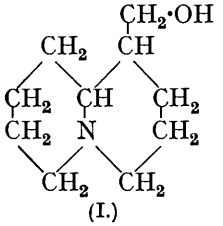
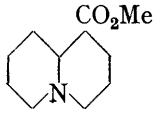
199. *The Lupin Alkaloids. Part XII. The Synthesis of* dl-*Lupinine and* dl-iso*Lupinine.*

By G. R. Clemo, W. McG. Morgan, and R. Raper.

Karrer and his co-workers (*Helv. Chim. Acta*, 1928, **11**, 1062), on the basis of degradation evidence, advanced formula (I) for lupinine, and we have been engaged for some time on its synthesis. In Part V (J., 1931, 3190) we described work leading to the production of (II), and from this, by the Bouveault reaction, we obtained a substance from which, although it should have structure (I), we could not obtain *l*-lupinine. The substance (II), however, was obtained from methyl 1-keto-octahydropyridocoline-9-carboxylate by the Clemmensen reduction; but we have since shown (Part XI; J., 1936, 1429) that, whereas the Clemmensen reduction of 1-keto-octahydropyridocoline gives the B form of octahydropyridocoline, differing from the A form obtained from lupinine, the Wolff reduction gives the latter,


(I.)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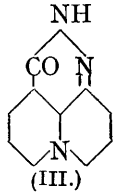
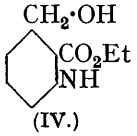
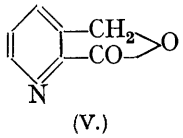

(III.)

and hence it appeared to be desirable to carry out the latter reduction on the 9-keto-ester in order to see if *dl*-lupinine could be obtained from the product. The reduction of quinolinic acid to the hexahydro-compound and the separation of this into its *cis*- and *trans*-forms through the nitrosoamines (Besthorn, *Ber.*, 1895, **28**, 3151) are tedious, and so the mixed stereoisomers were condensed with γ-bromobutyronitrile, and the product ring-closed, after hydrolysis and esterification, to methyl 1-keto-octahydropyridocoline-9-carboxylate (Part V; J., 1931, 3197). This compound on treatment with hydrazine hydrate gave the *pyridazine* derivative (III), but only in poor yield, and it was clear that this method could not be used in a satisfactory lupinine synthesis.


(IV.)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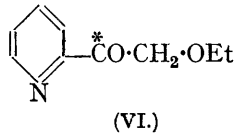

(VI.)

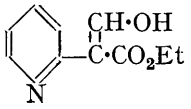
Attention was then turned to the preparation of 2-carbethoxy-3-piperidylcarbinol (IV), from which it was hoped to prepare *dl*-lupinine by the methods used in previous papers of this series for the production of the octahydropyridocoline ring system. We were, however, unable to reduce quinolinimide (Sucharda, *Ber.*, 1925, **58**, 1727) to quinolinide (V) by the methods which work well for phthalimide, and the method of Zincke (*Annalen*, 1896, **290**, 332) for the production of the unreduced form of (IV) is so long as to be unsatisfactory for our present purposes. Quinolinimide was also recovered unchanged from catalytic hydrogenation under the Adams–Shriner conditions.

We then attempted to prepare 2-ω-ethoxyacetylpyridine (VI), into which we hoped to introduce a trimethylene chain at the carbon atom * by means of the Grignard reaction, but the Claisen condensation of ethyl picolinate with ethyl ethoxyacetate gave only a very small trace of condensation product. The *p*-toluenesulphonyl ester of the oxime of 2-acetylpyridine was treated with potassium ethoxide (compare Neber and Huh, *Annalen*, 1935, **515**, 292), and the crude hydrochloride of ω-aminoacetylpyridine so obtained converted by nitrous acid into the diazo-compound, but this, on boiling with methyl alcohol, gave only a red oil, analysis of whose derivatives suggested that it was impure ω-aminoacetylpyridine.

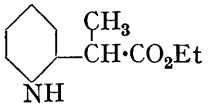
2-Acetylpyridine can be brominated to give the ω-*bromo*-derivative, but attempts to

replace the bromine by the methoxyl or phenoxyl group gave red tars from which nothing definite could be isolated, and no reaction occurred with potassium phthalimide.

