2. *The Alkaloids of* Ulex europaeus. *Part I.*

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Ulex europaeus, the common gorse, was first examined for alkaloids by Gerrard (*Pharm. J.*, 1886, **17**, 109, 227; 1888, **19**, 1029; 1889, **20**, 1017), who obtained from the seeds, bark, and shoots a crystalline base to which he gave the name ulexine and the formula $C_{11}H_{14}ON_2$. He stated that it differs from cytisine, but later workers (Partheil, *Ber.*, 1890, **23**, 3201; 1891, **24**, 634; van der Moer and Plugge, *Arch. Pharm.*, 1891, **229**, 48) asserted that the base from the seeds is cytisine. More recently Klein and Farkas (*Oester. Bot. Zeit.*, 1930, **79**, 107) were unable to find cytisine in the plant.

During the past two seasons we have examined the young shoots. Extracts of them in dilute hydrochloric acid were basified, and shaken with chloroform. Evaporation of this left a brown resinous mass, from an alcoholic solution of which we obtained a picrate, m. p. 242°, whereas cytisine picrate we find to decompose at 270°. The base recovered from this picrate was a lævorotatory resin, analysis of which, and of its picrate, picrolonate, platinichloride, and methiodide, suggested that it was anagyrine. Messrs. T. and H. Smith of Edinburgh kindly placed at our disposal some alkaloidal extract of the seeds of *Anagyris foetida*, and we find that the picrates of anagyrine and of the base from *Ulex europaeus* melt at 242° alone or mixed.

The presence of anagyrine in the plant is seasonal, and it only occurs in the young shoots from their budding in May till the end of July in quantity sufficient to allow of extraction. Our best yields (0·02% of the weight of shoots) were obtained in early June, decreasing to nil by the middle of August. On one occasion we isolated a few milligrams of a crystalline base, $C_{15}H_{20}O_5N_2$.

The work on this and related plants is being continued.

Experimental.

Extraction of the Alkaloid.—Freshly gathered shoots (7500 g.) were finely minced and soaked for 24 hours in hydrochloric acid (1%). After removal of plant debris in a filter-press the liquid

was mixed with 0·5% of its weight of Metasil A, passed through a Metafilter, basified (10*N*-sodium hydroxide), mixed with 1·5% of its weight of Metasil A, and again passed through the filter. The Metasil and slimy matter removed appeared to be free from the alkaloid. The clear brown filtrate was extracted five times with chloroform, on evaporation of which a brown, characteristically smelling resin was left. Addition of alcoholic picric acid to this precipitated a brown viscous mass, which soon became granular (4·2 g.) and on crystallisation from alcohol gave prisms, m. p. 242° (1·4 g.). The base recovered from this was a yellow varnish (0·6 g.), b. p. 195—200°/1 mm. (Found : C, 74·4, 73·5, 73·7; H, 8·6, 8·7, 8·7; N, 11·0, 11·8, 11·0. Calc. for $C_{15}H_{20}ON_2$: C, 73·7; H, 8·2; N, 11·5%). $[\alpha]_D^{20°}$ in chloroform — 148·5° (c = 0·75%). It gives a red colour with ferric chloride discharged by hydrogen peroxide, a brown amorphous precipitate with potassium tri-iodide, and a yellow precipitate with sulphur and hydrogen sulphide in ether.

The *picrate*, re-formed from the base, crystallises from alcohol in long prisms, m. p. 242° (Found : C, 53·6, 53·2, 53·5; H, 5·0, 5·6, 5·3; N, 14·1, 14·7, 14·7. $C_{15}H_{20}ON_2,C_6H_3O_7N_3$ requires C, 53·3; H, 4·9; N, 14·8%). The *picrolonate* forms brownish-red rosettes from alcohol, decomp. 254° (Found : C, 58·75, 58·9; H, 5·6, 5·25. $C_{15}H_{20}ON_2,C_{10}H_8O_5N_4$ requires C, 59·05; H, 5·5%). The platinichloride forms large orange-red prisms from hydrochloric acid (Found : C, 26·1, 26·6, 26·3; H, 3·8, 4·0, 3·85; N, 3·9; Pt, 28·0, 27·9, 28·4. Calc. for $C_{15}H_{20}ON_2,H_2PtCl_6,2H_2O$: C, 26·1; H, 3·8; N, 4·1; Pt, 28·3%). The methiodide, from the base and methyl iodide in warm acetone, forms square colourless plates from methyl alcohol, decomp. 264° (Found : C, 49·45; H, 5·7. Calc. for $C_{15}H_{23}ON_2I$: C, 49·7; H, 5·95%).

Anagyrine picrate, from authentic anagyrine and picric acid, forms yellow prisms indistinguishable under the microscope from the above picrate, m. p. 242° alone or mixed (Found : C, 53·2; H, 4·9%).

Cytisine picrate forms yellow prisms from alcohol, decomp. 270° (Found : C, 49·0; H, 4·2. $C_{11}H_{14}ON_2,C_6H_3O_7N_3$ requires C, 48·7; H, 4·05%).

On one occasion the solution from which the anagyrine had been extracted was acidified and evaporated to dryness in a vacuum, the residue basified (potassium carbonate) and extracted with ether, and the solvent removed; a small residue was left which solidified and then formed lustrous plates from ligroin, m. p. 170° (Found : C, 58·3; H, 6·2; N, 9·0. $C_{15}H_{20}O_5N_2$ requires C, 58·4; H, 6·5; N, 9·1%).

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