THE STRUCTURE OF SOPHORBENZAMINE

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On studying the alkaloid-bearing plant Goebelia pachycarpa C. A. M., we have isolated a new base which we have called sophorbenzamine. Sophorbenzamine, with the composition $C_{22}H_{26}N_2O$, forms white acicular crystals with mp 118-119°C (from hexane), $[\alpha]_D^{25}$ +90° (c 1.0; chloroform); picrate mp 122-123°C (from ethanol); mol. wt. 334 (mass spectroscopically).

According to its UV spectrum [λ_{max} 238 and 310 nm (log ε 4.10 and 4.16)], the base is very similar to the quinolizidine alkaloids containing an α-pyridone ring in their structure [1, 2]. The IR spectrum of the base has characteristic absorption bands of C=C bonds (1550, 1600 cm^{-1}), an =N−CO group (1645 cm^{-1}), a trans-quinolizidine system (2580, 2630, 2700 cm^{-1}), and pyridone ring (810 cm^{-1}) [3].

The oxidation of sophorbenzamine with chromic acid yielded succinic and benzoic acids, and glycine, β-alanine and γ-aminobutyric acid were identified chromatographically, which is characteristic for alkaloids of the quinolizidine series [4]. The formation of benzoic acid shows the presence of an aromatic substituent in the molecule.

The mass spectrum of sophorbenzamine is characterized by the presence of the molecular ion as the strongest peak and the peak of the $[M-1]^+$ ion is far weaker than that of the M^+ ion. The peak of an ion with m/e 91 shows the presence of a side benzyl chain in the base. The appearance of peaks of ions with m/e 305 (214 + 91) and 291 (200 + 91), and also the absence of the displacement of the peaks with m/e 149, indicates that this radical is in fact located in ring D. The general pattern of decomposition resembles that of quinolizidine alkaloids containing the matrine skeleton [4, 7].

In the CMR spectrum of sophorbenzamine there are 18 signals of different intensities. The signals were assigned by analogy with the spectra of other matrine alkaloids [8] in the following way: In the weak-field region (162-102 ppm) there are eight signals, which shows the presence of a pyridone fragment and a benzene radical; the signal at 64.0 ppm belongs to a tertiary carbon present in the α position to nitrogen, C_2 and C_{10} resonate at 54.7 ppm, and the C_{17} signal is shifted upfield as a result of the influence of an N−CO fragment (its chemical shift is 48.7 ppm), while C_7 and C_5 tertiary carbon atoms are responsible for signals at 41.1 and 36.1 ppm, respectively, and the C_6 carbon for a signal at 35.5 ppm. The difference in the chemical shifts is due to the influence of the $C_{11}=C_{12}$ bond on C_7, which is not transmitted to C_5. The C_4 and C_8 signals resonate at 28.7 and 28.3 ppm. The signals in the strongest field at 24.6 and 24.0 ppm correspond to C_3 and C_9. To interpret the signals relating to olefinic carbon atoms in the weak-field region, it is necessary in the first place to isolate the signals due to the phenyl radicals. A comparison with the spectrum of toluene showed that a signal at 125.5 ppm belongs to a meta carbon atom and two doublet signals at 128.5 and 127.8 ppm to ortho and para carbon atoms of the phenyl radical. The tertiary carbon atom of the phenyl radical resonates at 139.4 ppm.

For a more accurate assignment of the signals of the pyridone system we compared the chemical shifts of the other observed lines with the signals of the unsaturated carbon atoms of α-pyridone, cytisine, thermopsine, and isosophoramine: The C_{14} signal of the alkaloid differed substantially (by 10 ppm) from the chemical shifts of the signals of the carbon atoms present in the same position relative to an N−CO group. This means that the benzyl fragment is attached to the α-pyridone part of the alkaloid sophorbenzamine in position 14. The difference between the C_3 and C_9 chemical shifts in sophorbenzamine and in isosophoramine [8] is very small.

On the basis of the information obtained, we propose structure (I) as the most probable for sophorbenzamine.

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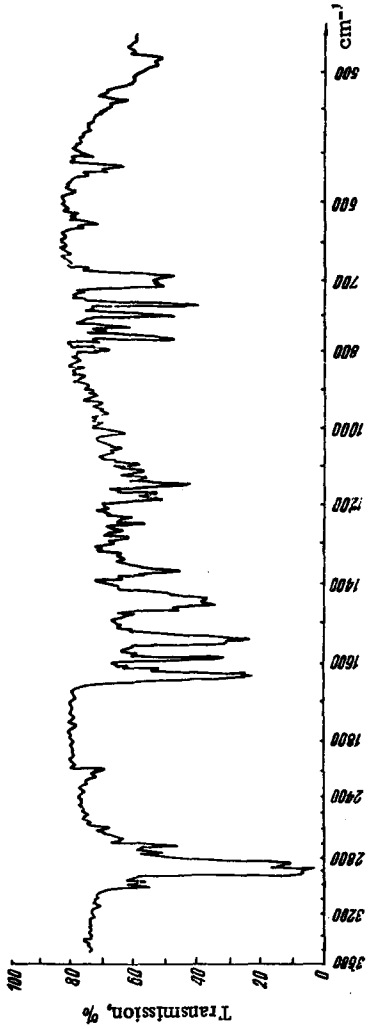
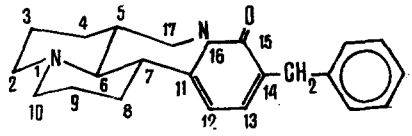


Fig. 1. IR spectrum of sophorbenzamine.



EXPERIMENTAL

The UV spectrum was taken on an SF-4A spectrometer, the IR spectrum on a UR-10 double-beam spectrometer, the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectra at the natural content of the ^{13}C isotope on a Varian XL-100 spectrometer.

Isolation of Sophorbenzamine. The dried and comminuted epigeal part of G. pachycarpa (10 kg) collected in the flowering period in the suburbs of Tashkent on the banks of canals was extracted with chloroform. The combined alkaloids obtained after the solvent had been distilled off (300 g) were passed through a column of alumina with elution by means of chloroform. The fractions containing sophorbenzamine were rechromatographed on a column of alumina and were eluted with ethyl acetate. After the solvent had been distilled off the fractions containing sophorbenzamine were crystallized from hexane. Yield 0.48 g, mp 118-119°C, $[\alpha]_D^{25}$ +90° (c 1.0; ethanol). Sophorbenzamine is soluble in alcohols, ether, and chloroform, sparingly soluble in n-hexane and cyclohexane, and insoluble in water.

Oxidation of Sophorbenzamine with Chromium Trioxide. A mixture of 52 mg of sophorbenzamine and 80 mg of chromium trioxide in 2 ml of 56% sulfuric acid and 1 ml of water was heated in a water bath for 3 h and was then boiled for 8 h. After cooling, ether extracted succinic and benzoic acids from the reaction mixture. The mother solution was treated with barium hydroxide, the precipitate was filtered off, and the filtrate was evaporated to dryness. When the residue was chromatographed on "Filtrak" No.3 paper, β-alanine (R_f 0.36), glycine (R_f 0.14), and γ-aminobutyric acid (R_f 0.32) were isolated. The solvent system used was butan-1-ol–formic acid–water (18:2:9).

SUMMARY

A new base with the composition $C_{22}H_{26}N_2O$ has been isolated from G. pachycarpa and has been called sophorbenzamine.

On the basis of UV, IR, mass, and CMR spectra, and also the results of a chemical investigation, sophorbenzamine has been assigned to the quinolizidine alkaloids of the matrine series and a most probable formula has been proposed for it.

LITERATURE CITED

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