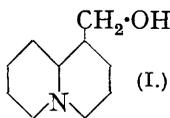


295. *The Lupin Alkaloids. Part XIII. The Resolution of dl-Lupinine.*

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

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 ($c = 1.034\%$) (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°, $[\alpha]_D - 15.3^\circ$ (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; $[\alpha]_D - 20.35^\circ$ (micro-determination) in alcohol ($c = 5.639\%$). The authentic base showed $[\alpha]_D - 21.3^\circ$

(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°, $[\alpha]_D - 15.8^\circ$ (Found : C, 52.4; H, 8.1%). *d*-Lupinine recovered from this had m. p. 68°, $[\alpha]_D + 19.9^\circ$ (Found : C, 70.6; H, 11.2%).

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