8. *The Alkaloids of* Ormosia dasycarpa *Jacks.*

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(—)-Sparteine has been identified as a constituent of the seeds of *Ormosia dasycarpa*. Two new alkaloids have been isolated and characterised.

The constituents of the seeds of *Ormosia dasycarpa* Jacks, a member of the Leguminosae, were examined by Hess and Merck;[1] two isomeric alkaloids, $C_{20}H_{33}N_3$, were characterised. The major alkaloid, ormosine, was obtained as a hydrate, m. p. 85—87°; the anhydrous compound was not crystalline. The minor alkaloid, ormosinine, crystallised from ethanol in prisms, m. p. 203—205°.

Lloyd and Horning[2] recently isolated three isomeric alkaloids, $C_{20}H_{33}N_3$, from *Ormosia panamensis* Benth. One compound, m. p. 219—220°, was thought to be identical with Hess and Merck's ormosinine. A second alkaloid, ormosanine, m. p. 167—168°, contained at least one imino-group but no *N*-methyl group. The major alkaloid, panamine, was similar to, but apparently not identical with, ormosine. Panamine formed a hydrate. m. p. 38—40°, and contained an imino-group and an *N*-methyl group.

Lloyd and Horning[2] investigated a number of *Ormosia* species, not including *Ormosia dasycarpa*, and showed by paper chromatography that they contained ormosinine, ormosanine, and panamine. *N*-Methylcystisine was the only alkaloid present in *Ormosia stipitata*.[3]

We have re-examined the alkaloids of *Ormosia dasycarpa.*

Exhaustive extraction of the powdered seeds with boiling methanol gave an alkaloid fraction (1·47%), yielding a crystalline compound (0·038%), which was insoluble in ether. A major alkaloid was isolated from the ether-soluble bases as its crystalline hydrobromide (0·57%). Chromatography and distillation of the remaining bases afforded (—)-sparteine (0·09%).

The failure of Hess and Merck to isolate sparteine from *Ormosia dasycarpa* may have been due to their use of ethanol for extraction; we found that ethanol gave an alkaloid fraction (0·82%) not containing sparteine. Further extraction with methanol gave a basic fraction (0·58%) from which (—)-sparteine was isolated.

The major alkaloid was not crystalline, but was shown to be homogeneous by paper chromatography. The base, for which we propose the name dasycarpine, is apparently, not identical with either ormosine or panamine. Thus dasycarpine formed a tripicrate, a trihydrobromide, and a triperchlorate, while panamine formed derivatives with only two mols. of picric and perchloric acid. Ormosine gave a dipicrate. The most likely molecular formula for dasycarpine is $C_{20}H_{35}N_3$. Dasycarpine, in contrast to panamine, did not contain an *N*-methyl group, but the presence of at least one secondary amino-group was shown by infrared absorption. Dasycarpine showed only very weak absorption in the 1800—1500 cm.$^{-1}$ region, but its hydrobromide had a strong infrared peak at 1578 cm.$^{-1}$ ($\supset NH_2^+$).[4] The alkaloid resisted catalytic reduction.

The crystalline alkaloid appears to have the composition $C_{20}H_{37}O_3N_3$, and is thus not identical with ormosinine, although the melting points of the two compounds are similar.

Experimental

Isolation of the Alkaloids.—(*a*) Powdered seeds of *Ormosia dasycarpa* (5 kg.) were defatted with hexane and then extracted with boiling methanol until a portion no longer gave a positive

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[1] Hess and Merck, *Ber.*, 1919, **52**, 1976.
[2] Lloyd and Horning, *J. Amer. Chem. Soc.*, 1958, **80**, 1506.
[3] Lloyd and Horning, *J. Org. Chem.*, 1958, **23**, 1074.
[4] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

test with Mayer's reagent. The methanol was evaporated and the brown residue treated with water (1 l.). After filtration, the aqueous solution was made alkaline with ammonia and extracted with ether (3 + 1 l.), and the ether solution was concentrated to 500 c.c. Alkaloid I (1·9 g., 0·038%) was deposited slowly.