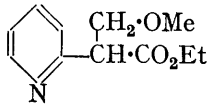
Meanwhile we made many attempts starting from ethyl 2-pyridylacetate. This condenses with ethyl formate to give the *hydroxymethylene* derivative (VII) in good yield. This crystalline compound is somewhat unstable, and, with picric and picrolonic acids, gives the salts of ethyl pyridylacetate. Unsuccessful attempts were made to methylate the hydroxyl group by means of methyl iodide and sulphate and diazomethane, and by successive treatments with phosphorus pentachloride and sodium methoxide, and it could not be benzoylated. Attempts to obtain quaternary salts with ethyl β-chloro-, -bromo-,



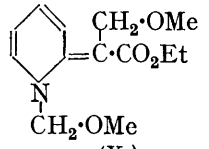
(VII.)



(VIII.)



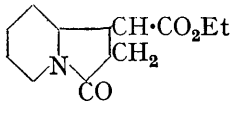
(IX.)



(X.)

and -iodo-propionates gave either (in the cold) no action, or, on warming, only 1-carbethoxy-4-keto-3-(2′-pyridyl)pyridocoline (Part X; J., 1936, 1026). Reduction of (VII) with sodium or aluminium amalgam was unsatisfactory, catalytic reduction with hydrogen and palladised charcoal did not affect the substance, and aluminium *iso*propoxide gave only the corresponding iso*propyl* ester. Catalytic reduction under the Adams–Shriner conditions gave an oil, which, treated with ethyl β-chloro- or -bromo-propionate, gave a condensation product from which two *picrolonates*, m. p.'s 136° and 115°, were obtained. If the picrolonate of the reduction product is very carefully fractionated from methyl alcohol, it is possible to obtain from it the picrolonate of ethyl pyridylacetate, a small amount of a *picrolonate*, m. p. 124°, not further investigated, and two *picrolonates* (C and D) of m. p.'s 209° and 185°. Analyses of these and the bases recovered from them showed that the latter were the two stereoisomeric forms of ethyl piperidyl-2-α-propionate (VIII), the catalytic reduction having converted the hydroxymethylene group into methyl. Condensation of the base from C with ethyl β-chloropropionate yielded an oil which gave the picrolonate, m. p. 115°, and similarly we obtained the picrolonate, m. p. 136°, from D. The Dieckmann reaction, carried out with either the mixed or the separated *ethyl piperidyl*-1-β-*propionate*-2-α-*propionates*, gave the same 2-keto-1-methyloctahydropyridocoline, but, as this could not be reduced by the Clemmensen method, and it could not lead to *dl*-lupinine, no further work on its reduction was carried out.

We then condensed ethyl 2-pyridylacetate with chloromethyl ether, but analysis of the product indicated it was a mixture of (IX) and (X). The condensation of ethyl pyridylacetate with ethyl chloroacetate yields *ethyl* 2-*pyridylsuccinate*, which is easily reduced to the piperidyl ester; this, however, cannot be purified, as, on distillation, it cyclises to *ethyl* 3-*keto-octahydropyrrocoline*-1-*carboxylate* (XI). Attempts to condense ethyl 2-piperidylsuccinate with ethyl β-bromopropionate, with the idea of ring-closing the condensation product by the Dieckmann reaction to ethyl 2-keto-octahydropyridocoline-1-acetate and thence obtaining structure (I) by a Curtius degradation, also failed, as no condensation on the imino-group could be effected.



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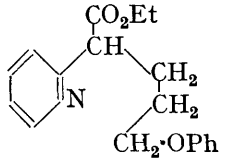
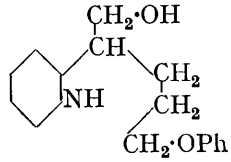


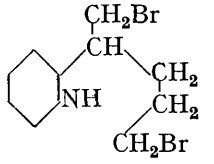
(XII.)

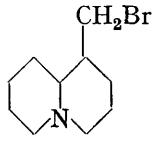


(XIII.)

Success in the synthesis of structure (I) was finally achieved by condensing ethyl pyridyl-2-acetate with γ-phenoxy-*n*-propyl bromide, yielding (XII), catalytic reduction, followed by Bouveault reduction, of which gave the *carbinol* (XIII). When this was treated with fuming hydrobromic acid, a mixture was obtained consisting mainly of (XIV).

In the course of working up this mixture the dibromo-compound cyclised, yielding the bromo-base (XV) together with a little unbrominated product. The whole was therefore

(XIV.) 

