

ALKALOIDS OF VERATRUM LOBELIANUM. II

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From Veratrum lobelianum Bernh. growing in the Northern Caucasus, we have isolated two steroid alkaloids—protoveratrine A and alkamine X.

The separation of the combined bases was carried out on a column of cellulose impregnated with formamide. The chloroform from fraction 1 was distilled off under vacuum to 1/5 bulk and the residual solution was treated with 6% acetic acid and then with 25% aqueous ammonia to pH 8.7, and was again treated with ether. The precipitates formed in the ethereal and aqueous layers were filtered off and combined. Evaporation of the ethereal solution to 1/5 bulk gave crystals of alkamine X.

After recrystallization from methanol and diethyl ether, the precipitate formed prismatic crystals with mp 259°–262° C (decomp.), $[\alpha]_D^{20} - 43.7^\circ$ (in pyridine), composition $C_{41}H_{69}O_{14}N$. The results obtained and those of a spectroscopic analysis are in agreement with literature data for protoveratrine A [1]. Protoverine $C_{27}H_{43}O_9N$ with mp 220°–222° C, $[\alpha]_D^{20} - 14.2^\circ$ (in pyridine) was isolated from the products of the alkaline hydrolysis of this compound by means of chloroform [1].

Further identification of protoverine, besides the spectroscopic and analytical data [2], was effected via the products of alkali isomerization.

The isomers of steroid alcohols generally have lower R_f values than the amino alcohols, and the pseudo-compounds, conversely, have higher R_f values [3].

On chromatography in the butan-1-ol–acetic acid–water (4:1:5) system, the R_f value of protoverine was 0.35, that of isoprotoverine was 0.33, and that of pseudoprotoverine was 0.61.

The aqueous alkaline solution after the elimination of protoverine was acidified with sulfuric acid, treated with diethyl ether and chromatographed on paper in the butan-1-ol–1.5 N aqueous ammonia (1:1) system with reference materials [4].

The following acids were identified: acetic (R_f 0.14), α -methyl- α -hydroxybutyric (R_f 0.24), and α -methylbutyric (R_f 0.81).

The number of ester groups [5] proved to be four.

Alkamine X crystallizes from methanol in the form of large needles with mp 215°–217° C. IR spectrum: 3500–3100 (OH and NH groups), 2975–2850 ($-\text{CH}_3$ and $-\text{CH}_2-$), 1470 (deformation vibrations of δ -CH methyl and methylene groups), 1385–1350 (deformation vibrations of δ -CH methyl groups with splitting), and 1668 (double bonds) cm^{-1} [6].

Alkamine dissolves in concentrated sulfuric acid with an orange coloration changing after 5 min to pink-orange, after 10 min to crimson, and after 1 hr to red-purple.

REFERENCES

1. A. Stoll and E. Seebeck, *Helv. Chim. Acta.*, 36, 718, 1953.
2. H. A. Nash and R. M. Brooker, *J. Am. Chem. Soc.*, 75, 1942, 1953.
3. H. Auerhoff and F. Günter, *Arch. Pharm.*, 288/60, 455, 1955.
4. H. Máček, S. Vaneček, and L. J. Vejdelek, *Chem. Listy*, 49, 539, 1955.
5. Ya. V. Rashkes, *ZhAKh*, 20, 238, 1965.
6. K. Nakanishi, *Infrared Spectra and the Structure of Organic Compounds* [Russian translation], Moscow, 1965.

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