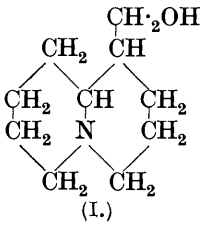
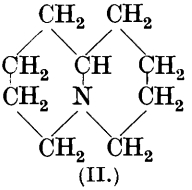
CCCCXLIII.—*The Lupin Alkaloids. Part V.*

By George Roger Clemo, George Rowntree Ramage, and Richard Raper.

In Part IV two of us recorded results having an adverse bearing on the formula (I) advanced by Karrer and co-workers (*Helv. Chim. Acta*, 1928, **11**, 1062) for lupinine. It was shown that synthetic octahydropyridocoline (II) differed from norlupinane ($C_9H_{17}N$)

prepared by distilling lupininic acid with soda-lime. It was inferred, therefore, that either (I) does not represent lupinine, or structural


(I.)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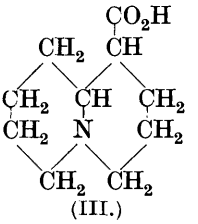
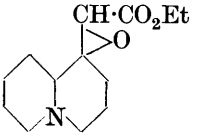
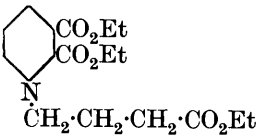

(III.)

changes had taken place in the somewhat drastic expulsion of carbon dioxide from lupininic acid. The preparation of norlupinane by milder methods was clearly desirable, and although Schöpf (*Annalen*, 1928, **465**, 104) states that lupininamide could not be obtained, it has now been found that the *hydrazide* can be readily prepared. This is unchanged by treatment with sodium nitrite in dilute acetic acid, but the action of amyl nitrite on a solution in ethyl-alcoholic hydrogen chloride gives a good yield of the *urethane*. The latter is not hydrolysed by refluxing with methyl-alcoholic potash, but is converted by boiling concentrated hydrochloric acid into *aminonorlupinane*, which on treatment with nitrous acid gives mainly d-*norlupinene* ($C_9H_{15}N$), together with some *hydroxynorlupinane* and other bases (see experimental part). This behaviour is in marked contrast to that of 1-hydroxyoctahydropyridocoline, which shows no such ready tendency to lose water. Norlupinene is reduced by hydrogen in acetic acid in the presence of palladised charcoal (compare this vol., p. 439), giving norlupinane, whose picrate, chloroaurate, and methiodide are identical with those prepared from the $C_9H_{17}N$ base obtained by the soda-lime distillation of lupininic acid. The possibility that a structural change has occurred in the earlier preparation of norlupinane is thus much reduced and the case against formula (I) for lupinine is correspondingly strengthened.

In continuation of the synthetic work recorded in Part IV, structure (III) has now been synthesised. It was thought that the carbon side chain could be introduced by the action of potassium cyanide on 1-bromo-octahydropyridocoline, but this was, unfortunately, only obtained in poor yield from 1-hydroxyoctahydropyridocoline. Next, 1-keto-octahydropyridocoline was treated with ethyl chloroacetate and sodamide, giving the *glycide* ester (IV), but it has not yet been possible to isolate either the free acid or the aldehyde expected to be formed from it by the loss of carbon dioxide. *Methyl octahydropyridocoline-1-carboxylate* was eventually prepared by condensing ethyl piperidine-2 : 3-dicarboxylate with γ-bromobutyronitrile, the resulting nitrile giving, with ethyl-alcoholic

hydrogen chloride, the *tricarboxylic* ester (V). After this had been submitted to the Dieckmann reaction, hydrolysis with hydrochloric

(IV.) 


