

226. *Sophora Alkaloids. Part II. The Alkaloids of the Seeds of S. Tetraptera.*

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The seeds of *Sophora tetraptera* are shown to contain mostly matrine, a little methylcytisine, and a base (aurichloride, m. p. 186°).

IN continuance of the investigation of the alkaloids of *Sophora* species endemic to New Zealand (Part I, J., 1937, 1795), the seeds of *Sophora tetraptera*, syn. *Edwardsia tetraptera*, have now been examined. The crystalline portion of the crude alkaloid (yield, 3%) proved to be almost entirely matrine with a little methylcytisine. These are also the chief alkaloids from the seeds of *S. microphylla*, where they occur, however, in almost equal amount. A considerable amount of basic resinous material accompanies these alkaloids, from which a small amount of a base was obtained through the hydriodide, giving an aurichloride, m. p. 186° (decomp.). The m. p. approximates to that of sophoramine (aurichloride, m. p. 183—184°) isolated by Orechov (*Ber.*, 1933, 66, 948) from the foliage of *S. alopecuroides*, but the amount obtained was too small for further characterisation.

EXPERIMENTAL.

S. tetraptera is a tree very similar to *S. microphylla*, and the material used in this research was collected from trees in the Hawkes Bay district.

7.54 Kg. of crushed seeds were worked up as described in Part I except that the final extract of the alkaloids in aqueous solution was made with trichloroethylene in a continuous extractor (Briggs, *Ind. Eng. Chem. [Anal.]*, 1937, 9, 250). The brown semicrystalline mass of crude alkaloids (232 g.; ca. 3% yield) so obtained was hygroscopic and was very soluble in water and the usual organic solvents except light petroleum and benzene. An aliquot portion (130 g.) of the crude material was extracted exhaustively with successive portions of petroleum (b. p. 80—100°), leaving a dark brown, vitreous residue (M) (41 g.). The alkaloid which separated from the evaporated extracts was distilled in two lots in order to make use of any fractional extraction. Both distilled as pale yellow oils, b. p. ca. 200°/ < 1 mm. (total yield, 76 g.), solidifying on standing. The undistillable residue was a dark tarry mass amounting to 11 g. from both experiments, which could not be crystallised nor converted into crystalline derivatives.

Both distillates were then fractionally recrystallised from petroleum of different boiling points, and the mother-liquors systematically worked up in a series of over fifty recrystallisations.

The distilled bases were repeatedly extracted with light petroleum (b. p. below 40°) to completion. The material separating was repeatedly crystallised from the same solvent until crystals of base A, of constant m. p. 77°, were obtained. The portion insoluble in light petroleum was then repeatedly crystallised from petroleum (b. p. 80—100°) and yielded base B, m. p. 137.5—138°. The mother-liquors were worked up separately, the light petroleum yielding further quantities of base A, whereas the mother-liquors of the petroleum (b. p. 80—100°) first yielded crystals of base B and then those of base A. Both distillates contained bases A and B, the material from the first series of extractions containing three times as much of base B as the material from the latter extractions. It is essential that all apparatus and solvents should be quite dry—if these precautions are not observed, the alkaloids, especially base A, tend to resinify readily and reduce the yield of pure alkaloid.

When no more crystalline material could be obtained, the mother-liquors were evaporated to dryness under reduced pressure, and the residue taken up in water (charcoal) and converted into picrates. By fractional crystallisation further quantities of bases A and B were obtained as pure picrates.

From 76 g. of distilled bases, 55.8 g. of base A, 3.3 g. of base B, 5.4 g. of base A picrate and 0.2 g. of base B picrate were obtained. No evidence could be obtained for the presence of other alkaloids in the distilled material.

Base A.—This base, m. p. 77°, has been identified as α -matrine by mixed m. p. determinations with authentic specimens of the free base and their derivatives. $[\alpha]_D^{18} + 32.06^\circ$ ($l = 1, c = 2.246$ in water); b. p. 230°/10 mm., 224°/5 mm., 190°/0.5 mm.

Methodide. The isomeric methodides, m. p. > 300° and m. p. 254° (decomp.), described in Part I were again obtained with no trace of lower-melting isomerides.

