Thus, we have established that daurine has the structure (I).

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ALKALOIDS OF *Veratrum lobelianum*.

VIII. THE STRUCTURE OF GERMINALINE

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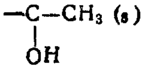
The isolation of a base with mp 220-222°C has been recorded previously. By a study of the products of alkaline hydrolysis, it was characterized as germanitrine [1, 2]. A determination of its elementary composition (mol. wt. 793, $C_{41}H_{63}NO_{14}$) on a MKh-1310 high-resonance mass spectrometer and a renewed study of its PMR spectrum (JNM-4H 100/100 MHz, internal standard HMDS) of the alkaloid showed that the compound was germitetrine (I) (melting point, IR spectrum) [3, 4].

Continuing the separation of the total alkaloids of the epigeal part of *V. lobelianum* collected in the Caucasus [5, 6] on a column of silica gel (eluent benzene—acetone), we have isolated an alkaloid with the composition $C_{39}H_{61}NO_{13}$, mol. wt. 751 (mass spectrometry), mp 138-140°C (II). The IR spectrum of (II) had absorption bands at (cm^{-1}) 3450 (OH), 1745, and 1250 (ester C=O). The main chemical shifts of the protons in the PMR spectrum of alkaloids (I) and (II) taken in $CDCl_3$ are given below (δ, ppm: s — singlet; d — doublet; t — triplet; m — multiplet):

	Gemitetrine (I)	*Alkaloid (II)*
19-CH_3 (s)	0,94	0,89
21-CH_3 (s)	1,10	1,11
27-CH_3 (d)	1,02	1,00
$OCOCH_3$ (s)	1,88; 2,00	1,89
<u>CH</u>—O-acyl (m)	5,71; 5,04 (3H)	4,98; 5,23; 5,91
Side chain:		
 $-\underset{\substack{\mid \\ OH}}{C}-CH_3$ (s)	1,28	1,26
$-CH-CH_3$ (d)	1,06; 1,22	1,08; 1,21
$-CH_2-CH_3$ (t)	0,82	0,82

On acetylation, the alkaloid (II) formed a diacetyl derivative (III) with mp 210-212°C, M^+ 835, and a triacetyl derivative (IV) with mp 200-202°C M^+ 877. This alkaloid proved to be identical with germinaline (melting point and IR spectrum) [7]. However, a comparison of the elementary composition of (II) (M^+ 751) with that of germinaline, which we isolated previously from the epigeal part of *V. lobelianum* [7] showed that they differed by one oxygen atom. We have compared the acetyl derivatives of (III) and (IV) with the corresponding acetyl derivatives of germerine (V) [8-10] — diacetylgermerine (VI), with mp 220-222°C, M^+ 777, and triacetylgermerine (VII) with mp 200-202°C, M^+ 819.

In spite of the identical R_f values of (III) and (VI), and of (IV) and (VII), these substances differ from one another by 58 mass units, respectively. Consequently, the elementary composition of germaline was previously determined incorrectly, and the acetyl derivatives of germinaline are not identical with those of germerine.

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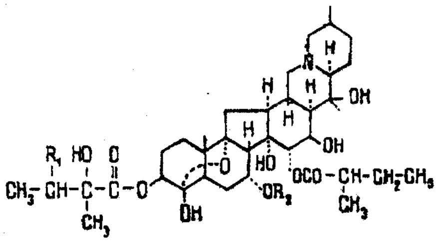
The triacetyl derivative (IV) of the alkaloid (II) was identical with diacetylgermitetrine (VIII), M^+ 877 (melting point, IR spectrum). Consequently, the *l*-2-methylbutyric acid residue in (II) is located at C_{15} and the *l*-2,3-dihydroxy-2-methylbutyric acid residue at C_3. To determine the location of the acetyl group in (II), germitetrine (I) was subjected to partial hydrolysis in aqueous methanolic solution. This yielded deacetylgermitetrine (IX) M^+ 751 [3], identical with the alkaloid (II), (melting point, IR spectrum). Consequently the acetic acid in (II) esterifies the β-hydroxy group of the dihydroxymethylbutyric acid residue.



I. $R_1=OCOCH_3, R_2=COCH_3$. II. $R_1=OCOCH_3, R_2=H$. V $R_1=R_2=H$

Thus, germinaline has the structure of deacetylgermitetrine 3β-[(*l*)-3-acetoxy-2-hydroxy-2-methylbutyryl]-15α-[(*l*)-2-methylbutyryl]germine, obtained from germitetrine [3]. This is the first time that germinaline has been obtained from a plant.

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