(V.)

acid removed carbon dioxide, and the resulting 9-keto-octahydropyridocoline-1-carboxylic acid was reduced by Clemmensen's method. If at the keto-acid stage the product was esterified and fractionated, a considerable quantity of 1-keto-octahydropyridocoline was always obtained, indicating the ready loss of a second molecule of carbon dioxide. Esterification of the reduction product with methyl-alcoholic hydrogen chloride produced an oil which gave the analytical results required for methyl octahydropyridocoline-1-carboxylate and from which a crystalline *picrate*, m. p. 187°, depressed to 175—178° by admixture with the picrate of methyl *d*-epilupininate, has been obtained. Schöpf (*loc. cit.*) states that the latter melts at 185°, and that methyl lupininate itself gives only a gummy picrate, both of which results we have confirmed. Methyl lupininate reacted readily in aqueous solution with ammonium *d*-bromocamphorsulphonate, eliminating ammonia and forming the highly crystalline *methyl lupininate* d-*bromocamphorsulphonate*. The *l*-bromocamphorsulphonate showed no indication of crystallisation after several weeks. The synthetic ester of (III) is somewhat unstable and did not react with ammonium *d*-bromocamphorsulphonate, which was recovered unchanged under similar conditions to those used above. In both of these respects the methyl ester of (III) behaves very differently from methyl lupininate.

It was realised, however, that there was a distinct possibility that the Dieckmann reaction on (V) might result in ring closure to some extent with the β-carbethoxy-group, but this has been shown (see preceding paper) not to be the case. An important point is that the reduction of 1-keto-octahydropyridocoline, which is always formed as a by-product (see above), gave octahydropyridocoline, the picrate of which was always homogeneous, having m. p. 213°, no matter whether the starting material was *cis*- or *trans*-hexahydroquinolinic acid (*Ber.*, 1895, **28**, 3151) or the unseparated mixture. This result indicates that octahydropyridocoline does not occur in *cis*- and *trans*-forms and supports the view of Kenner and ourselves, referred to in the previous paper, that in polycyclic systems the configuration of tervalent nitrogen is probably planar.

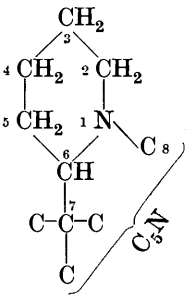
When submitted to the Bouveault reaction, the ester of (III) gave an oil which has not yet been induced to crystallise. This substance

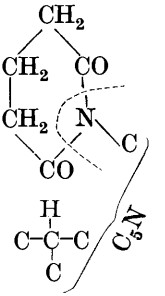
and *d*-tartaric acid gave a non-crystallisable salt, again contrasting markedly with the highly characteristic tartrate of the natural alkaloid.

These results show that lupinine is probably not (I), and, further, we have obtained degradation products from lupanine which are difficult to reconcile with any formula for the alkaloid yet advanced. When an aqueous solution of oxylupanine (Part I; J., 1928, 1819) is treated with potassium permanganate at 40—50°, a *compound* "*A*," $C_{15}H_{22}O_3N_2$, m. p. 212°, is obtained. Its production involves the highly unusual insertion, in a permanganate oxidation, of an oxygen atom without the removal of hydrogen. The compound does not react with phenyl *iso*cyanate, and so is presumably not an alcohol, nor does it give the standard reactions of keto- or reactive methylene groups. Further, it does not liberate iodine from acidified potassium iodide solution, or revert to oxylupanine on treatment with sulphurous acid, in which process sulphuric acid is not produced, thus indicating that in all probability it is not an amine oxide. This conclusion is supported by the fact that oxylupanine does not possess a reactive tertiary nitrogen atom (Part I; *loc. cit.*). In the sulphurous acid treatment, however, the compound recovered gives the correct analytical results for $C_{15}H_{22}O_3N_2$, and is indistinguishable from " A " under the microscope, but shows a variable melting point; this behaviour is possibly due to keto–enol tautomerism in a compound of structure such as " A," which contains probably several carbonyl groups. When substance " A " is hydrolysed by heating in sealed tubes with aqueous barium hydroxide, it gives glutaric acid and at least three other substances. One of these, obtained in only minute amount, gives a picrate, decomp. 290°. A second substance is a colourless crystalline *compound*, $C_{10}H_{20}O_4N_2$, m. p. 248°, and another is gummy, but gives a *picrate*, m. p. 231°. After oxylupanine has been treated with barium hydroxide at 200°, it can be recovered unchanged, but at 270° glutaric acid is formed. An isomeride " B " of $C_{15}H_{22}O_3N_2$ is obtained in small amount as a by-product in the oxidation of lupanine (compare Part I; *loc. cit.*).

