

When (I) was subjected to periodate oxidation, one of the xylose residues was split out, and the same treatment of derivative (II) led to the splitting out of both these residues, which indicated the attachment of the sulfate group to one of the xylose residues.

The enzymatic cleavage of (I) with cellulase gave the progenin (III) with mp 215-217°C, $[\alpha]_D^{20} -104.3^\circ$ (c 1.7; pyridine). The catalytic hydrogenation of (I) in water over Adams catalyst to the corresponding dihydro derivative (IV) with mp 211-212°C, $[\alpha]_D^{20} -62.5^\circ$ (c 1.6; pyridine) followed by Smith degradation led to the progenin (V) with mp 238-240°C, $[\alpha]_D^{20} -23.8^\circ$ (c 1.17; pyridine). The structures of the progenins (III) and (V) were confirmed by their ^{13}C NMR spectra, by hydrolysis with the formation of a mixture of xylose and quinovose (2:1) from (III) and of xylose, quinovose, glucose, and 3-O-methylglucose (1:1:1:1) from (V), and also by the results of the methylation of the corresponding desulfated derivatives followed by methanolysis and acetylation.

The position of the sulfate group at C-4 in the xylose residue was established by comparing the ^{13}C NMR spectra of glycoside (I) and of the progenin (III) with the spectra of their desulfated derivatives. The C-5 and C-3 signals in the spectra of the sulfate-containing compounds were located 1.3 ppm upfield, and the C-4 signal 5-6 ppm downfield as compared with the spectra of (II) and (VI) [3].

On the basis of all the results obtained, the structure of cucumarioside A₂-2 has been determined unambiguously as 3 β -{O-[O-(3-O-methyl- β -D-glucopyranosyl)-(1 \rightarrow 3)-O- β -D-glucopyranosyl-(1 \rightarrow 4)][O- β -D-xylopyranosyl-(1 \rightarrow 2)]-O- β -D-quinovopyranosyl-(1 \rightarrow 2)-[4-O-(sodium sulfato)- β -D-xylopyranosyloxy]}holosta-7.25-dien-16-one.

In contrast to the glycosides isolated from homothurins known previously, glycoside (I) has an odd number of disaccharide residues.

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ALKALOIDS OF *Aconitum zerafschanicum*

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We have investigated the alkaloids of the epigeal part of *Aconitum zerafschanicum* Steinb., collected from two growth sites. The alkaloids heteratizine (zarafshanine) [1-3] and azrafshanidine [1] have previously been isolated from the epigeal part of this plant in the budding-flowering phase from Alauddinsae (Alai range).

By chloroform extraction of the epigeal part of *A. zerafschanicum* collected in the budding phase at Alauddinsae (Alai range) we obtained 0.95% of total alkaloids. Similar extraction of the epigeal part of the plant collected in the budding-flowering phase in the gorge of the R. Berksu (Trans-Alai range) gave 0.67% of combined alkaloids. By separation into phenolic and nonphenolic fractions, separation according to solubility in organic solvents and according to basicity, and the preparation of salts, and also by chromatography on columns of alumina and silica gel, from the first group of alkaloids we isolated: heteratizine (I); base (II) with the composition C₂₀H₂₇NO, M^t 297.2093, mp 258-259°C (ethanol); base (III) with mp 148-150°C (acetone); base (IV) with mp 87.5-88.5°C (chloroform); base (V) with mp 130-131°C (acetone); amorphous base (VI), the hydrochloride of which had mp 296°C (ethanol, decomp.); and the amorphous base (VII).

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By the similar separation of the second group of alkaloids, in addition to the alkaloids (I) and (III)-(VI) we obtained a base (VIII) with mp 235-237°C (ethanol, with foaming) and a base (IX) with mp 206.5-207.5°C (acetone). The properties of base (VII), having the composition $C_{19}H_{23}NO_4$, M^+ 329, $[\alpha]_D^{20} +20$, (c 0.43; ethanol) were identical with those of the benzyl-tetrahydroisoquinoline alkaloid reticuline. A direct comparison of (VII) with an authentic sample of the alkaloid isolated from *Berberis integerrima* Bge. [4] showed their identity.

This is the first time that reticuline has been isolated from plants of the genus *Aconitum*.

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ALKALOIDS OF THE NARCISSUS VARIETY FORTUNE

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Continuing the search for new sources of galanthamine among plants of the family Amaryllidaceae we have investigated the leaves of the narcissus of the Fortune variety, which belongs to the group of large-corona narcissuses of garden origin *Narcissus hybridus* hort. and grows in the Pervomaiskii sovkhos [state farm], Moscow province.

Analysis of the material showed that the leaves collected in the period of mass flowering contained a total of 0.93% of bases (chloroform extraction). By chromatographing the combined alkaloids on a fixed layer of KSK silica gel + 2% of Na_2CO_3 in the chloroform-ethyl acetate-methanol (2:2:1) system, three main alkaloids were found with R_f 0.25, 0.46, and 0.56. The amounts of the individual alkaloids determined by the chromatophotocolorimetric method were, respectively, 0.17, 0.14, and 0.27% on the weight of the dry leaves.

The alkaloid with R_f 0.46, isolated from an acetone solution of the combined alkaloids in the form of the hydrobromide, was identified as galanthamine from its IR, UV, and NMR spectra and from the melting points of the base and its hydrobromide, and also by mixed melting points [1-4].

The addition of concentrated hydrochloric acid to the mother solution after the separation of galanthamine hydrobromide yielded the hydrochloride of an alkaloid with mp 208-209°C (ethanol), R_f 0.25. The base $C_{16}H_{19}NO_3$ obtained from the hydrochloride has mp 160-162°C (methanol) $[\alpha]_D^{20} +66.7^\circ$ (c 0.23%, ethanol), mol. wt. 273 (mass spectrum). UV spectrum: λ_{max} 285 nm ($\log \epsilon$ 3.53); shoulder λ 226 nm ($\log \epsilon$ 3.79). The 1H NMR spectrum (100 MHz, $CDCl_3$) contained the signals of an aromatic methoxy group (3.75 ppm), of a vinyl proton (5.50 ppm), of two aromatic protons in the form of singlets (6.45 and 6.78 ppm), of two hydroxylic protons (5 ppm), and of the proton of a $HCO-$ grouping (4.23 ppm). The compound gave a blue-violet coloration with ferric chloride and consequently had a phenolic hydroxyl. The absence of a N-methyl group and also of vinyl protons in the vicinal position to one another permitted the assumption that the compound isolated was of the lycorine type. The presence in the mass spectrum of the peaks of the ions M^+ 273, 272 (100%) and 228, 229 was also characteristic for alkaloids of the lycorine group [5, 6].

The alkaloid with R_f 0.56, $C_{17}H_{19}NO_4$, isolated by the chromatography of the evaporated mother solutions (after the removal of the alkaloids with R_f 0.46 and 0.25) on alumina (with benzene as the eluent) - with mp 203-204°C (methanol); mol. wt. 301 (mass spectrum); UV spec-

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