CONTINUING THE SEPARATION OF THE MIXTURE OF BASES FROM THE EPIGEAL PART OF VERATRUM LOBELIANUM [1, 2] WE HAVE ISOLATED A NEW ALKALOID VERALODISINE C29H44O4N (I). THIS IS A TERTIARY BASE WHICH FORMS WITH DIGITONIN A SPARINGLY SOLUBLE DIGITONIDE SHOWING THAT SUBSTANCE (I) HAS A 3β-OH GROUP AND BELONGS TO THE TYPICAL STEROID ALKALOIDS. THE IR SPECTRUM OF VERALODISINE SHOWS ABSORPTION BANDS AT (cm⁻¹) 3475 (OH), 2940, 1460, 1435 (−CH₃, −CH₂), 3030, 1680 (CH = C), 1680 (C = N), 1730, 1270 (ester carbonyl), 1700 (carbonyl in a six-membered ring). The UV spectrum of (I) [λmax 275 nm (log ε 3.63)] is similar to that of tomatillidine [3]. In the NMR spectrum of substance (I) there are signals at (ppm) 0.64 (3 H, 18-CH₃), 0.92 (3 H, 19-CH₃), and 1.99 (3 H, OCOCH₃); doublets at 0.93 and 1.00 (two secondary methyl groups, J = 6 Hz); and multiplets at 3.71 (H, CH-OH), 4.96 (H, CH-OCO-CH₃), and 5.26 (one olefinic proton).

Consequently, veralodisine contains four C-methyl groups. The nitrogen is present in a C = N system, two oxygen atoms in the residue of an ester grouping and the other two oxygen atoms in the form of hydroxy and carbonyl groups. The mass spectrum of (I) (Fig. 1) has the main peaks of ions with m/e 83, 94, 110, 111, 139, 140, 164, 177, 272, 281, 298, 299, 300, 314, 326, 352, 366, 381, 382, 394, 398, 409 (100%) (M-CH₃ COOH) +, 426 [M-(CH₃ + CO)] +, 427 (M-42) +, 441 (M-CO) +, 454 (M-CH₃) +, 469 (M⁺). A similar pattern is given in the mass-spectrometric decomposition of tomatillidine [3].

Veralodisine is saponified in an aqueous methanolic solution of potassium carbonate. From the products of its saponification we isolated the amino alcohol veralodisinol C27H42O₃N (II) and acetic acid (paper chromatography). The IR spectrum of (II) lacks the absorption band of an ester carbonyl, and the absorption band of the C = O group (1690 cm⁻¹) and the C = N group (1652 cm⁻¹) are shifted in the low-frequency direction. In the NMR spectrum there are singlets at (ppm) 0.61 (3 H, 18-CH₃) and 0.91 (3 H, 19-CH₃), and a six-proton doublet at 0.98 ppm from two secondary methyl groups, and multiplets at 3.60 and 4.10 (2 H, 2CH-OH) and 5.23 (olefinic proton), the signal of the protons of an acetyl group being absent.

Fig. 1. Mass spectrum of veralodisine (I).
The reduction of (I) with lithium tetrahydroaluminate gave a tetrahydro derivative C_{27}H_{45}O_{3}N (III) with mol. wt. 431 (mass spectrum), in the IR spectrum of which the absorption bands of C = N and C = O groups had disappeared. The Oppenauer oxidation of (II) yielded an \( \alpha, \beta \)-unsaturated ketone (IV). Its UV spectrum \( \lambda_{\text{max}} \) 241 nm (log \( \epsilon \) 4.15) is similar to those of the unsaturated oxo derivatives of tomatillidine, verasine, and veralosidine [3–5]. The facts given above permit the assumption that compound (I) is based on the heterocyclic skeleton of tomatillidine and veralosidine [3–5].

From the products of the Huang-Minlon [6] reduction of (II) we isolated deoxoveralodisinol with mp 153–155°C, the IR spectrum of which lacked the absorption band characteristic for a carbonyl group but clearly showed the absorption band of the C = N system. Deoxoveralodisinol proved to be identical with veralosidine (V) [5] (Scheme) from the melting point of a mixture and from the IR spectrum. Thus, veralodisine is a carbonyl derivative of veralosidine acetate [5].

In the mass spectrum of tetrahydroveralodisinol, the maximum peak is that of the ion with m/e 114 due to the fragment of the side chain at C_{20} of the compounds hexahydrotomatillidine, veratramine, isojer- vine, and hexahydrokorservevne[3, 7, 8], which is formed as a result of the cleavage of the C_{20}–C_{22} bond.

The facts given confirm that the carbonyl group in veralodisine is located in the heterocyclic part of the molecule. It may be positioned at C_{23}, C_{24}, or C_{25}. Veralodisine does not possess the properties of an amide or of an \( \alpha, \beta \)-unsaturated ketone. These facts exclude the C_{23} and C_{25} positions for the carbonyl group, and only the C_{24} position remains for it.

The formation of a sparingly soluble digitonide by veralodisine shows that the acetate group in (I) is located at C_{16}. This is shown by the fact that the signal of the proton geminal to the acetate group in veralodisine resonates at 4.96 ppm and in veralodisinol the signal of this proton is shifted upfield by 0.86 ppm. Such a shift of the signal of the proton geminal to an acetate group on passing from (I) to (II) shows that the acetate group in veralodisine is located in the five-membered ring at C_{16} [9]. The configurations of the asymmetric centers of veralodisine follow from the structure of veralosidine [5].

Consequently, veralodisine has the most probable structure and configuration of 16\( \alpha \)-acetyl-3\( \beta \)-hydroxy-22,26-linocholesta-5,22(\( \alpha \))-dien-24-one.

**EXPERIMENTAL**

Thin-layer chromatography (TLC) was performed with KSK silica gel (100 nm) and the following solvent system: 1) butyl acetate–ethanol–chloroform (3:2:20); 2) benzene–ethanol (9:1.5); 3) benzene–