# *Dehydration of Lycorine.**

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Dehydration of lycorine yields 9 : 10-methylenedioxy-7*H*-dibenzo[*f,hi*]-pyrrocoline (V) and its 4 : 5-dihydro-derivative (IV). These compounds, which were identified by synthesis through *N*-4′ : 5′-methylenedioxy-2′-nitrobenzoylindoline, readily undergo aerial oxidation forming the 7-oxo-derivatives (VI) and (III) respectively.

Formula (I), proposed for lycorine by Kondo and Katsura (*Ber.*, 1940, **73**, 1424), represents the alkaloid by a structure which should readily undergo dehydration to a more highly aromatic form. Dehydration is certainly known to occur in course of degradative reactions but the independent process has not been described and relevant information available is both scanty and obscure (cf. survey by Cook and Loudon, " The Alkaloids," Ed. Manske and Holmes, Academic Press Inc., New York, 1952, Vol. II, p. 331). It was from this point of view that the experiments here described were initiated some years ago.

Lycorine was isolated from *Narcissus pseudonarcissus* L., essentially in the manner described by Ewins (*J.*, 1910, **97**, 2406). It was characterised as its hydrochloride, picrate, and dihydro-derivative but its specific rotation was much lower than that usually recorded although, curiously enough, the value for the derived hydrochloride agreed with that recorded (Ewins, *loc. cit.*; cf. Asahina and Sugii, *Arch. Pharm.*, 1913, **251**, 357; Gorter,

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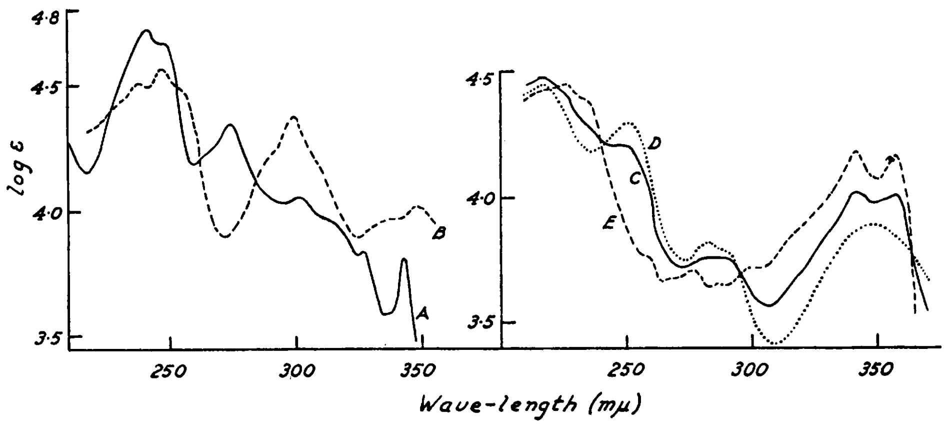
* After this paper had been written, a preliminary notice of work in the same field, and embracing (without experimental data) some of the compounds now described, was published by Taylor, Thomas, and Uyeo (*Chem. and Ind.*, 1954, 929).

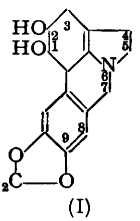
*Bull. Jard. Bot. Buitenzorg*, 1920, [iii], I, 352; II, 331; Yurashevskii, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 949; Greathouse and Rigler, *Amer. J. Bot.*, 1941, **28**, 702; Hunger and Reichstein, *Helv. Chim. Acta*, 1953, **36**, 824). Lycorine distilled unchanged in a high vacuum, a behaviour which denotes a fair degree of thermal stability. On the other hand, similar distillation from a mixture with alumina yielded dehydration products. These proved to be highly sensitive compounds, difficult to purify or characterise. The principal product was a rather feeble base for which the formula, $C_{16}H_{13}O_2N$, was preferred to $C_{16}H_{11}O_2N$ on the basis of analyses of its picrate and methiodide. Moreover, under quantitative hydrogenation conditions the base *evolved* one mol. of gas, and by simple heating with palladium in methanol it afforded a product, $C_{16}H_{11}O_2N$. This same dehydro-compound was also detected as a by-product of the dehydration experiments on lycorine. From colour tests it appeared that the new compounds might well be related as an indoline to the corresponding indole. Neither of the compounds was stable, each on fusion and also in hot solvents yielding higher-melting materials which are referred to later (see also Experimental Section).