Evaporation of the ether solution gave a yellow gum (71·5 g., 1·43%). A solution in ethanol was acidified with hydrobromic acid; the precipitate of dasycarpine hydrobromide crystallised from ethanol in needles (54·0 g., 0·57%).

The acid solution was evaporated, an aqueous solution of the residue was made alkaline with ammonia, and the alkaloids were obtained by ether-extraction. Their solution in benzene was chromatographed on alumina.

Distillation of the benzene eluates at 50—60° (bath)/0·0001 mm. gave (—)-sparteine (4·5 g., 0·09%).

(*b*) The powdered seeds were extracted exhaustively with boiling ethanol. The total alkaloids (0·82%), obtained as described in (*a*), were shown by paper chromatography not to contain sparteine.

Further extraction of the seeds with boiling methanol gave a basic fraction (0·58%). The alkaloids in benzene were chromatographed on alumina. Distillation of the benzene eluates gave (—)-sparteine (0·09%).

(—)-*Sparteine*.—A sample, b. p. 86°/0·002 mm., was obtained as an oil, $[\alpha]_D^{22}$ —14·7° (*c* 1·0 in ethanol), n_D^{20} 1·5275 (Found: C, 78·0; H, 11·5; N, 12·2. Calc. for $C_{15}H_{26}N_2$: C, 77·9; H, 11·2; N, 12·0%), shown to be identical with an authentic sample by paper chromatography and by comparison of infrared spectra.

The picrate separated from ethanol in yellow needles, m. p. 203—205° (decomp.) (Found: C, 46·6; H, 4·5; N, 16·2. Calc. for $C_{27}H_{32}O_{14}N_8$: C, 46·8; H, 4·7; N, 16·2%), shown by a mixed-m. p. determination, and by a comparison of infrared spectra to be identical with an authentic sample, m. p. 205—206° (decomp.).

Dasycarpine.—After recovery from its hydrobromide, the *base* was obtained by distillation as an oil, $[\alpha]_D^{20}$ +12·5 (*c* 1·1 in ethanol), b. p. 160—165° (bath)/0·5 mm. (Found: C, 75·5; H, 11·0; N, 13·1; *N*-methyl, 0·0%; *M*, by mass spectrography, 314. $C_{20}H_{35}N_3$ requires C, 75·6; H, 11·1; N, 13·2%; *M*, 315).

A sample of the *hydrobromide* separated from ethanol in needles, m. p. 270—274° (Found: C, 39·3; H, 7·2; N, 6·8; Br, 38·8. Found, after being dried at 110°: C, 40·2; H, 7·1. $C_{20}H_{35}N_3,3HBr,3H_2O$ requires C, 39·1; H, 7·2; N, 6·8; Br, 39·0. $C_{20}H_{35}N_3,3HBr,2H_2O$ requires C, 40·3; H, 7·1%).

The *perchlorate*, prepared in ethanol with perchloric acid, crystallised from ethanol–ether in needles, m. p. 240° (decomp.) (Found: C, 39·5; H, 6·4; N, 7·0. $C_{20}H_{35}N_3,3HClO_4$ requires C, 39·0; H, 6·3; N, 6·8%).

Picrate. Dasycarpine (117 mg.) in ethanol was treated with excess of a solution of ethanolic picric acid. The *picrate* (342 mg., 96%), separated from ethanol–methanol as an amorphous powder, m. p. 150—152° (Found: C, 44·7; H, 4·6; N, 16·0. $C_{20}H_{35}N_3,3C_6H_3O_7N_3,1H_2O$ requires C, 44·6; H, 4·5; N, 16·4%).

Alkaloid I.—This *base* crystallised from ethanol–ether in needles, $[\alpha]_D^{20}$ +25·3 (*c* 1·0 in chloroform), m. p. 205—207° (Found: C, 65·2; H, 10·0; N, 11·1. $C_{20}H_{37}O_3N_3$ requires C, 65·4; H, 10·1; N, 11·4%).

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