ACTA CHEMICA SCANDINAVICA 1 (1947) 656—658

Lunarine, an Alkaloid from *Lunaria biennis*

OLAV ROSENLUND HANSEN

The Chemical Laboratory of the University and A/S Ferrosan, Copenhagen, Denmark

From the cruciferae only one alkaloid has so far been isolated in a pure state, *viz.*, the lunarine found by Hairs[1] and Reeb[2] in seeds of *Lunaria biennis.*

Recently Steinegger and Reichstein[3] have isolated the alkaloid in fairly large quantities, and their product seems to be identical with that of Hairs. The Swiss chemists propose the empirical formula $C_{19}H_{26}N_2O_4$ for lunarine with one basic nitrogen atom.

The present author also has isolated lunarine following the directions of Hairs. The substance was purified chromatographically on aluminum oxide. Contrary to the findings of Steinegger and Reichstein (*l. c.*) the analysis, a molecular weight determination and a microhydrogenation were found to be in agreement with the formula $C_{25}H_{33}N_3O_5$. The analysis of a chloroaurate showed the presence of two basic nitrogen atoms.

Lunarine is soluble in ethanol' chloroform, pyridine, aqueous hydrochloric acid and aqueous sodium hydroxide, but insoluble in water, ether, benzene and the week bases. The solution in sodium hydroxide is yellow, perhaps due to enolization. Lunarine is precipitated by the usual alkaloid reagents (picric acid etc.) the precipitates being amorphous. *p*-Diazobenzenesulphonic acid produces a red colour when dropped into a solution of lunarine in sodium hydroxide. Lunarine gives a positive colour reaction for enols[4] but doubtful reactions for reactive metylene groups with sodium 1,2-naphthaquinone-4-sulphonate[5] and for phenols with Millon's reagent[6]. The reaction with ferri chloride as well as reactions for primary and secondary amino groups with flourescein chloride[7] and for the indole ring with the reagent of Hopkins-Cole-Winkler[8] were negative. Methoxyl-, methylenedioxy-[9] and N-methyl groups could not be found.

EXPERIMENTAL

Isolation of lunarine

900 g of finely ground seeds of *Lunaria biennis* were mixed with 1 l of gasoline and left standing for 24 h. The mixture was filtered and the seeds extracted once more in the same way. Now the well dried seeds were extracted several times with boiling ethanol and the combined ethanolic extracts evaporated in vacuum to sirupy consistence. The residue was shaken with a solution of 15 g of tartaric acid in 500 ml of water, the mixture filtered and the filtrate extracted with chloroform. The aqueous layer was made alkaline with soda and extracted twice with 500 ml of chloroform. After drying with sodium sulphate the chloroform solution was evaporated to dryness and the residue (10 g) dissolved in 40 ml of boiling ethanol. The solution was partly decolourized with a little charcoal and filtered. On cooling, 3 g of yellowish needles separated. The crude material was repeatedly recrystallized from ethanol. Micro m. p. 224°—226°.

Purification by chromatography

One g of the crude product was dissolved in 25 ml of chloroform and poured through a column of aluminum oxide, 1 cm in diameter. A yellow band, 2 cm high, was formed, and the column was eluated with a mixture of chloroform and ethanol (20 : 1) and four fractions of about 25 ml were collected. Fraction II contained the yellow band and yielded the alkaloid in a pure crystalline state by evaporation of the solvent.

$C_{25}H_{33}N_3O_5$ (455.5)	Calc. C 65.91	H 7.30	N 9.23	
	Found » 66.09	» 7.52	» 9.14	(Kjeldahl)
			9.23	(Dumas)

The molecular weight was determined osmometrically (Barger's method). Azobenzene was used as comparison substance.

Found: 460, 470 (in chloroform) 410 (in pyridine).

The hydrogen absorption was measured in the apparatus of Clauson-Kaas and Limborg[9]. Ethanol and acetic acid were used as solvents.

In ethanol: equiv. wt. found 152.5
calc. for 2 ⊢: 151.8
In acetic acid: equiv. wt. found 92.5
calc. for 5 ⊢: 91.1

Chloroaurate

A saturated solution of hydrogen auri chloride was added dropwise to a solution of 20 mg of lunarine in 2 ml of 4 *N* hydrochloric acid. The amorphous precipitate was filtered and dried in vacuum at 20°. Micro m. p. 170° (dec.).

$C_{25}H_{33}N_3O_5$, 2 $HAuCl_4$ (1135.6)	Calc. Au 34.73	Cl 24.98	
	Found » 34.55	» 24.40	

Colour reaction with diazobenzenesulphonic acid

A few mg of lunarine were dissolved in 1 ml of 4 *N* hydrochloric acid and the solution made alkaline with 5 ml of 2 *N* sodium hydroxide. Hereby a yellow solution was obtained, to which diazotized sulfanilic acid was added dropwise. A red colour immediately occurred but after a few seconds the colour became orange. Acidification with hydrochloric acid produced a yellow colour.

SUMMARY

The alkaloid lunarine from *Lunaria biennis* has been isolated and the empirical formula $C_{25}H_{33}N_3O_5$ is proposed.

The author wishes to thank the director of the Chemical Laboratory of the University of Copenhagen, Professor Dr. A. Langseth for permission to carry out this work in his laboratory, and Dr. K. A. Jensen for his encouragement during the investigation.

I am indebted to Mr. N. Clauson-Kaas and Mr. F. Limborg for their assistance in performing the microanalyses.

REFERENCES

1. Hairs, E. *Bull. acad. roy. med. Belg.* 1909. 1042.
2. Reeb, E. *Les nouvelles remèdes* **27** (1910) 481.
3. Steinegger, E., and Reichstein, T. *Pharm. Acta. Helv.* **22** (1947) 258.
4. Feigl, F. *Spot Tests* (1939) p. 277.
5. *Ibid.* p. 325.
6. *Ibid.* p. 276.
7. *Ibid.* p. 307.
8. Winkler, S. *Z. physiol. Ch.* **228** (1934) 54.
9. Rosenlund Hansen, O. To be published in this journal.
10. Clauson-Kaas, N. and Limborg, F. To be published in this journal.

Received October 4, 1947.