FIG. 1. FIG. 2.

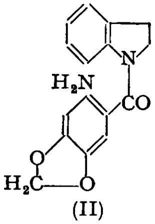


*A, Phenanthridone derivative* (III). *C, Degradative and, D, synthetic sample of* (VI).
*B, Phenanthridone derivative* (VI). *E, Compound* (V).

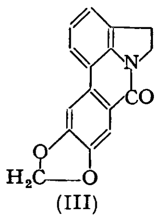
Concurrently with the degradative study synthetic work designed to yield the indoline derivative (IV) was undertaken. To this end *N*-2′-amino-4′ : 5′-methylenedioxybenzoylindoline (II) was prepared and diazotised, and the diazonium solution was heated in order to form the phenanthridone (III). It has recently been shown that this type of reaction, when applied to 2-amino-*N*-methylbenzanilides which contain an *o*-substituent, may lead to abnormal results (Hey and Turpin, *Chem. and Ind.*, 1954, 216, 219). In the present case a gum was formed and afforded a crystalline constituent, $C_{16}H_{11}O_3N$, which was immediately suspect because of its relatively low melting point. It was not identical with 4′ : 5′-methylenedioxybenzoylindoline ($C_{16}H_{13}O_3N$) and is regarded as 4′ : 5′-methylenedioxybenzoylindole since on attempted reduction with lithium aluminium hydride it gave much indole. On the other hand, when the diazonium solution from (II) was



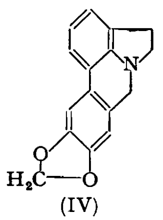
(I)



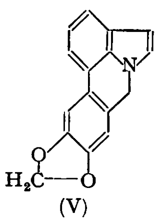
(II)



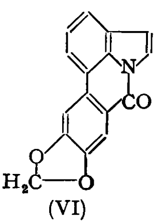
(III)



(IV)



(V)



(VI)

decomposed in a neutral environment or, better, in presence of precipitated copper, there was formed—albeit in poor yield—another product, $C_{16}H_{11}O_3N$, which appears to be the phenanthridone (III). The ultra-violet absorption spectrum of this product is given in Fig. 1 and is comparable with that of *N*-methylphenanthridone (Karrer, Szabo, Krishna, and Schwyzer, *Helv. Chim. Acta*, 1950, **33**, 295). Reduction of (III) with lithium aluminium hydride gave the dihydrophenanthridine (≡ indoline) derivative (IV) and this compound was essentially identical with the dehydration product of lycorine.

Because of the instability of (IV) it was not easy to establish the absolute identity of the two samples as obtained by degradation and synthesis respectively. Their melting behaviour was similar and their ultra-violet absorption spectra are given in Fig. 2. The absorption curve for the synthetic sample generally resembles that of authentic dihydro-*N*-methylphenanthridine (Karrer *et al.*, *loc. cit.*), and the curve for the degradative material may be brought into conformity on the plausible assumption that this particular sample is contaminated with the indolic compound, $C_{16}H_{11}O_2N$, already recognised as a by-product of degradation. The ultra-violet absorption spectrum of the latter compound is also shown in Fig. 2 The infra-red spectra of the samples (IV) were kindly measured by Dr. L. A. Duncanson who reported that although the spectra (of the solids in Nujol) were not identical, the similarity between them was such as could hardly be fortuitous. Methiodides prepared from the two samples had virtually identical ultra-violet absorption spectra. Moreover, on dehydrogenation the samples afforded the same dehydro-compound, now formulated as (V), of which the respective specimens were identical in m. p., in ultra-violet (Fig. 2) and in infra-red spectra.

