295. *The Lupin Alkaloids. Part XIII. The Resolution of* dl-*Lupinine.*

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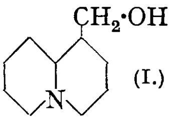
1-Octahydropyridocolylcarbinol (I) has been resolved, and the *l*-component shown to be identical with lupinine.



(I.)

The synthesis of two geometrically isomeric racemic forms of 1-octahydropyridocolylcarbinol (I) was described in Part XII (J., 1937, 965), and by repeatedly crystallising the *d*-tartrate of the form " N," of m. p. 59°, from alcohol, we have separated the *l*-form of the base, which is identical with *l*-lupinine obtained from the seeds of *Lupinus luteus*, thus establishing the formula for the alkaloid advanced by Karrer (*Helv. Chim. Acta*, 1928, **11**, 1061); the d-*base* also has been isolated with the aid of *l*-tartaric acid.

Experimental.

l-*Lupinine* d-*Tartrate*.—*l*-Lupinine (0·85 g.) and *d*-tartaric acid (0·75 g.), when mixed in alcoholic solution, deposited the tartrate (1·3 g.), which crystallised from alcohol in prisms, m. p. 170°, $[\alpha]_D$ 15·5° ± 0·5° in alcohol ($c = 1{\cdot}034\%$) (Found: C, 52·5; H, 7·6. Calc. for $C_{10}H_{19}ON,C_4H_6O_6$: C, 52·7; H, 7·8%).

l-*Lupinine* d-*Camphorsulphonate*.—The base (0·35 g.) and the acid (0·45 g.) were mixed in acetone, and the *salt* (0·22 g.) crystallised from the same solvent, forming prisms, m. p. 182°, $[\alpha]_D$ 22·5° (Found: C, 59·8; H, 8·1. $C_{10}H_{19}ON,C_{10}H_{16}O_4S$ requires C, 59·8; H, 8·7%). The l-*camphorsulphonate*, similarly prepared, had m. p. 184°, $[\alpha]_D$ − 15·3° (Found: C, 59·4; H, 8·4%).

l-*Lupinine picrolonate* crystallised from alcohol in orange plates, m. p. 191° (Found: C, 55·6; H, 6·2. $C_{10}H_{19}ON,C_{10}H_8O_5N_4$ requires C, 55·4; H, 6·2%).

Resolution of Octahydropyridocolylcarbinol (dl-*Lupinine*).—The base (3·4 g.) and *d*-tartaric acid (3 g.) were dissolved in alcohol (10 c.c.), seeded with *l*-lupinine *d*-tartrate, and left overnight in the ice-chest. The crude tartrate (3·0 g., m. p. 136—139°) was recrystallised twelve times from alcohol, the last fraction (0·15 g.) having m. p. 167° (mixed m. p. with authentic *l*-lupinine *d*-tartrate, 168—169°) and $[\alpha]_D$ 14·9° ± 0·5° (Found: C, 52·8; H, 7·9%). The base recovered from the above crystallised from light petroleum (b. p. 40—60°) in long prisms indistinguishable from *l*-lupinine, m. p. 69—70°, not depressed by the alkaloid; $[\alpha]_D$ − 20·35° (micro-determination) in alcohol ($c = 5{\cdot}639\%$). The authentic base showed $[\alpha]_D$ − 21·3°

(Found: C, 70·9; H, 11·4. Calc. for $C_{10}H_{19}ON$: C, 71·0; H, 11·2%). The picrolonate was identical with that obtained from *l*-lupinine, m. p. 192°, mixed m. p. 191° (Found: C, 55·4; H, 6·1%).

d-*Lupinine* l-*Tartrate*.—The mother-liquor from the first crop of *l*-lupinine *d*-tartrate was evaporated, the residue dissolved in water, basified, and extracted with ether, giving the crude *d*-base (1·2 g.). This was combined with *l*-tartaric acid (1 g.) in alcohol (10 c.c.), and the resulting salt (1·25 g., m. p. 140—145°) repeatedly crystallised from alcohol, the final fraction (0·2 g.) having m. p. 167—168°, $[\alpha]_D$ — 15·8° (Found: C, 52·4; H, 8·1%). d-*Lupinine* recovered from this had m. p. 68°, $[\alpha]_D$ + 19·9° (Found: C, 70·6; H, 11·2%).

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[*Received, July 28th,* 1938.]