93. *Sophora Alkaloids. Part III. The Alkaloids of the Seeds of* S. chrysophylla.

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The alkaloids from the seeds of *Sophora chrysophylla* are shown to consist chiefly of cytisine and anagyrine with a third base in small quantity probably identical with an unidentified base isolated from *S. microphylla* and *S. tetraptera*, for which the name sophochrysine is suggested.

Sophora chrysophylla (native name, " Mamami ") is an inland species endemic to Hawaii, resembling the New Zealand " Kowhai " (*S. microphylla*). The alkaloids from the seeds have been isolated and examined by methods similar to those described in Parts I and II (J., **1937**, 1795; **1938**, 1206). The distilled alkaloids from the mixture of crude bases (yield, *ca.* 2%) have been separated by fractional crystallisation of the free bases and their salts and shown to consist mainly of cytisine and anagyrine in the approximate proportion of 1 : 4. *S. chrysophylla* therefore resembles *Anagyris fœtida*, which contains the same alkaloids (Ing, J., 1943, 504; Partheil and Spasski, *Apoth.-Ztg.*, 1895, **10**, 903). From material insoluble in acetone, a third base, m. p. 284—287°, has been isolated. Although it could not be obtained crystalline, it formed a crystalline aurichloride, m. p. 190—192° (decomp.), picrate, m. p. above 360°, and a picrolonate, m. p. 255—258° (decomp.). This base is, in our opinion, identical both with base D, from *S. microphylla* (cf. Part I), which has m. p. 293—296° (picrate, m. p. above 350°, and picrolonate, m. p. 261° with sintering at 257—258°), and with a third base from *S. tetraptera* (cf. Part II), which gave a crystalline aurichloride, m. p. 186° (decomp.), although direct comparisons could not be made owing to the minute amounts of alkaloid separated from *S. microphylla* and *S. tetraptera*. All three bases were obtained from fractions insoluble in light petroleum, and the first two bases had similar solubilities and failed to give the van der Moer reaction. We suggest the name sophochrysine for this new alkaloid (cf. also Part IV to follow). Analyses of the *picrate* and *picrolonate* did not confirm the original formula suggested, $C_{15}H_{23}O_4N_3$, but the analytical data are still too meagre for a definite formula, a more probable decision lying between $C_{13-15}H_{21-19}O_2N_3$.

EXPERIMENTAL.

3·22 Kg. of the seeds of *S. chrysophylla* were worked up as described in Part II, yielding after 18 days of continuous extraction with trichloroethylene 60 g. of a dark brown, viscous oil (K), (yield, *ca.* 2%). Since basic material still remained in the aqueous solution, extraction was continued with chloroform for 15 days, giving a further 4 g. of deep red, hygroscopic material (L). Since even this treatment failed to extract all the basic material, precipitation of the remaining alkaloids was brought about by the addition of Mayer's reagent, 3·3 g. of dark amorphous material (M) being recovered. Fractions L and M gave positive tests for nitrogen and pyrrole bases on dry distillation (pine shaving test), but no crystalline material could be obtained as a free base or as a salt and fraction L could not be distilled in low vacuum without decomposition.

Distillation of (K) gave a product (35 g.), b. p. 192—195°/0·15 mm., solidifying to a yellowish-brown glassy solid containing some crystalline material. The residue (N) in the neck of the flask was worked up later. The distilled alkaloids were again distilled and collected in two fractions : (*a*) 21·31 g., b. p. 175—180°/0·1—0·2 mm., and (*b*) 8·61 g., b. p. 200—215° (mainly 207°)/0·1 mm. The first fraction partly crystallised on standing while the second fraction remained as a clear glass.

18% of fraction (*a*) was obtained crystalline by treatment with acetone, followed by recrystallisation from benzene and light petroleum (b. p. 80—100°), to give a pure base A, m. p. 153·5—154·5°. No other crystalline base could be obtained from the mother-liquors, but 50% of another base B could be obtained as the picrate, m. p. 243—244·5° (decomp.).

Fraction (*b*) did not yield base A, but mainly dissolved in acetone, leaving an amorphous residue of base C, m. p. 284—287° after darkening at *ca.* 228° (yield, 220 mg. from 6·68 g.).

From another aliquot portion, 76% of base B could be obtained as the perchlorate, m. p. 292° (decomp.).

Base A.—This base has been identified as cytisine by mixed m. p. determinations with authentic specimens of the free bases and their derivatives (Found : C, 69·3; H, 7·3. Calc. for $C_{11}H_{14}ON_2$: C, 69·4; H, 7·4%). $[\alpha]_D^{25^\circ}$ − 114·6° (l = 1, c = 0·8460 in water). Partheil (*Arch. Pharm.*, 1892, **230**, 448) records $[\alpha]_D^{25^\circ}$ − 119·5°. The m. p.'s of the base and its derivatives compared with recorded values are as follows (for references, see Part I) : base, m. p. 153·5—154·5° (150—156°); picrate, m. p. 277° (decomp.) (278°, decomp.); aurichloride, m. p. 218—220° (decomp.) (219°, decomp.); methiodide of methylcytisine, m. p. 271—275° (270—280°). Ing (J., 1933, 506) refers to a perchlorate but gives no m. p. The *perchlorate*, prepared by addition of 20% aqueous perchloric acid to the base in ethyl acetate, crystallised from alcohol in long colourless needles, m. p. 296° (decomp.) (Found : N, 9·6. $C_{11}H_{14}ON_2,HClO_4$ requires N, 9·8%). The picrolonate, prepared from the components in hot alcohol, crystallised from alcohol in bright yellow needles, m. p. 270° (decomp.) with sintering at 265°.