The two degradation products, thus identified by synthesis as (IV) and (V), are clearly accountable in terms of Kondo and Katsura's formula for lycorine but they neither establish this formula nor rule out more recently proposed alternatives (Robinson *et al.*, *Chem. and Ind.*, 1953, 946, 1317: Govindachari and Thyagarajan, *ibid.*, 1954, 374; Kelly, Taylor, and Wiesner, *J.*, 1953, 2094). Their further transformations as observed during the present investigation relate to their instability when heated in solvents or in air. Thus their melting behaviour was frequently complicated by the formation of cloudy melts in which higher-melting material developed fairly rapidly. This was eventually traced to oxidation whereby the phenanthridone (III) was produced from (IV) and its dehydro-analogue (VI) was formed from (V). The ultra-violet absorption spectra of these phenanthridone derivatives are shown in Fig. 1.

## EXPERIMENTAL

*Extraction of Lycorine.*—Washed bulbs (35 kg.) of *Narcissus pseudonarcissus* L. were sliced, dried at room temperature, and disintegrated to a coarse powder (10 kg.) which was extracted with ethanol under reflux (24 hr.). The cold, filtered extract deposited (12 hr.) a colourless solid which was removed before the solution was concentrated. The clarified concentrates (750 c.c.) were treated with water (750 c.c.) and, after 12 hr. at 0°, filtered from a sludge which was washed with 40% ethanol and then with a little cold 5N-hydrochloric acid. The combined filtrate and washings were concentrated (to 750 c.c.) under reduced pressure, cooled, clarified, and extracted with ether (6 × 250 c.c.). The ethereal solution was washed with 20% hydrochloric acid (2 × 100 c.c.), and the combined aqueous phases were treated with an excess of a saturated solution of sodium carbonate. After 12 hr. at 0° the partly crystalline solid was collected, washed with sodium carbonate (which removed some amorphous acidic material), and repeatedly extracted with hot dilute hydrochloric acid (wherein a dark, resinous acid remained undissolved). Crude lycorine, liberated from the acid solution by aqueous sodium carbonate, was partly purified by renewed dissolution in hot acid (charcoal), recovery, and washing with small quantities of cold methanol (which removed some yellow solid). It (20 g.) was now converted into the hydrochloride, which was repeatedly crystallised from N-hydrochloric acid and (twice) from 90% ethanol, affording colourless needles, m. p. 212—214° (decomp.), $[\alpha]_D^{24}$ +44·9° (*c*, 2·94 in $H_2O$). The recovered lycorine formed colourless prisms, m. p. *ca.* 270° (decomp.) (from ethanol), $[\alpha]_D^{21}$ −72·7° [*c*, 0·612 in pyridine–ethanol (1 : 1 v/v)], $[\alpha]_D^{20}$ −83·8° (*c*, 0·1432 in 98% ethanol) (Found: C, 66·45; H, 6·0; N, 5·0. Calc. for $C_{16}H_{17}O_4N$: C, 66·9; H, 6·0; N, 4·9%). It was distilled at 175—185°/2 × $10^{-3}$ mm. without change in

m. p. or $[\alpha]_D$, and afforded the picrate as yellow leaflets, m. p. 196—197° (decomp.; heated at rate of 2°/min.) (Found: C, 51·4; H, 4·1. Calc. for $C_{16}H_{17}O_4N,C_6H_3O_7N_3$: C, 51·2; H, 3·9%).

*Dehydration of Lycorine.*—In a series of experiments lycorine (0·5 g.) was intimately mixed with powdered alumina (1·7—2 g.) and, after careful evacuation to remove air-pockets, the mixture was heated in a sublimation tube at 175—185°/4 × $10^{-5}$ mm., for periods ranging from 8 to 24 hr. In general there was formed a solid sublimate accompanied by varying quantities of gum. The latter could be removed by preferential dissolution in warm ethanol but in most cases the total sublimate was dissolved in a mixture of peroxide-free ether (20 c.c.) and 0·1N-sulphuric acid, and the water-washed, dried, ethereal layer (which had a blue fluorescence) was evaporated to afford a crystalline solid. The acid layer usually contained unchanged lycorine (isolated as the hydrochloride) together with amorphous basic material which was not investigated.