 (XV.)

treated with phosphorus pentabromide; the resulting *bromo-base* (XV) gave two *picrolonates* (J), m. p. 202°, and (K), m. p. 169°, by means of which it was separated into its two racemic forms. In Part VI (J., 1932, 2959) we showed that ring-closures of the type (XIV) ⟶ (XV) lead exclusively to the A form of octahydropyridocoline, and thus the occurrence of only two racemates is accounted for satisfactorily. The two forms, L and M, of *dl*-bromolupinane (XV) recovered from J and K respectively were hydrolysed by refluxing with sodium acetate solution, giving the two racemic forms of 1-*octahydropyridocolylcarbinol* (I), N and O. One of these should be *dl*-lupinine and the other *dl-iso*lupinine (Winterfeld and Holschneider, *Ber.*, 1931, **64**, 137; Schöpf, Schmidt, and Braun, *ibid.*, p. 683, name this base *epi*lupinine), but the amounts available so far have been too small for resolution, and work is in hand to prepare sufficient quantities of the two racemic bases to allow this to be effected.

Experimental.

3-*Ketodecahydro*peri*pyridazopyridocoline* (III).—Methyl 1-keto-octahydropyridocoline-9-carboxylate (0·2 g.) and hydrazine hydrate (0·3 g.) were mixed; heat was developed, and the *pyridazine* (III) (0·1 g.), m. p. 125—135°, deposited. Recrystallised from water, this had m. p. 137° (Found: C, 57·2; H, 8·0. $C_{10}H_{15}ON_3,H_2O$ requires C, 56·9; H, 8·0%).

2-ω-*Bromoacetylpyridine*.—2-Acetylpyridine (2 g.) in benzene (20 c.c.) and glacial acetic acid (5 c.c.) was gradually treated with bromine (2·65 g.) in benzene (12·6 c.c.). The colourless precipitate (3·65 g., decomp. 226°) was collected and treated with an excess of saturated potassium carbonate solution, and the liberated oil taken up in ether, dried, and distilled, giving acetylpyridine (0·15 g.), b. p. 37—40°/1 mm., identified as the picrate, m. p. 136° (given as 131° in Beilstein's " Organische Chemie "), and ω-*bromoacetylpyridine* (0·9 g.), b. p. 88°/1 mm. (Found: C, 42·5; H, 3·3. C_7H_6ONBr requires C, 42·0; H, 3·0%). The base (0·6 g.) was heated for 2 hours with potassium permanganate (1 g.) in water (15 c.c.) and concentrated sulphuric acid (5 c.c.), and the whole basified (sodium carbonate) and evaporated to dryness. The residue was mixed with soda-lime and distilled, the distillate dissolved in concentrated hydrochloric acid and evaporated to dryness, and the residue basified; the pyridine obtained was identified as the picrate, m. p. and mixed m. p. 163°.

Ethyl Hydroxymethylene-2-pyridylacetate (VII).—Potassium (2 g.) was dissolved in dry ether (50 c.c.) and alcohol (7·2 c.c.), and ethyl 2-pyridylacetate (8 g.) and ethyl formate (4 g.) added with ice-cooling. After 18 hours water was added, the ethereal layer separated, and the aqueous layer acidified to Congo-red, basified (potassium carbonate), and ether-extracted. The ether was removed, and the residue recrystallised from light petroleum, giving a felt of pale yellow needles (6 g.), m. p. 97° (Found: C, 62·0; H, 5·5. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7%). The substance gives an intense red coloration with ferric chloride. The *hydroxymethylene* compound (1·9 g.), aluminium *iso*propoxide (0·15 g.), and *iso*propyl alcohol (2 c.c.) were slowly distilled through a column. No acetone distilled (negative reactions with sodium nitroprusside and *p*-nitrophenylhydrazine). The residue was concentrated, taken up in dilute hydrochloric acid, basified (potassium carbonate), and ether-extracted. On removal of the ether and recrystallisation of the residue from light petroleum, unchanged material (0·8 g., m. p. 96° alone or mixed) was obtained. The concentrated mother-liquor deposited an oil, which solidified after distillation. Recrystallised from light petroleum, it melted at 78° alone or mixed with authentic iso*propyl hydroxymethylene-2-pyridylacetate* prepared in the same way as the ethyl ester (Found: C, 63·4; H, 6·6. . $C_{11}H_{13}O_3N$ requires C, 63·7; H, 6·3%).