It is hoped to discuss the full structural significance of these and our earlier results in a later communication, for synthetic and degradation work is being actively pursued. Meanwhile, as already pointed out in Part II (J., 1929, 1933), no formula hitherto advanced for sparteine or lupanine explains the oxidation results, but as these have now been considerably extended, it is tentatively suggested that the partial formula (VI) may represent the part of the sparteine molecule concerned. The production of " A " would then involve the breaking of the 6—7 link to give (VII), from which hydrolysis as shown would give glutaric acid, and a similar fission of a carbon–

carbon link at the same or another quaternary carbon atom would account for the formation of " B." The carbonyl group of lupanine

(VI.) 

 (VII).

is probably at position 2. It is improbable that there is a methylene group in position 8 in sparteine, as it would probably be oxidised to the carbonyl group in oxysparteine and *iso*lupanine, and the second $-CO-$ in oxylupanine is presumably in the same position. In this case " A " would have three carbonyl groups attached to the same nitrogen. It is, in fact, very doubtful if such a group occurs in any compound, although Aschan (*Ber.*, 1886, **19**, 1400) describes acetylphthalimide as a compound unstable to water; hence it is improbable that " A " contains such a group. The C_5N residue, together with four of the carbon atoms not in the piperidine ring, forms a second dicyclic nitrogen system to which at present we assign no definite constitution. The fact, however, that norlupinene is dextrorotatory, whereas norlupinane and its methiodide are inactive, strongly suggests that the ring structures in it are symmetrical.

Experimental.

Lupininhydrazide.—Methyl lupininate (20 g.) was heated for 48 hours with hydrazine hydrate (20 c.c., 90—95%) in sealed tubes placed horizontally in a boiling water-bath. On cooling, the resulting solution set to a colourless crystalline mass. This was collected, washed with a small volume of light petroleum (b. p. 60—80°), dried on the water-bath (17—18 g., m. p. 114—117°), and crystallised from boiling light petroleum (800 c.c.), giving colourless prisms (16 g.), m. p. 118—119° (Found: C, 60·9; H, 9·4; N, 21·5. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6; N, 21·3%). The *hydrazide* is very easily soluble in water and alcohol. A by-product is obtained in the above reaction, m. p. 218° approx., but insufficient has been obtained for its investigation.

Methylnorlupinanylurethane Hydrochloride.—Lupininhydrazide (3 g.) in ethyl alcohol (6 c.c.) was cooled in ice-water, and amyl nitrite (3·75 c.c.) added. Ethyl-alcoholic hydrogen chloride (4 c.c.; 0·6 g HCl) was then run into the dull reddish solution with shaking, and the

resulting pale yellow solution left over-night. The mixture, which had usually deposited a mass of colourless prisms, was evaporated to dryness (in this and all subsequent cases this was done on the water-bath under reduced pressure), and the crystalline residue recrystallised from ethyl alcohol (6 c.c.), colourless prismatic aggregates (2·5 g.), m. p. 270° (decomp.), being obtained. Recrystallisation raised the m. p. to 277—278° (decomp.) (Found: C, 55·2; H, 9·1; N, 10·7. $C_{12}H_{22}O_2N_2$,HCl requires C, 54·9; H, 8·8; N, 10·7%). The free *urethane*, obtained from the hydrochloride by treatment with methyl-alcoholic potash or silver oxide, was a colourless oil, b. p. 125—128°/1 mm. (Found: C, 63·8; H, 9·9. $C_{12}H_{22}O_2N_2$ requires C, 63·7; H, 9·7%).

Aminonorlupinane.—The urethane hydrochloride (3·9 g.) was refluxed for 16 hours with concentrated hydrochloric acid (8 c.c.), the solution evaporated to dryness, the residue dissolved in water (3—4 c.c.),* aqueous potassium hydroxide (50%) added, and the liberated base extracted with ether and dried over potassium carbonate. Fractionation gave *aminonorlupinane* (2·2 g.), b. p. 73—75°/1 mm. (Found: N, 17·9. $C_9H_{18}N_2$ requires N, 18·2%).