The main crystalline product was unstable and deteriorated in air, in hot solvents, or during attempted chromatography (even under nitrogen) in light petroleum (b. p. 60—80°) on alumina. It was best purified by rapid crystallisation from ethanol and thereby formed colourless or pale brown leaflets, considered to be *4 : 5-dihydro-9 : 10-methylenedioxy-*7H*-dibenzo*[f,hi]*pyrrocoline* (IV), which melted variously within the range 112—123° (corr.) (Found, in sample of m. p. 122—123°: C, 76·65; H, 4·95. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2; N, 5·6%. Other samples of m. p. 119—120° had C, 77·3, 77·45, 77·4; H, 4·9, 5·2, 5·5; N, —, —, 5·55. Calc. for $C_{16}H_{11}O_2N$: C, 77·1; H, 4·4; N, 5·6%). Light-absorption max. in EtOH: 217, 249, 281—289, 342, 352, 357 mμ; log ε 4·48, 4·21, 3·76, 4·02, 3·99, 4·00. With picric acid in cold methanol it afforded the *picrate* as brownish-red needles, m. p. *ca.* 250° (decomp.; bath preheated to 230°) (Found: C, 55·2; H, 3·2; N, 11·6. $C_{16}H_{13}O_2N,C_6H_3O_7N_3$ requires C, 55·0; H, 3·3; N, 11·7%), and with methyl iodide (18 hr. at room temperature) it gave the *methiodide* as flattened needles (from ethanol), m. p. 216—217° (decomp. and cloudy melt in a capillary tube; single crystals when unenclosed became opaque at *ca.* 230° but were unmelted even up to 253°) (Found: C, 51·9; H, 4·4. $C_{17}H_{16}O_2NI$ requires C, 51·9; H, 4·1%). Light-absorption max. of the methiodide in EtOH: 300, 318 mμ; log ε 4·03, 4·10: inflexion at 236—245 mμ; log ε 4·25.

*Dehydrogenation of* (IV) *to* (V).—A solution of the dehydration product (IV) (20 mg.) in methanol (2 c.c.) was heated under reflux (3 hr.) with palladium black (20 mg.). The hot filtered solution deposited *9 : 10-methylenedioxy-*7H*-dibenzo*[f,hi]*pyrrocoline* (V) as colourless needles (10 mg.), m. p. 159—161° (corr.) (from methanol) (Found: C, 77·2; H, 4·5. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·4%). Light-absorption max. in ethanol: 226, 258, 277, 286, 342, 358 mμ; log ε 4·47, 3·79, 3·73, 3·67, 4·18, 4·17: inflexions at 232, 269, and 300—305 mμ; log ε 4·41, 3·70, and 3·73. The compound gave a well-marked Ehrlich reaction and afforded a picrate as reddish-brown needles, m. p. 143—145° (decomp.). The same compound (V) had earlier been encountered (*a*) on a single occasion as by-product in the dehydration of lycorine and (*b*) as contaminant of the methiodide prepared from a much-crystallised sample of (IV).

*4′ : 5′-Methylenedioxy-2′-nitrobenzoylindoline.*—Indoline, b. p. 226—230°, characterised as the picrate of m. p. 177—178° (from ethanol) (Found: C, 48·4; H, 3·6; N, 16·1. Calc. for $C_8H_9N,C_6H_3O_7N_3$: C, 48·3; H, 3·45; N, 16·1%), was prepared from 2-*o*-aminophenylethanol and benzenesulphonyl chloride in presence of sodium hydroxide as described by Bennett and Hafez (*J.*, 1941, 287), the yield being increased through hydrolysis of the incidentally formed benzenesulphonylindoline by heating the latter under reflux with 70% sulphuric acid. Indoline (7·2 g.) in ether (25 c.c.) was added with cooling to an ethereal solution (25 c.c.) of 4 : 5-methylenedioxy-2-nitrobenzoyl chloride, prepared from the acid (12·6 g.) (Bedi and Narang, *J. Indian Chem. Soc.*, 1936, **13**, 253) and thionyl chloride. Powdered potassium carbonate (12·5 g.) was then added, and the whole shaken for 15 hr. at room temperature, heated under reflux for 2 hr., and freed from ether. The residue, washed with water, N-hydrochloric acid, and again with water, afforded *4′ : 5′-methylenedioxy-2′-nitrobenzoylindoline* as greenish-yellow prisms (10·5 g.), m. p. 219—220° (corr.), from ethanol (charcoal) (Found: C, 61·5; H, 4·2; N, 8·8. $C_{16}H_{12}O_5N_2$ requires C, 61·5; H, 3·85; N, 9·0%).