*iso*Propyl 2-pyridylacetate gives a *picrolonate*, m. p. 187° (Found: C, 54·5; H, 5·1. $C_{10}H_{13}O_2N,C_{10}H_8O_5N_4$ requires C, 54·2; H, 4·75%).

Ethyl 2-*Piperidyl-α-propionate*.—Ethyl hydroxymethylene-2-pyridylacetate (8·5 g.) in

glacial acetic acid (60 c.c.) was shaken with platinum oxide (0·5 g.) in hydrogen at 100 lb./sq. in. for 40 hours; the product, worked up in the usual way, yielded an oil (5 g.), b. p. 80°/1 mm. Its picrolonate, prepared in ethyl alcohol and recrystallised from methyl alcohol, aided by hand-picking, gave (a) ethyl pyridylacetate picrolonate, m. p. 157° alone or mixed with an authentic specimen, (b) a small amount of a *picrolonate*, m. p. 124°, probably of ethyl pyridyl-α-propionate (Found: C, 54·2; H, 4·8. $C_{10}H_{13}O_2N$,$C_{10}H_8O_5N_4$ requires C, 54·2; H, 4·8%), (c) *picrolonate C*, m. p. 209° (Found: C, 53·4; H, 6·1%), and (d) *picrolonate D*, m. p. 185° (Found: C, 53·8; H, 6·25. $C_{10}H_{19}O_2N$,$C_{10}H_8O_5N_4$ requires C, 53·4; H, 6·0%).

Ethyl 1-*Piperidyl*-β-*propionate*-2-α-*propionates E and F*.—The base (0·5 g., b. p. 80°/1 mm.) recovered from picrolonate C (1·6 g.) was heated with ethyl β-chloropropionate (0·9 g.) and anhydrous potassium carbonate (1·4 g.) in a sealed tube for 5 hours in the water-bath, water and excess of potassium carbonate added, and the oil taken up in ether. The basic portion was shaken out in dilute hydrochloric acid, liberated (50% potassium carbonate), ether-extracted, dried, and distilled, giving some unaltered base and an oil (0·25 g.), b. p. 145—150°/1 mm., whose *picrolonate G* had m. p. 115° (Found: C, 54·8; H, 6·8. $C_{15}H_{27}O_4N$,$C_{10}H_8O_5N_4$ requires C, 54·6; H, 6·4%). *Ethyl piperidyl*-1-β-*propionate*-2-α-*propionate E* recovered from this picrolonate had b. p. 136—138°/1 mm. (Found: C, 63·1; H, 9·6; N, 4·9. $C_{15}H_{27}O_4N$ requires C, 63·2; H, 9·5; N, 4·9%).

The base recovered from picrolonate D, similarly treated with ethyl β-chloropropionate, gave an oil, b. p. 145—150°/1 mm. This gave *picrolonate H*, m. p. 136° (Found: C, 54·2; H, 6·5. $C_{15}H_{27}O_4N$,$C_{10}H_8O_5N_4$ requires C, 54·6; H, 6·4%), and the *ethyl piperidyl*-1-β-*propionate*-2-α-*propionate F* recovered from it had b. p. 145°/1 mm. (Found: C, 62·9; H, 9·6. $C_{15}H_{27}O_4N$ requires C, 63·2; H, 9·6%). The esters E and F are more readily obtained by treating the mixed isomers of ethyl 2-piperidyl-α-propionate with ethyl β-chloropropionate as above; picrolonates G and H are then readily separated by fractional crystallisation from alcohol of the mixture obtained from the crude condensation product.

2-*Keto*-1-*methyloctahydropyridocoline*.—The mixture of esters E and F obtained as above (2·5 g.) was added to powdered potassium (0·9 g.) in toluene (20 c.c.), and the whole heated for 6 hours on the water-bath. Alcohol was added to dissolve unused potassium, then water (10 c.c.) and concentrated hydrochloric acid (30 c.c.), and the whole heated for a further 18 hours and evaporated to dryness. The residue was basified (50% potassium hydroxide) and ether-extracted, and the extract distilled, giving 2-keto-1-methyloctahydropyridocoline (0·6 g.) as a colourless oil, b. p. 78—80°/1 mm. The homogeneous *picrate* had m. p. 202° (from alcohol) (Found: C, 48·7; H, 5·0. $C_{10}H_{17}ON$,$C_6H_3O_7N_3$ requires C, 48·5; H, 5·05%). The separated base E gave the same result [picrate (m. p. 202° alone or mixed) and a *picrolonate*, m. p. 209° (Found: C, 55·1; H, 6·1. $C_{10}H_{17}ON$,$C_{10}H_8O_5N_4$ requires C, 55·6; H, 5·8%)].