Norlupinene.—The solution of the hydrochloride above (*) was cooled in ice, and aqueous *N*-sodium nitrite solution (15 c.c.) run in with shaking. After 15 minutes, the solution was heated for 15† minutes on the water-bath, then concentrated to a few c.c., and made strongly alkaline with potassium hydroxide (50%). The liberated bases were extracted with ether, and the extract dried over potassium carbonate and fractionated, giving "C" (1 g.), b. p. 40—50°/1 mm., and "D" (0·8 g.), b. p. up to 120°/1 mm. On redistillation of the "C" fraction, practically the whole passed over between 40—43°/1 mm. as a colourless oil which turned brown in the air (Found: C, 78·8; H, 10·85; N, 10·5. $C_9H_{15}N$ requires C, 78·8; H, 10·9; N, 10·2%. $[\alpha]_D$ in acetone, + 33·7°). *Norlupinene* is only slightly soluble in water, but the solution is strongly alkaline to litmus, and does not give either the pine shaving or the *p*-dimethylaminobenzaldehyde pyrrole colour reactions. It forms a *picrate*, bright yellow, rectangular prisms, m. p. 175°, from alcohol (Found: C, 49·5; H, 5·25. $C_9H_{15}N,C_6H_3O_7N_3$ requires C, 49·2; H, 4·9%), and a *methiodide*, compact prisms, m. p. 308—310° (decomp.), from acetone (Found: C, 43·0; H, 6·8. $C_9H_{15}N$,MeI requires C, 43·0; H, 6·5%).

When the "D" fraction (3 lots combined) was refractionated, about one-third of the material passed over between 68° and 72°/1 mm., and further approximately equal amounts up to 100°/1 mm. and 100—120°/1 mm. (Found for the first fraction: C, 69·7, 69·2; H, 11·15, 11·2. $C_9H_{17}ON$ requires C, 69·7; H, 11·0%). *Hydroxy-*

norlupinane rapidly turns brown on exposure to the air, and gives an oily methiodide. The intermediate fraction gave a gummy methiodide, but a picrate was obtained as yellow warts, m. p. 207—208° (decomp.), from alcohol, and the same picrate was obtained from the final fraction (Found : C, 47·5, 47·7 ; H, 5·9, 5·7 ; N, 16·1. $C_{15}H_{27}O_3N_3$,$C_6H_3O_7N_3$ requires C, 47·8 ; H, 5·7 ; N, 16·0%). The exact nature of these intermediate and final fractions has not yet been determined. If in the preparation of norlupinene the amino-norlupinane (2·2 g.) was first isolated and then dissolved in two equivalents of *N*-hydrochloric acid (no reaction occurred with only one equivalent), repetition of the above experiment gave the same result. If, however, the 15 minutes'† standing was extended to about 6 hours until the evolution of nitrogen ceased, a slightly larger yield of norlupinene and a smaller one of " D " resulted.

Norlupinane.—A solution of the above crude " C " fraction of norlupinene (1 g.) in glacial acetic acid (25 c.c.) was stirred with palladised charcoal (0·2 g. ; see Part IV, this vol., p. 439) for some hours in an atmosphere of hydrogen : reduction was rapidly effected. After filtration and the addition of concentrated hydrochloric acid (1 c.c.) and a fragment of granulated zinc, the solvent was removed, aqueous potassium hydroxide added, and the mixture extracted with ether. On fractionation a colourless inactive oil (0·65 g.) was obtained, b. p. 43—45°/1 mm. (Found : C, 77·45 ; H, 12·5 ; N, 10·3. Calc. for $C_9H_{17}N$: C, 77·7 ; H, 12·2 ; N, 10·1%). The picrate, m. p. 149°, chloroaurate, m. p. 164°, and inactive methiodide, m. p. 340—343° (decomp.) in place of 333—335° recorded in Part IV, all confirm the conclusion that the $C_9H_{17}N$ base obtained by the soda-lime distillation of lupininic acid is identical with norlupinane.

Ethyl β-1-*Octahydropyridocolylglycidate* (IV).—Finely powdered sodamide (1·2 g.) was added during 2 hours to freshly distilled 1-keto-octahydropyridocoline (3·7 g.) and ethyl chloroacetate (3 g.) in dry ether (7 c.c.). After 2 days, water was added, and the solution extracted with ether. On fractionation 1-keto-octahydropyridocoline (0·8 g.) was recovered, and *ethyl* β-1-*octahydropyridocolylglycidate* (2·3 g.) obtained as a yellowish oil, b. p. 152°/0·1 mm. (Found : C, 65·1 ; H, 8·7. $C_{13}H_{21}O_3N$ requires C, 65·3 ; H, 8·8%).

