the mono- and dimethylamine hydrochlorides, no value of Δj exceeded 0.02; for the trimethylamine hydrochloride some values rose as high as 0.03.

Discussion of Results

It is difficult to set up an absolute degree of accuracy in the values given. By a consideration of the possibilities of heat leakage, stray electromotive forces, contact electromotive forces, precision of measuring devices, etc., it is estimated that most of the observed freezing point lowerings are accurate to approximately one two-thousandth of the freezing point depression. The method of determining the concentration was, ultimately, a graphical one. The conductance measurements are estimated to be accurate to within one-hundredth of one per cent. and the concentrations to at least that accuracy.

The behavior of the methylamine hydrochlorides is similar to that of the ammonium salts, as found by Scatchard and Prentiss[3] and to some of the tetraalkylammonium halides, as described by Jörn Lange.[15] Lange found that the j-values of these halides asymptotically approached the limiting law line from below in some cases and from above in other cases. In the case of tetramethylammonium chloride, the limiting law was approached from below, which is opposite to the approach of the salts of this investigation.

Summary

A differential freezing point apparatus was utilized to determine the freezing point depressions of aqueous solutions of mono-, di- and trimethylamine hydrochlorides over a concentration range 0.0025 to 1.0 molal.

The data are presented in terms of j-values at rounded concentration values.

From these j-values, provisional values for the activity coefficients were calculated.

Conductivity data for the methylamine hydrochlorides are presented.

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[CONTRIBUTION FROM THE INSTITUTO BACTERIOLÓGICO D.N.H., BUENOS AIRES]

Studies on Argentine Plants. III. Alkaloids from Lycopodium Saururus[1]

BY V. DEULOFEU AND J. DE LANGHE

The presence of alkaloids in a plant of the genus *Lycopodiaceae* was first shown by Bödeker,[2] who isolated *lycopodine* from *L. Complanatum.* Shortly thereafter Arata and Canzoneri[3] isolated from *L. saururus* a substance, $C_{15}H_{20}ON_2$, m. p. 64–65°, to which the name *pillijanine* was assigned. More recently Orechoff[4] has mentioned the presence of alkaloids in *L. annotinum*, and Muszynski[5] has confirmed this finding, and extended his study to other European species with similar results. From one of the latter, *L. clavatum*, Achmatowicz and Uzieblo[6] isolated lycopodine, as well as clavatine and clavatoxine.

We have re-studied *L. saururus*, a plant which is widely distributed not only in Argentina, but in other South American countries, and in Africa. From it we have isolated two bases. The first, and most important, substance for which we propose the name *saururine*, was obtained as a sirup, from which a crystalline picrate, $C_6H_3O_7N_3 \cdot C_{10}H_{19}N$, and methiodide, $C_{10}H_{19}N \cdot CH_3I$, could be obtained. Its nitrogen atom is tertiary, and the base is isomeric with lupinanes. Further, a crystalline levorotatory alkaloid, $C_{17}H_{26}ON_2$, m. p. 198°, was obtained in small amounts. This substance forms a monomethiodide, has one tertiary nitrogen atom, and no methoxyl groups. Although the formula of our substance bears some resemblance to that of pillijanine, obtained from the same plant by Arata and Canzoneri,[3] the properties of the two substances differ markedly. For the new alkaloid we propose the name *sauroxine.* We were not able to isolate any substance having the properties of pillijanine, even when employing the method of extraction described by the earlier investigators.

Experimental

Extraction of the Plant.—Seventy-four hundred grams of air-dried *L. saururus* leaves was allowed to stand for two weeks with fifty liters of 2% hydrochloric acid. This operation was repeated twice.

The combined extracts were evaporated to a volume of

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(1) Part II, *J. Chem. Soc.*, 1051 (1940).

(2) Bödeker, *Ann.*, **208**, 363 (1881).

(3) Arata and Canzoneri, *Gazz. chim. ital.*, **22**, 146 (1892).

(4) Orechoff, *Ber. deut. pharm. Ges.*, **272**, 673 (1934).

(5) Muszynski, *ibid.*, **273**, 452 (1935).

(6) Achmatowicz and Uzieblo, *Roczniki Chem.*, **18**, 88 (1938).

ten liters, made alkaline with sodium hydroxide, and extracted with ether (ten liters). After the extraction the water solution gave only a faint Mayer test.

