



I

LITERATURE CITED

1. A. M. Khashimov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 339, 343 (1970).
2. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 770 (1970).
3. R. Shakirov and S. Yu. Yunusov, Khim. Prir. Soedin., 852 (1971).
4. I. Nakhatov, R. Shakirov, É. M. Tashkanova, and S. Yu. Yunusov, Khim. Prir. Soedin., 131 (1980).
5. S. M. Kupchan and M. J. Suffness, J. Am. Chem. Soc., 90, 2730 (1968).
6. H. Budzikiewicz, Tetrahedron, 2267 (1964).
7. T. Masamune, N. Sato, K. Kobayashi, J. Yamazaki, and Y. Mori, Tetrahedron, 1591 (1967).
8. R. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).