*2′-Amino-4′ : 5′-methylenedioxybenzoylindoline* (II), m. p. 143—144° (from methanol), was obtained when a solution (formed by heating and rapid cooling) of the foregoing nitro-compound (4·5 g.) in ethyl acetate (350 c.c.) was hydrogenated (6 hr.) over palladised strontium carbonate (5 g. of 1·5%) (Found: 68·1; H, 4·8; N, 10·1. $C_{16}H_{14}O_3N_2$ requires C, 68·1; H, 5·0; N, 9·9%). It afforded the *picrate* as golden-yellow needles, m. p. *ca.* 218° (decomp.) (from methanol) (Found: C, 51·7; H, 3·7. $C_{16}H_{14}O_3N_2,C_6H_3O_7N_3$ requires C, 51·7; H, 3·3%), and the *hydrochloride* as slender needles, m. p. *ca.* 245° (decomp.), from dilute hydrochloric acid (Found: C, 60·2; H, 4·35; N, 8·8. $C_{16}H_{14}O_3N_2$,HCl requires C, 60·4; H, 4·7; N, 8·8%).

*Pschorr-type Cyclisation of* (II).—(*a*) The amine (II) (0·5 g.) dissolved in 0·5N-sulphuric acid (30 c.c.) was treated at 0° with sodium nitrite (0·17 g.) in water (1 c.c.) and the mixture, in which orange-coloured crystals had separated, was slowly heated to 100°. The solid dissolved, gas was evolved, and a tar separated. After 10 min. the whole was cooled and extracted in ether containing a little benzene from which a yellow gum was recovered and was chromatographed on alumina in the same solvent, affording colourless leaflets, m. p. 90—92°, from methanol (charcoal) (Found: C, 72·3; H, 4·25; N, 5·4. $C_{16}H_{11}O_3N$ requires C, 72·45; H, 4·15; N, 5·3%). This compound is regarded as 4′ : *5′-methylenedioxybenzoylindole* since (i) it was not identical with 4′ : *5′-methylenedioxybenzoylindoline*, m. p. 120—122° (from ethanol) which was prepared from the corresponding acid chloride in reaction with indoline (Found: C, 72·15; H, 5·3; N, 5·1. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9; N, 5·2%), and (ii) it yielded indole, recovered as a low-melting solid (picrate, m. p. 178—179° raised to 180—181° by admixture with indole picrate) from the water-washed reaction solution after reduction (9 hr.) with lithium aluminium hydride in anhydrous ether.

(*b*) The suspension, obtained by diazotising the amine (II) (1 g.) in 2N-sulphuric acid (25 c.c.) with aqueous sodium nitrite (0·26 g. in 1·6 c.c.) at 0°, was diluted with water (25 c.c.), neutralised (methyl-red) with sodium carbonate, and heated to 100° during 1 hr. The solid obtained from the cooled mixture was heated with charcoal in methanol, recovered as a brown powder (0·62 g.), and separated by rubbing with cold benzene (3 c.c.) into a soluble fraction (0·4 g. of m. p. 90°, from methanol) and a residue (0·07 g. of m. p. 228—232°). The combined residues from several preparations afforded 4 : *5-dihydro-*9 : *10-methylenedioxy-*7*-oxo-*7H*-dibenzo-*[f,hi]*pyrrocoline* (III) as colourless needles, m. p. 246—247°, from ethanol (charcoal) (Found: C, 72·8; H, 4·4; N, 5·4. $C_{16}H_{11}O_3N$ requires C, 72·4; H, 4·2; N, 5·3%). Light-absorption max. in EtOH: 242, 249, 275, 303, 327, 343 mμ; log ε 4·66, 4·62, 4·32, 4·03, 3·84, 3·86.