Ethyl Piperidine-2 : 3-*dicarboxylate.*—Pyridinedicarboxylic acid (*Ber.*, 1925, **58**, 1727) was reduced by sodium (70 g.) and absolute ethyl alcohol (500 c.c.) (compare Besthorn, *Ber.*, 1895, **28**, 3154). The acidified solution obtained as described was evaporated to dryness, the residue extracted three times with absolute alcohol, the solvent removed, and the residual acid esterified by 12 hours' refluxing with ethyl-alcoholic hydrogen chloride (25 c.c.). After removal of the alcohol and refluxing again for 4 hours with a

further quantity of alcoholic hydrogen chloride (15 c.c.), the residue was made alkaline with aqueous potassium carbonate and extracted with ether. Fractionation gave ethyl piperidine-2 : 3-dicarboxylate as a colourless oil (6 g.), b. p. 114—117°/0·2 mm. (Found : N, 6·4. Calc. for $C_{11}H_{19}O_4N$: N, 6·1%).

Ethyl γ-2 : 3-Dicarbethoxypiperidinobutyrate (V).—Ethyl piperidine-2 : 3-dicarboxylate (2·3 g.), γ-bromobutyronitrile (1·5 g.), and powdered anhydrous potassium carbonate (1·5 g.) were heated for 1½ hours in the water-bath with occasional stirring. Water was added to four similar experiments, and the liberated oil collected in ether. After removal of the ether and any unchanged bromonitrile and dicarboxylic ester, the crude γ-2 : 3-dicarbethoxypiperidinobutyronitrile (9·5 g.) was refluxed with ethyl-alcoholic hydrogen chloride (30 c.c.). After filtration of the ammonium chloride and distillation of the alcohol, excess of aqueous potassium carbonate solution was added to the residue, and the insoluble ester taken up in ether. Fractionation of the dried extract gave *ethyl γ-2 : 3-dicarbethoxypiperidinobutyrate* as a colourless oil (9 g.), b. p. 160—166°/0·1 mm. (Found : C, 59·7; H, 8·3; N, 4·3. $C_{17}H_{29}O_6N$ requires C, 59·5; H, 8·5; N, 4·1%).

Methyl Octahydropyridocoline-1-carboxylate.—The above tricarboxylic ester (6 g.) was gently refluxed with powdered sodium (1 g.) in toluene (25 c.c.) until a vigorous reaction set in and then heated for two hours in the water-bath. Hydrochloric acid (1 : 1) was added till neutral, followed by concentrated acid (10 c.c.), and the solution was heated in the water-bath until carbon dioxide evolution almost ceased (3 hours). The solution was evaporated to dryness, and the residue extracted three times with methyl alcohol. Removal of the solvent left a substance (E), which was esterified by refluxing it for 12 hours with methyl-alcoholic hydrogen chloride (20 c.c.). Removal of the alcohol, followed by ether extraction of the mixture, made strongly alkaline with aqueous potassium carbonate, gave a low-boiling fraction of 1-keto-octahydropyridocoline (0·6 g.), b. p. 110°/17 mm. (methiodide, m. p. 210°; semicarbazone, m. p. 230°) (Found : N, 26·4. Calc. : N, 26·7%). The m. p. recorded for the original semicarbazone, which gave correct analytical results, is 215°. We now find that repeated crystallisation raises this to 230°, and this is apparently another instance of the variability of the m. p.'s of semicarbazones (compare Bryant and Clemo, this vol., p. 2080). The higher-boiling fraction (1·4 g.), b. p. 127—130°/0·3 mm., was methyl 9-keto-octahydropyridocoline-1-carboxylate, since on hydrolysis with hydrochloric acid and reduction as below it gave methyloctahydropyridocoline-1-carboxylate. The latter was better obtained, however, when the residue (E) above was treated with

