ALKALOIDS OF *Veratrum lobelianum*. THE STRUCTURE OF GERMINALININE

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The alkaloid with mp 157-159°C, $[\alpha]_D$ + 8.02° [1] forms an acetyl derivative (II) with mp 205-207°C and is germbudine [3β-(d)-2,3-dihydroxy-2-methylbutyryl-15α-(*l*)-2-methylbutyrylgermine] [2, 3].

Continuing the separation of the combined alkaloids (31.5 g) of the soluble metaphosphate part fractionated by Salzberger's method [4] we chromatographed it on a column of silica gel. A benzene eluate was separated by means of an acetate buffer, pH 4.0. This led to the isolation of the new alkaloid germinalinine (III), $C_{39}H_{61}NO_{13}$ with mp 168-170°C (ether), $[\alpha]_D$−52.08° (pyridine). The IR spectrum of (III) had absorption bands at 3490 cm^{-1} (OH) and 1750 and 1255 cm^{-1} (ester C=O).

The saponification of (III) gave the amino alcohol germine (IV) [5]. Paper chromatography showed the presence of 1-2-methylbutyric, d-2,3-dihydroxy-2-methylbutyric, and acetic acids. The characteristics of the NMR spectra of (I) and (III) are given in Table 1.

The acetylation of (III) with acetic anhydride in pyridine gave an acetyl derivative with mp 205-207°C (V). In the acetylation of compounds (I) and (III), the secondary hydroxy groups of the side chains were also acetylated, as was shown by the presence in the NMR spectra of (II) and (V) of the signals on the protons of three acetyl methyl groups at 1.98 ppm (3H) and 2.05 ppm (6H), showing the formation of germbudine triacetate (II) and germinalinine diacetate (V).

The methanolysis of (III) led to a base with mp 157-159°C identical with germbudine (I). Furthermore, germinalinine diacetate (V) proved to be identical with germbudine triacetate (II). Consequently, the d-2,3-dihydroxy-2-methylbutyric acid residue in germinalinine is located at C_3 and the *l*-2-methylbutyric acid at C_{15}. The acetic acid residue may be present either at C_7 or C_{16}. In the NMR spectrum of (III), the signal from the 19-CH_3 proton is shifted by 1 Hz downfield as compared with the corresponding signal for germbudine (I). The results of a comparative study of the NMR spectra of (I) and (III) and of the gentle methanolysis of germinalinine show the position of the acetic acid residue at C_7.

TABLE 1. Chemical Shifts (δ, ppm)

Substance	19—CH_3 s	21—CH_3 s	27—CH_3 d	Methyl protons of the side chain					H, H—C—O-acyl d	H, H—C—O-acyl d
				CH_2—CH_3 t	CH—CH_3 d	CH—CH_3 (OH) d	C—CH_3 (OH) s	$OCOCH_3$ s		
I	0,92	1,13	1,02	0,84	1,09	1,16	1,39	—	5,26	4,96
III	0,93	1,13	1,02	0,81	1,05	1,12	1,38	2,03	5,10	4,99 5,72

Note: s) singlet; d) doublet; t) triplet; m) multiplet.

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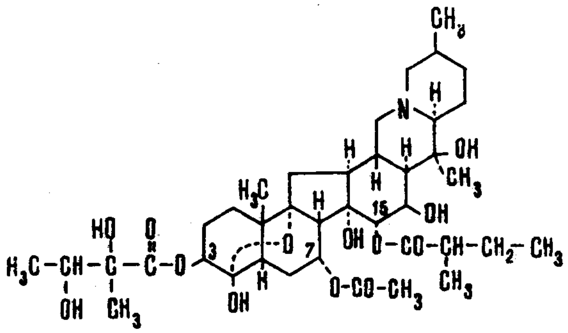
On the basis of the facts given, germinalinine has the structure and configuration of 7α-acetyl-3β-(d)-2,3-dihydroxy-2-methylbutyryl-15α-(*l*)-2-methylbutyrylgermine.



III

Thus, germbudine, for the first time, and the new alkaloid germinalinine (III) have been isolated from *V. lobelianum*.

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