(*c*) To the faintly turbid diazonium solution, prepared from (II) (0·5 g.) in 2N-sulphuric acid (25 c.c.) by treatment at 0° with sodium nitrite (0·135 g.) in water (1·35 c.c.), was added freshly precipitated copper powder (0·25 g.), and the whole was shaken for 15 hr. at room temperature. After a further 10 hr. the mixture was slowly heated to 70—85° whereupon a pale-brown solid gradually separated (10 min.); this was dissolved in benzene which was added to the hot suspension. The benzene extract was washed with dilute aqueous sodium hydroxide, dried, and concentrated (to 2 c.c.), affording the phenanthridone (III) (0·066 g.) which was purified from ethanol (charcoal). The benzene mother-liquor contained the lower-melting product.

4 : *5-Dihydro-*9 : *10-methylenedioxy-*7H*-dibenzo*[f,hi]*pyrrocoline* (IV).—A suspension of the phenanthridone (III) (0·455 g.) and lithium aluminium hydride (0·7 g.) in dry ether (100 c.c.) was heated under reflux for 24 hr. before being cooled and treated with fragments of ice. The ethereal solution (which had a blue fluorescence), combined with ethereal washings of the aluminium hydroxide, was dried and evaporated, affording a yellowish mass (0·414 g.) of stout needles which softened at 80° and had (micro-)m. p. 108—111° (forming a melt in which some crystals survived and became centres for the subsequent growth of tiny needles; the latter began to sublime at *ca.* 200° and melted at 210°). Crystallisation from methanol afforded colourless leaflets (0·371 g.) which softened at 100°, (micro-)melted at 110—115°, re-solidifying and re-melting at 225—230°. Moreover, except that the values were slightly higher, this melting behaviour was reproduced when simultaneously examined with a mixture of this compound and a sample of (IV) obtained by dehydration of lycorine. Attempts to purify the material further failed because of the tendency of the compound to deteriorate. Light-absorption max. in EtOH: 217, 251, 282, 349 mμ; log ε 4·45, 4·29, 3·82, 3·89. The compound formed a methiodide as straw-coloured needles which, when crushed, gave a cloudy melt at 216—218° (decomp.) (corr.), undepressed by admixture with the methiodide of the degradation product (IV) (Found: C, 52·05; H, 4·2; N, 3·9%). Light-absorption max. of the synthesised methiodide in EtOH: 301, 318 mμ; log ε 4·03, 4·1: inflexion, 238—244 mμ; log ε 4·26.

Dehydrogenation of synthetic (IV) was conducted as described for the specimen of (IV) obtained by degradation and afforded the indole derivative (V) as colourless needles, m. p. (after softening at 153°) 160—163° (corr.), and mixed m. p. with the specimen from degradation, 159—161° (Found: C, 77·3; H, 4·4; N, 5·6%). Light-absorption max. in EtOH: 226, 258, 276, 287, 300, 341, 358 mμ; log ε 4·45, 3·77, 3·71, 3·65, 3·72, 4·18, 4·16: inflexions 233, 269—270 mμ; log ε 4·395, 3·68. The compound gave a positive Ehrlich reaction even in the cold. On continued heating above the m. p. the melt (and mixed melt) developed into a mass of tiny needles which remelted at *ca.* 210—218°. The picrate, prepared from the components in hot methanol, formed dark-red needles, m. p. (and mixed m. p. with the degradation specimen) 144—145° (decomp.) (corr.).