The ethereal extracts were evaporated to dryness, and the residue triturated with 10% hydrochloric acid (100 cc.). Water was added to 200 cc., the insoluble material removed by filtration and re-extracted three times in like manner. The acid solution containing the bases was extracted with ether, and the ethereal solution discarded. The water solution was then made alkaline and again extracted with ether, about 1500 cc. being employed. The ether extract was washed with water, dried well and evaporated. Nine-tenths of a gram of residue was obtained per kilo of plant.

The residue was dissolved in acetone, cooled and treated with a solution of 5 g. of picric acid in 5 cc. of acetone. After some minutes, crystals of saururine picrate began to separate. After twenty-four hours, 3.3 g. of crystalline material, m. p. 188–190°, was collected. Concentration of the mother liquor afforded another, much less pure, fraction of picrate.

After separation of the picrate the acetone mother liquor was evaporated to dryness and the residue triturated with 50 cc. of hydrochloric acid (10%). The first extract was removed and the insoluble material, after a second trituration with a similar volume of acid, was discarded. The acid extracts were combined, made alkaline with sodium hydroxide and extracted with ether.

The extract was well washed with water and evaporated. The residue was dried thoroughly in a desiccator and dissolved in 4 cc. of absolute ether. A crystal of sauroxine was added and the material which had separated after twenty-four hours was collected. Concentration of the mother liquor afforded a new crop. In all, 0.5 g. of sauroxine, m. p. 190–191°, was obtained. The alkaloid does not crystallize readily without seeding. Crystals were first obtained by spontaneous crystallization of the saururine mother liquors.

The residue after the separation of sauroxine gave a strong positive Mayer alkaloid test but no new pure base could be obtained from it.

Saururine Picrate.—The crude picrate after recrystallization three times from 75% acetone gave yellow prisms, m. p. 202°.

Anal. Calcd. for $C_6H_3O_7N_3 \cdot C_{10}H_{19}N$: C, 50.26; H, 5.76; N, 14.65. Found: C, 50.17; H, 5.13; N, 14.11, 14.18.

Saururine.—The picrate was twice triturated with dilute hydrochloric acid (1:1). The combined acid extracts were made alkaline and extracted with chloroform. The chloroform solution was washed with water and evaporated to dryness. The residue was taken up in dilute acid, the insoluble material was removed by filtration, the solution was made alkaline and extracted with ether.

Evaporation of the well-dried ether solution left a pale yellow, very viscous sirup, soluble in all organic solvents except petroleum ether, insoluble in water. The substance was dextrorotatory in alcoholic solution and levorotatory in dilute hydrochloric acid. It could not be induced to crystallize from solvents or on long standing in a desiccator.

The oil was not steam-volatile, but could be distilled *in vacuo*. The distillate was a colorless sirup from which the picrate described above, m. p. 201–202°, was easily obtained.

Saururine Methiodide.—The free base was dissolved in acetone and treated with an excess of methyl iodide. A violent reaction ensued, and the methiodide separated. The material was collected and crystallized from water, from which it separated in fine needles, m. p. 242–244°.

Anal. Calcd. for $C_{10}H_{19}N \cdot CH_3I$: C, 44.74; H, 7.45; N, 4.74; I, 43.05. Found: C, 44.79; H, 7.14; N, 4.19; I, 43.21.

A water solution of the methiodide made alkaline gives a base soluble in water and insoluble in ether.

Sauroxine.—The alkaloid was obtained as prismatic needles, m. p. 198°, by recrystallization of the crude sauroxine from acetone; $[\alpha]^{20}_D$ −71.8° (*c*, 0.792 in alcohol; *l*, 2 dm.).

Anal. Calcd. for $C_{17}H_{26}ON_2$: C, 74.45; H, 9.49; N, 10.21. Found: C, 73.88; H, 9.29; N, 10.27.

Sauroxine Methiodide.—When sauroxine was boiled with excess methyl iodide in acetone for one hour, the crystalline methiodide separated. After cooling, the precipitate was collected and crystallized from aqueous acetone as fine needles, m. p. 258°.

Anal. Calcd. for $C_{18}H_{29}ON_2I$: C, 51.92; H, 6.97; N, 6.73; I, 30.52. Found: C, 51.87; H, 6.90; N, 6.55; I, 30.20.

Like saururine methiodide, sauroxine methiodide in aqueous solution was transformed by alkali into a water-soluble, ether-insoluble base.

We are indebted to Professor O. Orias (Córdoba) who collected the plants used in our work.

Summary

Two new alkaloids, *saururine*, $C_{10}H_{19}N$, and *sauroxine*, $C_{17}H_{26}ON_2$, have been isolated from *Lycopodium saururus*.

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