40. Delphinium *Alkaloids. Part II. Ajacine.*

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Ajacine yields as products of hydrolysis lycoctonine and acetic and anthranilic acids and hence has the formula $C_{34}H_{46}O_9N_2,2H_2O$.

Ajacine was first isolated from the seeds of *Delphinium ajacis* by Keller and Völker (*Arch. Pharm.*, 1913, **251**, 209), who assigned to it the formula $C_{15}H_{21}O_4N,H_2O$. Recently, Hunter (*Pharm. J.*, 1943, **150**, 82) proposed the formula $C_{32}H_{44}O_8N_2,2H_2O$.

As it was thought that ajacine might be closely related to lycaconitine from *Aconitum lycoctonum*, which Schulze and Bierling (*Arch. Pharm.*, 1913, **251**, 8) showed to be succinylanthranoyl-lycoctonine, and to methyllycaconitine from *D. elatum*, which Goodson (J., 1943, 139) found to be methylsuccinylanthranoyl-lycoctonine, it has been submitted to hydrolysis. Alkaline hydrolysis gives acetylanthranilic acid and lycoctonine according to the equation $C_{34}H_{46}O_9N_2 + H_2O = C_{25}H_{39}O_7N + C_9H_9O_3N$ and acid hydrolysis yields acetic acid and anthranoyl-lycoctonine: $C_{34}H_{46}O_9N_2 + H_2O = CH_3{\cdot}CO_2H + C_{32}H_{44}O_8N_2$. From this it follows that ajacine is acetylanthranoyl-lycoctonine and has the empirical formula $C_{34}H_{46}O_9N_2,2H_2O$.

Experimental.

The m. p.'s are corrected.

Ajacine crystallised from the concentrated ethereal solution of the alkaloids liberated by sodium bicarbonate from the solution of the total alkaloids of *D. ajacis* seeds in dilute hydrochloric acid. The *base*, purified by crystallisation from 70% alcohol, gave needles with two molecules of water, m. p. 154° (sintering at 150°), $[\alpha]_D^{22°} + 49{\cdot}5°$ ($c = 2$ in dry alcohol), $[\alpha]_D^{22°} + 30{\cdot}8°$ ($c = 2$ in N/5-hydrochloric acid) (Found: C, 61·5; H, 7·8; N, 4·5; OMe, 17·5; NMe, 4·0; loss at 105° in a vacuum, 5·4. $C_{34}H_{46}O_9N_2,2H_2O$ requires C, 61·6; H, 7·6; N, 4·2; 4OMe, 18·7; NMe, 4·4; $2H_2O$, 5·4%).

Alkaline Hydrolysis of Ajacine.—Ajacine (5 g.) was dissolved in alcohol (125 c.c.) and heated on the water-bath with 17 c.c. of N-sodium hydroxide until most of the alcohol had evaporated. On addition of water (125 c.c.), 2·54 g. of crude crystalline lycoctonine separated. A further 0·71 g. was extracted from the filtrate by chloroform. Crude crystalline acetylanthranilic acid (0·71 g.) separated on the addition of dilute sulphuric acid; a further 0·69 g. was obtained by extraction of the filtrate with chloroform. The lycoctonine, purified by recrystallisation from 70% alcohol, had $[\alpha]_D^{16°} + 53{\cdot}0°$, m. p. 141°, not depressed by lycoctonine obtained from the hydrolysis of methyl-lycaconitine from the seeds of *D. elatum* (Goodson, J., 1943, 141) (Found: equiv., by titration with N/10-sulphuric acid with methyl-red as indicator, 485. Calc. for $C_{25}H_{39}O_7N,H_2O$: equiv., 483).

The acetylanthranilic acid, recrystallised from boiling water, had m. p. 185°, not depressed by authentic acetylanthranilic acid (Found : C, 60·6; H, 5·2; N, 7·9; equiv., by titration with N/5-sodium hydroxide with phenolphthalein as indicator, 179·5. Calc. for $C_9H_9O_3N$: C, 60·3; H, 5·1; N, 7·8%; equiv., 179·1). Hydrolysis with dilute hydrochloric acid gave acetic and anthranilic acids.

Acid Hydrolysis of Ajacine.—Ajacine (5 g.) was dissolved in 50 c.c. of 10% hydrochloric acid and kept in a closed vessel for 14 days. On addition of excess of saturated solution of sodium carbonate, 4·7 g. of crude anthranoyl-lycoctonine were precipitated. The filtrate from the anthranoyl-lycoctonine was acidified with dilute hydrochloric acid and extracted with chloroform, which only removed a portion of the acetic acid produced. This was identified by conversion into the silver salt (Found : Ag, 64·3. Calc. : Ag, 64·6%). A further quantity of acetic acid was separated from the solution after extraction with chloroform as silver salt.

The anthranoyl-lycoctonine, purified by recrystallisation from 70% alcohol, had $[\alpha]_D^{15^\circ}$ + 31·0° (c = 2 in N/5-hydrochloric acid), m. p. 172°, not depressed by anthranoyl-lycoctonine obtained by hydrolysis of methyl-lycaconitine from *D. elatum.* Its solution had a beautiful blue-violet fluorescence. On alkaline hydrolysis it gave anthranilic acid and lycoctonine.

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