*Aerial Oxidation of* (IV) *and* (V).—(*a*) Small quantities (10—60 mg.) of (IV), obtained from lycorine, were heated as thin films, first at 140° and then gradually (30 min.) to 200°, whereupon a vacuum (0·1 mm.) was applied and caused sublimation of a yellowish solid. Combined sublimates were re-sublimed and fractionally crystallised from methanol, affording first the phenanthridone (III) which was identified by m. p. and by its ultra-violet and infra-red absorption spectra (Found: C, 72·05; H, 4·6; N, 5·3%). The concentrated mother-liquor gave a second crystalline material which, from its m. p. (140—145°) and positive Ehrlich reaction, is regarded as the indole (V).

(*b*) Compound (V) (14 mg.), slowly heated in a sublimation tube to 200—230°, gave a partly crystalline sublimate which afforded 9 : 10-*methylenedioxy*-7-*oxo*-7H-*dibenzo*[f,hi]*pyrrocoline* (VI) as almost colourless needles, (micro-)m. p. 216—218° (from methanol) depressed by admixture with (III). Light-absorption max. in EtOH: 238, 248, 300, 348 m$\mu$; log $\varepsilon$ 4·51, 4·57, 4·36, 4·01 : inflexions at 232, 245, 292, 339 m$\mu$; log $\varepsilon$ 3·94, 4·49, 4·22, 3·96. The infra-red absorption of the solid in Nujol showed a carbonyl band at *ca.* 1670 cm.$^{-1}$ (Found in a second specimen of slightly lower m. p. : C, 72·6; H, 4·0. $C_{16}H_9O_3N$ requires C, 73·0; H, 3·4%). When mixed with picric acid in methanol the compound afforded a yellow crystalline substance of rather indefinite (micro-)m. p. appearing to " dissociate " at 115—120° and finally melt at 155—157°; there was insufficient for further examination.

(*c*) Mixtures of the phenanthridones (III) and (VI) were also encountered when the crude dehydration product of lycorine was subjected to much heating in solvents (light petroleum or ethanol) in presence of air. The high-melting product in such cases gave an ultra-violet absorption curve which was a composite of those shown in Fig. 1.

*Miscellaneous Experiments.*—Attempted quantitative hydrogenation of the dehydration product of lycorine gave varying results. When treated in acetic acid solution under hydrogen and with palladium as catalyst, different samples of the compound *evolved* 0·9 and 0·6 mol. of gas, while with a third sample evolution appeared to be followed by absorption of gas. In one case (0·9 mol. evolved) evaporation of the filtered solution *in vacuo* and washing of the residue with hot benzene afforded a water-soluble substance—apparently the acetate of a base—which with picric acid in ethanol gave a *picrate* as orange-yellow prisms, m. p. 267° (from methanol) (Found: C, 55·1; H, 3·3%); but in other experiments, although the m. p., 267—268°, was constant, analyses varied (Found, after intensive drying: C, 56·0, 55·7; H, 3·9, 3·0%). Attempts to isolate the free base failed since it rapidly changed in non-acidic media, and the only product identified (by m. p., and ultra-violet and infra-red spectra) was the phenanthridone (III).

Dihydrolycorine, m. p. 244° (decomp.), prepared from lycorine by hydrogenation in acetic acid with palladium as catalyst and purified *via* the nitrate, m. p. 247—248° (decomp.), sublimed unchanged at 160—165°/5 × $10^{-4}$ mm. For dehydration it was mixed with alumina and under sublimation conditions slowly heated (4·5 hr.) to 210°/5 × $10^{-4}$ mm. and then (18 hr.) at 200—215°/5 × $10^{-4}$ mm. At this stage the sublimate obtained was dissolved in 0·1N-sulphuric acid, and the solution was extracted with ether from which, when washed and dried, a gum was recovered. With picric acid in ethanol the gum formed a brick-red, crystalline picrate, m. p. *ca.* 247°. A later sublimate, obtained after further heating (8 hr.) at 250°/4 × $10^{-5}$ mm., was similarly treated, affording (from the ether-soluble fraction) a *picrate* as yellow-orange needles, m. p. 262—265° (from ethanol) (Found: C, 54·6; H, 3·7%). A mixture of the two picrate fractions had m. p. 249° and admixture of the higher-melting picrate with the picrate (m. p. 267°) mentioned in the preceding paragraph gave m. p. 265°.

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