Methyl matrinat methiodide. Orechov and Proskurnina (*Ber.*, 1935, **68**, 429) recommend this compound as the most suitable for the identification of matrine. The compound so obtained had m. p. 215—216°, undepressed by an authentic specimen kindly provided by Professor Orechov. Their observations on potassium matrinat, however, could not be confirmed. Potassium matrinat is hygroscopic and excessively soluble in water. It crystallises readily from absolute alcohol or better from alcohol-acetone (1 : 3) in fine long needles, m. p. 160—165°. Orechov and Proskurnina (*loc. cit.*) record the same m. p. (from water). They also state that this form is a hydrate, giving an extremely hygroscopic anhydrous salt, m. p. 237—239°. In our hands potassium matrinat was unaltered in m. p. after heating for some time at 137°/20 mm. over calcium chloride.

Hydriodide. Colourless plates, m. p. 267° with darkening at 250°, separate after long standing when the base in aqueous alcohol is mixed with the equivalent of concentrated hydriodic acid. The material decomposes on recrystallisation from hot water or alcohol.

Picrate. This is easily prepared and crystallised from hot water. It has m. p. 64—140°, the indefinite m. p. probably being due to water of crystallisation. A sharp m. p. is not obtained after long heating over phosphoric oxide in a vacuum, although the incipient m. p. is raised to 97°. The derivative is therefore not suitable for the identification of matrine.

Base B.—This base, m. p. 137·5—138°, $[\alpha]_D^{20} = 221·6^\circ$ ($l = 1$, $c = 2·157$ in water), has been identified as methylcytisine. The m. p. of the free base was not depressed by an authentic specimen, the following derivatives behaving similarly (the m. p.'s in parenthesis refer to those already recorded; cf. Part I, where full references to matrine and methylcytisine are also given): picrate, m. p. 230° (229°); picrolonate, m. p. 224—225°, decomp. (224°); aurichloride, m. p. 207°, decomp. (206°); perchlorate, m. p. 254°, decomp. (250—252°). The platinichloride, orange-red needles, obtained in alcoholic solution sintered at 265° but did not melt below 290° (cf. Part I). The methiodide, obtained after 15 minutes' refluxing of the reactants in acetone and standing, crystallised from methyl alcohol in colourless plates, m. p. 276·5°. Ing (J., 1931, 2200) records m. p. 276° (cf. also Part I).

Hydriodide. This separated in reddish needles, m. p. 246° (decomp.) with previous sintering at 232°, when concentrated hydriodic acid was added to the base in aqueous solution. Like matrine hydriodide, it decomposed when attempts were made to recrystallise it.

The original vitreous residue (M) insoluble in boiling petroleum was deliquescent, very soluble in alcohols and chloroform and partly soluble in ether, acetone, benzene, and xylene. From the latter solvents, only amorphous products separated which rapidly turned to viscous brown oils on exposure to the atmosphere. They gave pyrrole bases on dry distillation (pine shaving test).

The material could not be purified through re-solution in water and extraction, by salting out from concentrated solutions saturated with potassium carbonate, or by chromatographic adsorption on norit or calcium carbonate. Derivatives, sometimes crystalline but usually amorphous, became oily or tarry on short exposure to the atmosphere. The hydriodides alone were stable solids, partly crystalline, but decomposed when heated in solution for recrystallisation.

A portion of the crystalline hydriodide was dissolved in water, saturated with potassium carbonate, and extracted with chloroform. The drop of oily base obtained gave a yellow amorphous picrate, m. p. 140—180°, which could not be crystallised, and an aurichloride crystallising from aqueous acetone, m. p. 186° (decomp.). The material was too small in amount for further characterisation.

An aliquot portion of the residue (M) (28 g.) was then distilled; 5·2 g. of a pale yellow oil passed over at 170°/0·2 mm., which solidified after 3 weeks. Derivatives prepared from this material approximated in m. p. very closely to those of sophoridine (Orechov, *Ber.*, 1933, **66**, 948), but careful purification showed that they were derivatives of mixtures of methylcytisine and matrine. No other bases could be detected and the residue from the distillation could not be crystallised.

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