107. Sophora *Alkaloids. Part IV. The Alkaloids from the Seeds of the Chatham Islands Species.*

By L. H. Briggs and W. E. Russell.

Differences of opinion exist among botanists as to whether the *Sophora* from the Chatham Islands is a true species (*S. chathamica*) or whether it is identical with or a variety of *S. microphylla*. The alkaloids of the seeds are shown to consist of α-matrine, methylcytisine, and sophochrysine, which are all found also in the seeds of both *S. microphylla* and *S. tetraptera* but in different proportions. The chemical evidence is insufficient for a definite conclusion but tends to support the view that it is identical with *S. microphylla*.

Cockayne (*Trans. Roy. Soc. New Zealand*, 1902, **34**, 319), mainly in the differences exhibited by the juvenile forms, regards the *Sophora* of the Chatham Islands as a species distinct from *S. microphylla* growing on the mainland of New Zealand, which otherwise it resembles very closely, and has classified it as *S. chathamica*. Cheeseman, however ("Manual of the New Zealand Flora," 1925, p. 530), without supporting his contention, regards it as identical with or at the most a variety of *S. microphylla*. It was considered that a chemical investigation of the seeds of this *Sophora* for alkaloids would aid the botanical classification. Manske (*Canadian J. Res.*, 1939, **17**, *B*, 1) has already shown that species of *Senecio*, taxonomically indistinguishable, can be separated quite easily by the fact that they contain different alkaloids, and Baker and Smith ("A Research on the Eucalypts and their Essential Oils," 1920, Second Edition) have also demonstrated that eucalypt species, taxonomically indistinguishable, can be separated by differences in the constituents of their essential oils.

A small quantity of seeds of the *Sophora* species from the Chatham Islands has been examined for alkaloids by methods similar to those described in Parts I and II (J., 1937, 1795; 1938, 1206) for *S. microphylla* and *S. tetraptera* respectively. From the distilled bases (yield, 1·5%), three alkaloids have been identified, *viz.*, α-matrine, methylcytisine, and sophochrysine (cf. Part III, this vol., p. 507).

The same three bases also occur in *S. microphylla* and *S. tetraptera*, the main alkaloids being α-matrine and methylcytisine in both cases but in different proportion. The seeds of the former also contain cytisine and a fifth base (Base E) but these are only present to a very small extent (6 mg. and 3 mg. respectively were isolated from a much larger quantity of alkaloidal material) and would not be expected to be isolated in this case. With the small amount of material available from the Chatham Islands *Sophora* it has been impossible to separate the mixtures of bases in any way quantitatively and consequently a definite conclusion cannot be reached regarding the chemical evidence supporting the classification. The fact, however, that the alkaloids are the same as those of *S. microphylla*, together with the evidence of Manske's observations, would tend to support Cheeseman's view that the two species are identical.

The definite identification of sophochrysine from this *Sophora* supports our opinion (cf. Part III) that the base D of *S. microphylla* is identical with sophochrysine.

Experimental.

515 G. of the seeds of the Chatham Islands *Sophora* were worked up as described in Part II, trichloroethylene completely removing the alkaloids from the aqueous solution in 192 hours. The crude alkaloids on distillation afforded two fractions, (*a*) b. p. 180—185°/0·5 mm., (*b*) b. p. indefinite/0·8 mm. (bath temp. 260—340°)—total yield, 3·31 g. (1·5% based on weight of dry seeds).

Both fractions dissolved almost completely in hot light petroleum (b. p. 80—100°), leaving an amorphous residue (4 mg.) of base C, m. p. 284—288°. As no crystalline material had separated from the light petroleum solution after some months, the solvent was removed, and the residue digested successively with light petroleum (b. p. below 40°) and (b. p 80—100°). After concentration of the former extract colourless needles separated, m. p. 56—64°, raised by repeated crystallisation from the same solvent to 73—77° (base A). The latter extract on concentration gave colourless needles of base B, m. p. 128—132°. The yield in both cases was less than 50 mg.

Base A.—This base, m. p. 73—77°, has been identified with α-matrine, an authentic specimen causing no depression of the m. p. The picrate, crystallised from hot water, had m. p. 58—145°. The same indefinite m. p. is recorded in Part II. The aurichloride from the base (10 mg.) crystallised from the reaction mixture in golden-yellow needles, m. p. 197—199° with sintering at 195°, undepressed by an authentic specimen.

The following two new salts were prepared from matrine *ex S. tetraptera*: The perchlorate separated as an oil on addition of 20% aqueous perchloric acid to a solution of the base in ethyl acetate, but crystallised from absolute alcohol–

chloroform in colourless needles, m. p. 214·5—216°. The hydrobromide, prepared in absolute alcohol, crystallised from absolute alcohol–ethyl acetate in colourless needles, m. p. 272—275° with sintering at 266°.

Base B.—This base, m. p. 128—132°, has been identified as methylcytisine by its m. p., and by preparation of the following derivatives ; in all cases the m. p.'s were not depressed by authentic specimens. The picrate crystallised from hot water in long yellow needles, m. p. 223—225° with sintering at 212° (lit., m. p. 229°; cf. Part I). The picrolonate crystallised from dilute alcohol in needles, m. p. 218° (decomp.) (Part II records 224—225°).

Base C.—This base, m. p. 284—288°, has been identified as sophochrysine by its m. p. The aurichloride prepared from it (4 mg.) crystallised in yellow needles, m. p. 187—189°. In each case the m. p. was undepressed by an authentic specimen.

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AUCKLAND UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, May 15th,* 1942.]