Ethyl 2-*Pyridylsuccinate*.—Ethyl 2-pyridylacetate (12·8 g.) was added to an ice-cold solution of potassium (3·2 g.) in alcohol (40 c.c.); after ½ hour ethyl chloroacetate (9·6 g.) was added, and the whole left overnight. The alcohol was removed, water added, and the solution extracted with ether. The basic part was shaken out with dilute hydrochloric acid, liberated (potassium carbonate), and ether-extracted. Distillation gave unchanged ethyl pyridylacetate (6·75 g.), b. p. 93—110°/1 mm., identified as picrate and picrolonate, and *ethyl* 2-*pyridylsuccinate* (3·4 g.), as a pale yellow oil, b. p. 143—147°/1 mm. (Found: C, 62·2; H, 6·9. $C_{13}H_{17}O_4N$ requires C, 62·1; H, 6·8%). The *picrolonate* formed rosettes of yellow prisms from alcohol, m. p. 95° (Found: C, 53·75; H, 5·3. $C_{13}H_{17}O_4N$,$C_{10}H_8O_5N_4$ requires C, 53·6; H, 4·85%).

Ethyl 3-*Keto-octahydropyrrocoline*-1-*carboxylate*.—Ethyl 2-pyridylsuccinate (3·4 g.) in glacial acetic acid (20 c.c.) was shaken with platinum oxide (0·1 g.) in hydrogen at 100 lb./sq. in. for 48 hours. On being worked up in the usual way and distilled, the product underwent considerable decomposition, yielding *ethyl* 3-*keto-octahydropyrrocoline*-1-*carboxylate* (2·3 g.), b. p. 148—150°/1 mm. (Found: C, 62·3; H, 8·2. $C_{11}H_{17}O_3N$ requires C, 62·6; H, 8·1%).

Ethyl 2-*Piperidylsuccinate*.—After reduction of ethyl 2-pyridylsuccinate by the above method, the acetic acid was removed at 30—35° in a vacuum. After basification (potassium carbonate) and ether-extraction, the ether was evaporated at room temperature, leaving an oil (2·8 g.) which appeared to be ethyl 2-piperidylsuccinate, as it gave a *picrolonate*, m. p. 166° (Found: C, 52·6; H, 5·7. $C_{13}H_{23}O_4N$,$C_{10}H_8O_5N_4$ requires C, 53·0; H, 5·95%). This ester did not react in the cold with ethyl β-chloro- or -iodo-propionate or with β-cyanoethyl *p*-toluenesulphonate, and, on warming with any of these, immediate cyclisation took place.

Ethyl δ-*Phenoxy*-α-2-*pyridyl*-n-*valerate* (XII).—Ethyl 2-pyridylacetate (8·2 g.) was added to potassium powder (2·0 g.) suspended in dry ether (100 c.c.). After 18 hours γ-phenoxy-*n*-propyl bromide (11 g.) was added, and the whole refluxed for 6 hours. Water was added to dissolve

potassium bromide, the ethereal layer separated, and the aqueous layer extracted with ether. The basic part was shaken out (dilute hydrochloric acid), liberated (potassium carbonate), taken up in ether, dried, and distilled, giving *ethyl δ-phenoxy-α-2-pyridyl-*n*-valerate* (5 g.) as a golden-yellow oil, b. p. 205—207°/1 mm. (Found: C, 72·2; H, 7·3. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0%).

*Ethyl δ-Phenoxy-α-2-piperidyl-*n*-valerate.*—The above ester (5·0 g.) was shaken in glacial acetic acid (30 c.c.) with platinum oxide (0·2 g.) in hydrogen at 100 lb./sq. in for 18 hours. On working up, the *piperidyl* ester was obtained as a thick colourless oil (4 g.), b. p. 190—192°/1 mm. (Found: C, 70·6; H, 8·5; N, 5·0. $C_{18}H_{27}O_3N$ requires C, 70·8; H, 8·8; N, 4·6%). The ester gave the Liebermann reaction.