Base B.—This base has been identified as anagyrine. It gives a positive van de Moer test, is deliquescent, and is soluble in the common solvents except light petroleum, in which it is only slightly soluble. $[\alpha]_D^{25^\circ}$ − 146·9° (l = 1, c = 1·062 in absolute alcohol). Ing (*loc. cit.*) records $[\alpha]_D^{25^\circ}$ − 165·3° and Oréchov (*Ber.*, 1934, **67**, 1394) $[\alpha]_D^{25^\circ}$ − 151·7°. In agreement with these workers we have not been successful in crystallising the base.

The picrate crystallised from water or alcohol in slender yellow needles, m. p. 243—244·5° (decomp.). Oréchov (*loc. cit.*) records m. p. 242—243° and Clemo and Raper (J., 1935, 10) m. p. 242° (Found : C, 53·2; H, 4·8. Calc. for $C_{15}H_{20}ON_2$: C, 53·25; H, 4·9%). $[\alpha]_D^{25^\circ}$ − 145·7°. Clemo and Raper record $[\alpha]_D^{25^\circ}$ − 148·5°.

The picrolonate crystallised from aqueous alcohol in yellow needles, m. p. 253° (decomp.). Clemo and Raper (*loc. cit.*) record m. p. 254° (decomp.).

The mercurichloride crystallised from aqueous alcohol in clusters of colourless needles, m. p. 221·5—224°, and on standing prisms separated, m. p. 230—232°. Litterscheid (*Arch. Pharm.*, 1900, **238**, 191) records three forms : (*a*) with water of recystallisation, m. p. 225—226°; (*b*) anhydrous, slender white needles, m. p. 213—214°; (*c*) white nodular crystals, m. p. 231°. Oréchov (*Ber.*, 1934, **67**, 1394), however, records only one form, m. p. 220—222°.

The methiodide, from the base (200 mg.) in methyl alcohol and methyl iodide (0·5 c.c.), separated in colourless needles after the mixture had been heated for an hour; after repeated crystallisation from methyl alcohol it had m. p. 262° (decomp.). Clemo and Raper (*loc. cit.*) record colourless plates, m. p. 264° (decomp.).

The perchlorate, which Ing (*loc. cit.*) recommends as the most convenient means of separation from cytisine, is described as colourless needles decomposing at 270° without melting. In this case the perchlorate, after recrystallisation from water containing a little ethyl acetate, formed colourless needles which darkened at 267° and decomposed at 298·5°.

Base C.—This base, sophochrysine, m. p. 284—287°, could not be crystallised. It is freely soluble in water, ethyl and methyl alcohol, sparingly soluble in benzene and chloroform, and insoluble in acetone, ethyl acetate and light petroleum. It does not give the van de Moer reaction. $[\alpha]_D^{25^\circ}$ − 113·2° (l = 1, c = 0·795 in absolute alcohol). The *picrate*, formed on addition of alcoholic picric acid to an aqueous solution of the base (7 mg.), separated on cooling in short yellow needles which darkened at 250° but did not melt below 360° [Found : C, 47·9; H, 4·9; N, 17·1. $C_{13}H_{21}O_2N_3(?),C_6H_3O_7N_3$ requires C, 47·5; H, 5·0; N, 17·5%].

The *picrolonate*, prepared similarly from the base (13 mg.), after recrystallisation from water formed yellow needles, m. p. 265·5—267° (decomp.) [Found : C, 56·2; H, 4·8; N, 18·8. $C_{15}H_{19}O_2N_3(?),C_{10}H_8O_5N_4$ requires C, 55·9, H, 5·0; N, 18·3%].

The aurichloride, formed from the base (5 mg.) in the usual way, crystallised from dilute hydrochloric acid in clusters of bright yellow needles, m. p. 190—192° (decomp.). It was unsuitable for molecular weight estimations, as it darkened and decomposed on standing, but was apparently stable in suspension in the mother-liquors of the preparation.

The residue (N) from the first distillation of the bases was dissolved in water and aliquot portions were treated with picric acid and picrolonic acid. The former acid gave an amorphous picrate, m. p. 237° (decomp.), and, on standing, long yellow needles, m. p. 260° (decomp.). Both products, however, after crystallisation from water darkened at *ca.* 250° but did not melt below 360° and consisted apparently of sophochrysine picrate. From the latter acid an amorphous picrolonate was obtained which after crystallisation from aqueous alcohol had m. p. 260—261·5°, undepressed by sophochrysine picrolonate.

The analyses are by Dr. Burger.

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