Both for lipase 1 and for lipase 2 the greatest affinity was shown for fatty acids of medium chain length. An increase in the length of the acyl donor led to a rise in the percentage conversion from 26% for butyric acid to 54% for caprolic acid. The physicochemical characteristics of the menthyl esters synthesized agreed with those given in the literature.

Thus, the investigations performed have shown that D,L-menthol can be esterified by lipase 1 under the optimum conditions if a suitable acyl donor is selected.

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CHEMICAL COMPOSITION OF THE RHIZOMES WITH ROOTS OF VALERIANA WOLGENSIS FROM THE VALERIANA OFFICINALIS GROUP

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The quantitative level and qualitative composition of the essential oil and valepotriates [the main pharmacologically active substances in ecotypes (species) of *V. officinalis* L. *s. l.*] vary considerably. In view of this, we have studied the component composition of the essential oil and the valepotriates of the rhizomes with roots of the Volga valerian *V. wolgensis* Kazak. (= *V. nitida* Kreyer) cultivated in the sovkhozes [collective farms] of Lekrasprom [All-Union Combine for the Production, Collection, and Processing of Medicinal PLants, USSR Ministry of the Medical Industry].

ℓ,α-Pinene, ℓ-camphene, cadinene, and esters of borneol with isovaleric acid and with other acids have been isolated from this essential oil previously [1]. The component composition of the valepotriates had not been studied.

By the steam-distillation method, 97 ml of essential oil was obtained from the rhizomes with roots of Volga valerian grown in 1988 in the Voronezhskii sovkhoz (yield 0.61%). The following were isolated by column chromatography and also by preparative TLC on neutral alumina (activity grade III) and type L silica gel and were identified (from their IR, mass, and PMR spectra): ,α-pinene, terpinolene, fenchene, camphene, alloaromadendrene, β-bisabolene, ar-curcumene, valerenal, valeranone, valerenic acid, (−)-pacifigorgiol, fauronyl acetate, kessanyl acetate, and a previously undescribed sesquiterpene alcohol in the form of a viscous liquid, $C_{15}H_{24}O_4$, which we have called valerol. IR spectrum, ν_{max} (cm^{-1}): 3400-3370 (OH); 3070 and 1640 (C=C); 890 (CH_2=C). The UV spectrum gave no indication of the presence of a conjugated system of double bonds.

On the addition of bromine to a chloroform solution of valerol a deep blue coloration arose, which indicated the presence of an azulene skeleton, while the number of carbon atoms (C_{15}) in the valerol molecule showed that it contained a guaiane skeleton.

It followed from the ^{1}H NMR spectrum that the valerol molecule includes an isopropyl group (d, 6 H; 1.02 ppm); a methyl and a hydroxy group on the same carbon atom (s, 3 H; 1.28 ppm); an exocyclic double bond (two br.s, 2 H; 4.7-4.9 ppm) and a double bond in a ring (br.s, 1 H, 5.6 ppm).

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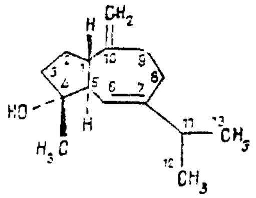
To determine the positions of the substituents in the valerol skeleton we employed the paramagnetic shift reagent (PSR) $Eu(fod)_3$ and INDOR.

On the addition of the PSR, the singlet signal of the olefinic proton (H_6) was converted into a doublet (J = 3.5 Hz). Such behavior of the signal indicated a closeness or coincidence of the chemical shifts of the allyl proton (H_5) and of one vicinal to it (H_1), i.e., the H_5 and H_1 protons are each in the α- position with respect to a double bond. The chemical shift of the H_5 proton (2.18 ppm) was determined by the INDOR method on the singlet of the olefinic proton (H_6). Consequently, the H_1 proton had a close value of the chemical shift. The signal of the methine proton (H_{11}) was also observed in this region (2.24 ppm), this being determined by the INDOR method on the line of the methyls of the isopropyl group; i.e., the methine proton is in the α- position to a double bond. It followed from these facts that double bonds are located at $C_6{-}C_7$ and $C_{10}{-}C_{14}$ and the OH group at C_4. The presence of the OH group at C_4 and the positions of the H_5 and H_6 protons were also confirmed by the results of a determination of the rate of displacement of the signals of these protons ($V_{PSR} = \Delta\delta/\Delta c_{PSR}$, where $\Delta\delta$ is the difference in chemical shifts at different concentrations of the PSR, C_{PSR} being the concentration of PSR). If we take the value of V for the $CH_3{-}\overset{|}{\underset{|}{C}}{-}O$ group as unity, then the rates of change of the other signals are as follows: CH_{isopr}) 0.11 and 0.13; $=C{<}^{H}_{H}$) 0.13 and 0.19; H_6) 0.9; H_5) 1.15. The considerable rate of change of the signals of the H_5 and H_6 protons showed their closeness to the hydroxy group.

The large value of the coupling constant $J_{5,1} = 11.0$ Hz (determined by the INDOR method) indicated the closeness of the dihedral angle between the H_5 and H_1 protons to 180°C and, consequently, the trans linkage of the five- and the six-membered rings.

It followed from a consideration of molecular models that if the hydroxylic proton and the H_5 proton are on the same side of the plane of the ring the distance between the OH group and the H_5 proton will be less than that between the OH group and the H_6 proton; if they are on different sides the opposite relationship exists. As has been stated above, the rate of displacement of the signal of the H_5 proton exceeded the rate of displacement of the signal of the H_6 proton. It followed from this that the H_5 proton is closer to the OH group than the H_6 proton is, and, consequently, the OH group and the H_5 proton are located on the same side of the plane of the ring. The results obtained point to the following structure for valerol:



From petroleum ether extracts of the rhizomes with roots of the Volga valerian we isolated and identified (with the aid of IR, NMR, and mass spectra) valtrate, IVHD-valtrate, β-sitosterol, acetylvalerenolic acid, and a glyceride of linoleic and linolenic acids.

Thus, the rhizomes with roots of Volga valerian contain valtrate, IVHD-valtrate, valerenal, valeranol, and valerenic and acetylvalerenolic acid – the main pharmacologically active substances responsible for the therapeutic activity of valerian.

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