*ε-Phenoxy-β-2-piperidyl-*n*-amyl Alcohol* (XIII).—The above ester (12 g.) in alcohol (150 c.c.) was added to sodium (18 g.) at 180°, followed by enough alcohol to dissolve the sodium. The solution was acidified (concentrated hydrochloric acid) and evaporated, the residue basified (50% aqueous potassium hydroxide), and the liberated oil extracted and distilled, giving the *carbinol* as a very thick, pale yellow oil (6 g.), b. p. 195—200°/1 mm. (Found: C, 72·9, 73·3; H, 9·25, 9·6; N, 5·6. $C_{16}H_{25}O_2N$ requires C, 73·0; H, 9·5; N, 5·3%).

1-*Bromomethyloctahydropyridocoline* (XV).—The above carbinol (12·5 g.) in hydrobromic acid (100 c.c., *d* 1·65) was kept for 18 hours and then refluxed for 7 hours, and the solution evaporated. The residue was basified (30% potassium hydroxide solution) and extracted with ether, and the ethereal extract, after standing for 18 hours, was again shaken with 30% potassium hydroxide solution, dried, and fractionated. The crude distillate, in benzene (15 c.c.), was refluxed for 1½ hours with phosphorus pentabromide (7 g.), the whole cooled, and ice added, followed by an excess of potassium hydroxide solution (20%). The benzene layer was separated, and the aqueous layer extracted twice with benzene. The united dried benzene extracts were evaporated, and the residue distilled, yielding an oil (6·6 g.), b. p. 110°/1 mm. This was converted into picrolonate (12 g.), and the latter fractionally crystallised from alcohol, giving *picrolonate J* (5·3 g.), m. p. 202° (Found: C, 48·5, 48·3; H, 5·6, 5·6. $C_{10}H_{18}NBr,C_{10}H_8O_5N_4$ requires C, 48·4; H, 5·25%), and *picrolonate K* (4·3 g.), m. p. 169° (Found: C, 48·4, 48·2; H, 5·5, 5·3%).

The *base L* recovered from picrolonate J (5·3 g.) had b. p. 107°/1 mm. (1·8 g.) (Found: C, 51·3; H, 7·7. $C_{10}H_{18}NBr$ requires C, 51·7; H, 7·8%), and gave a *methiodide*, m. p. 216° (Found: C, 35·1; H, 5·75. $C_{10}H_{18}NBr,CH_3I$ requires C, 35·3; H, 5·6%), and *picrate*, m. p. 135° (Found: C, 41·5; H, 4·9. $C_{10}H_{18}NBr,C_6H_3O_7N_3$ requires C, 41·6; H, 4·55%).

The *base M* was recovered from picrolonate K as an oil (2 g.), b. p. 107°/1 mm. (Found: C, 51·2; H, 7·6); it gave a *picrate*, m. p. 144° (Found: C, 41·3; H, 4·9%), and a methiodide, m. p. 186°.

1-*Octahydropyridocolylcarbinols N and O.*—The bromo-base L (1·7 g.) was refluxed with sodium acetate (7 g.) in water (15 c.c.) for 10 hours, and the solution acidified to Congo-red (hydrochloric acid) and evaporated to dryness. The residue was basified (potassium carbonate) and extracted with ether, and the extract fractionated, giving 1-*octahydropyridocolylcarbinol N* (0·42 g.), b. p. 107°/1 mm. This solidified, and formed prisms, m. p. 59°, from light petroleum (b. p. 40—60°) (Found: C, 71·3; H, 11·3. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%). The *methiodide* had m. p. 303° (decomp.) (Found: C, 42·4; H, 7·3. $C_{10}H_{19}ON,CH_3I$ requires C, 42·4; H, 7·1%), the *picrolonate*, m. p. 203° (Found: C, 55·7; H, 6·1. $C_{10}H_{19}ON,C_{10}H_8O_5N_4$ requires C, 55·4; H, 6·2%), and the *picrate*, m. p. 127° (Found: C, 48·6; H, 5·6. $C_{10}H_{19}ON,C_6H_3O_7N_3$ requires C, 48·2; H, 5·5%).

In a similar manner the bromo-base M gave the *carbinol O*, b. p. 122°/1 mm., m. p. 81° (Found: C, 70·8; H, 11·7%). This formed a *picrate*, m. p. 139° (Found: C, 48·0; H, 5·9%), *picrolonate*, m. p. 225° (Found: C, 55·5; H, 6·4%), and *methiodide*, m. p. 248° (Found: C, 42·6; H, 7·2%).

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