13,14-DEHYDROSOPHORIDINE FROM *Sophora alopecuroides*

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From 2 kg of the leaves of *Sophora alopecuroides* L., collected on the banks of the R. Naryn (Kirghiz SSR) in the period of complete ripeness of the fruit, we have obtained 38 g of combined alkaloids which have been separated into fractions according to solubility.

From a petroleum ether fraction we have isolated sophoridine, matrine, and a base with R_f 0.58 (system 1).

The alkaloid with R_f 0.58 ($C_{15}H_{22}ON_2$) is an unsaturated strongly monoacid base in which one matrine atom and the one oxygen atom are inactive.

The UV spectrum of the base shows absorption with λ_{max} 253 nm (log ε 3), which is characteristic for a carbonyl group conjugated with a double bond. The mass spectrum has the peaks of the molecular ion M^+ 246 (83%) the peaks of ions with m/e 245 (100%), 231 (8.1%), 217 (9.1%), 203 (13.4%), 192 (3%), 188 (4.5%), 177 (82%), 160 (12%), 150 (91%), 138 (53%), 122 (20%), 98 (18%), 96 (78%). Such mass-spectrometric fragmentation is characteristic for the quinolizidine alkaloids of the matrine group [1-3]. The ions with m/e 217 and 203 show the presence of a double bond in ring D [4, 5].

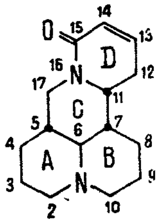
The IR spectrum of the base with R_f 0.58 has absorption bands at 2795-2672 cm^{-1} (Bohlmann bands) that are characteristic for a trans quinolizidine nucleus, at 1650 cm^{-1} (amide carbonyl) and at 1596 cm^{-1} (double bond conjugated with an amide carbonyl).

The PMR spectrum of the base has a number of signals: two signals of olefinic protons in the form of a doublet of triplets at 5.73-6.25 ppm; the signals of H_{17e} and H_{11} are observed in the 3.74-3.26 ppm region, and those of H_{2e}, H_{10e}, and H_{17a} in the 2.86-2.30 ppm region. The other protons give overlapping multiplet signals in the 2.24-0.82 ppm region.

The comparative study of the spectra of sophocarpine [1, 6], lehmanine [7], the deoxy base 7 [8], and the base with R_f 0.58 showed that they were possibly stereoisomers. However, it later appeared that the deoxy base 7 and the base with R_f 0.58 were identical.

For a definitive confirmation of this fact we performed catalytic hydrogenation in the presence of Raney nickel. Under these conditions each substance absorbed 1 mole of hydrogen and formed a saturated compound with the composition $C_{15}H_{24}ON_2$, mp 108-109°C, $[\alpha]_D^{20}$ −53.6° (c 0.6; ethanol) identical in its physicochemical constants and spectral characteristics with sophoridine.

On the basis of the facts given above, for the new alkaloid with R_f 0.58 we have proposed as the most probable structure that of 13,14-dehydrosophorodine:



EXPERIMENTAL

The UV spectra were taken on a Beckman spectrometer (in methanol), the IR spectra on a UR-10 spectrophotometer (thin film), the mass spectra on a Varian MAT-311 spectrometer, and the PMR spectra on a Varian-15 XL-100 instrument with a working frequency of 100 MHz (the chemical shifts are given in the δ scale relative to HMDS) with $CHCl_3$ as the solvent.

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We used Filtrak No. 1 paper for paper chromatography, and type LS 5/40 μ silica gel for thin-layer chromatography. The solvent systems were as follows: 1) butan-1-ol—water—hydrochloric acid (100:27:15); 2) ethyl acetate—isopropanol—25% ammonia (50:35:25). Chromogenic agents—the Dragendorff reagent and iodine vapor.

Isolation of the Alkaloids. The combined bases were isolated from *Sophora alopecuroides* (collected on July 31, 1976) by the method described previously [8]. This gave 38 g of the combined bases (yield 1.9%) which were fractionated according to their solubilities. The yield of the petroleum ether fraction was 0.61% (12.2 g), of the benzene fraction 0.76% (15.2 g), and of the chloroform fraction 0.4% (9.2 g).

Isolation of Sophoridine. The petroleum ether fraction (12.2 g) was boiled under reflux with the light fraction of petroleum ether for 30 min. The solution was poured off and the solvent was evaporated. This operation was repeated four times. The concentrated solution deposited crystals of sophoridine (8.2 g). Recrystallization from petroleum ether yielded sophoridine with mp 108-109°C, $[\alpha]_D^{20}$ −57.2° (c 0.9; ethanol).

Isolation of 13,14-dehydrosophoridine. The combined petroleum-ether-insoluble bases (4 g) were separated on a column of cellulose [8]. In this way we isolated sophocarpine (0.3 g), sophoridine (1.7 g), and matrine in admixture with 13,14-dehydrosophoridine (1.6 g). Of this mixture of matrine and 13,14-dehydrosophoridine, 1.6 g was separated by preparative chromatography in a fixed layer of silica gel in system 2 [8]. This yielded 0.8 g of matrine and 0.5 g of 13,14-dehydrosophoridine with mp 84-85°C, $[\alpha]_D^{20}$ +77.9° (c 0.56; ethanol); M^+ 246.

Catalytic Hydrogenation of 13,14-Dehydrosophoridine. 13,14-Dehydrosophoridine (146 mg) in solution in 50 ml of ethanol was hydrogenated over Raney nickel in a current of hydrogen with vigorous shaking at room temperature for 6 h. After the end of the reaction, the ethanolic solution was filtered and evaporated to dryness in vacuum. The residue was recrystallized from petroleum ether to give 125 mg of a base with mp 108-109°C, $[\alpha]_D^{20}$ −53.6° (c 0.6; ethanol); M^+ 248, identical with sophoridine.

SUMMARY

A new alkaloid, $C_{15}H_{22}ON_2$, with mp 84-85°C $[\alpha]_D^{20}$ +77.9° (c 0.56; ethanol) has been isolated from *Sophora alopecuroides* L. On the basis of UV, IR, PMR, and mass spectral characteristics and the hydrogenation reaction, its most probable structure has been determined as 13,14-dehydrosophoridine.

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