N^6-Trimethyl-L-lysine Betaine from Seeds of *Reseda luteola* L.

P. OLESEN LARSEN

Department of Organic Chemistry, The Royal Veterinary and Agricultural College, Copenhagen, Denmark

During a systematic investigation of the contents of free amino acids in species of Cruciferae and Resedaceae, seeds of *Reseda luteola* L. were examined and a number of constituents were previously isolated and identified.[1] A spot was observed on two-dimensional paper chromatograms (spot No. 6 in Fig. 1 of Ref. 1) which could not be assigned to any amino acid previously identified in Cruciferae or Resedaceae. The amino acid in question has now been isolated and identified as N^6-trimethyl-L-lysine betaine.

The fraction of neutral and basic amino acids from 750 g of seeds of *R. luteola* L. obtained as previously described [1] was applied to a strongly acid ion-exchange resin in the hydrogen form. Neutral amino acids were eluted with aqueous pyridine (1 M), and basic amino acids with ammonia (1 M). The fraction of basic amino acids containing arginine, lysine, and the unknown compound was applied to a strongly acid ion-exchange resin (Dowex 50 × 8, 1.1 × 80 cm, particle diameter 45—70 μ) in the ammonium form, and elution was performed with ammonia (0.5 M). Fractions of each 200 drops (*ca.* 10 ml) were collected. Lysine occurred in fractions 9—15, the unknown compound in fractions 20—25, and arginine in fractions 53—62. Final purification was accomplished by use of a small carbon column and a small ion-exchange column (strongly acid, elution with ammonia) as previously described.[2] Evaporation of the eluate from the last column produced the unknown amino acid as a colourless, chromatographically homogeneous, amorphous solid (12 mg).

Identification was easily achieved by NMR-spectroscopy (in D_2O, Varian A-60 instrument at the Chemical Laboratory II, University of Copenhagen). The nine methyl protons appeared as a sharp band at δ 3.1 ppm. The proton on C_2 and the two protons on C_6 exhibited signals within the same region, whereas the six protons on C_3, C_4, and C_5 appeared as a complex pattern between δ 1.4 and δ 2.2 ppm. Integration of the spectrum showed the ratio 2:1 between the two regions.

By addition of oxalic acid, and crystallization from aqueous ethanol, N^6-trimethyl-L-lysine betaine dioxalate hemihydrate was obtained ($[\alpha]_D^{24}$ + 8.9° (*c* 0.7, H_2O) (determined on a Perkin-Elmer photoelectric polarimeter 141). (Lit. value for the L-compound $[\alpha]_D^{18}$ + 10.8° (*c* 5, H_2O) (Ref. 3)). The compound was further identified upon comparison with an authentic sample [3] by use of IR-spectra and co-chromatography on paper. The free amino acid liberated from the authentic dioxalate by the use of an ion-exchange column furthermore exhibited an NMR-spectrum identical with that of the amino acid from *R. luteola* L.

That the occurrence of the amino acid is not restricted to seed material appeared from its presence also in green parts of *R. luteola* L.

The same amino acid (laminine [3]) has previously been isolated from the algae *Laminaria angustata* [3] and *Heterochordaria abietina*,[4] and a number of syntheses have been reported in the literature.[5-7]

The author is indebted to Professor T. Takemoto, University of Tohuku, Japan, for a generous sample of N^6-trimethyl-L-lysine betaine dioxalate hemihydrate.

1. Kjær, A. and Larsen, P. O. *Acta Chem. Scand.* **17** (1963) 2397.
2. Larsen, P. O. *Acta Chem. Scand.* **19** (1965) 1071.
3. Takemoto, T., Daigo, K. and Takagi, N. *Yakugaku Zasshi* **84** (1964) 1176.
4. Takemoto, T., Takagi, N. and Daigo, K. *Yakugaku Zasshi* **85** (1965) 843; *Chem. Abstr.* **64** (1966) 3964.
5. Enger, R. and Halle, H. *Z. physiol. Chem.* **191** (1930) 103.
6. Fr. Pat. 1.176.117; *Chem. Abstr.* **55** (1961) 19865.
7. Takemoto, T., Daigo, K. and Takagi, N. *Yakugaku Zasshi* **84** (1964) 1180.

Received April 22, 1968.