amalgamated zinc (15g.) and concentrated hydrochloric acid (10c.c.), first for 2 hours at room temperature and then for 12 hours on the water-bath. A further quantity of hydrochloric acid (5 c.c., *d* 1·195) was added, the heating continued for a further 8 hours, and the mixture finally refluxed for several hours after addition of more hydrochloric acid (5 c.c.). The solution was decanted from the zinc and evaporated to dryness, water (200 c.c.) added, and an excess of hydrogen sulphide passed into the solution whilst it was gradually made alkaline with sodium hydroxide. On steam-distillation, octahydropyridocoline (0·08 g.), b. p. 77°/18 mm., passed over. Its picrate melted at 211—213°, alone or mixed with an authentic specimen. The zinc sulphide was filtered off and washed, and the filtrate acidified with hydrochloric acid and evaporated to dryness. The residue was extracted with methyl alcohol, esterified, and worked up as for the corresponding keto-ester above, and *methyl octahydropyridocoline*-1-*carboxylate* (0·8 g.), b. p. 100—110°/0·5 mm., obtained. When redistilled, at least one half passed over between 102—105°/0·5 mm. as a colourless oil (Found : C, 67·35; H, 9·4. $C_{11}H_{19}O_2N$ requires C, 67·0; H, 9·65%). The ester darkened rapidly on standing and was slightly soluble in water, giving a solution alkaline to litmus. The *picrate* was prepared in alcohol, treated with charcoal, and allowed to cool, and the gum again dissolved; crystals were then deposited. A further crystallisation gave yellow prisms, m. p. 187° (Found : C, 47·4; H, 5·1. $C_{11}H_{19}O_2N,C_6H_3O_7N_3$ requires C, 47·8; H, 5·2%).

The separated *cis*- and *trans*-piperidinedicarboxylic acids were esterified, and the above operations repeated exactly with them. The 1-carbomethoxyoctahydropyridocoline picrates obtained could not be crystallised to constant m. p. (probably mixtures of stereoisomerides). From the octahydropyridocoline obtained as a by-product, picrates were obtained which melted after several recrystallisations at 212—213° and gave no depression with authentic octahydropyridocoline picrate.

Methyl Lupininate d-*Bromocamphorsulphonate*.—Authentic methyl lupininate (0·1 g.) and ammonium *d*-bromocamphorsulphonate (0·17 g.) in water (0·5 c.c.) were warmed for 20 minutes on the water-bath and the solution was evaporated to dryness in a vacuum desiccator. The crystalline residue, recrystallised from acetone, gave colourless needles, m. p. 171—173° (Found : C, 50·1; H, 6·9. $C_{21}H_{34}O_6NBrS$ requires C, 49·6; H, 6·8%).

Lupinine d-*tartrate*, formed from the alkaloid and *d*-tartaric acid in alcohol, crystallised from alcohol–acetone in colourless prisms, m. p. 171° (Found : C, 52·9; H, 8·1. $C_{14}H_{25}O_7N$ requires C, 52·7; H, 7·9%).

Oxylupanine was prepared as in Part I, lupanine (25 g.) being used, and the permanganate added during 5—6 hours. Yield, 8·5 g.; m. p. 123—124°. The manganese dioxide was well extracted with hot water, and the brown filtrate concentrated till crystallisation began. After cooling, the potassium oxalate was filtered off, and after some time crystalline material (0·35 g.) was deposited. Recrystallised from acetone, this formed needles of "B," m. p. 233° (Found: C, 64·7, 64·4; H, 8·4, 7·9; N, 10·1. $C_{15}H_{22}O_3N_2$ requires C, 64·7; H, 7·9; N, 10·1%).

The Substance "A."—Oxylupanine (2 g.) in water (80 c.c.) maintained at 40—50° was gradually treated with potassium permanganate (4·4 g.) with stirring. After removal of the manganese dioxide the liquid was evaporated to dryness, and the light brown residue exhaustively extracted with acetone. This was removed, and the residue (0·4 g.) recrystallised from acetone, giving colourless prisms (0·3 g.), m. p. 212° (Found: C, 64·6, 64·7; H, 8·0, 8·0; N, 10·3. $C_{15}H_{22}O_3N_2$ requires C, 64·7; H, 7·9; N, 10·1%). The residue from the acetone extract contained oxalate and carbonate.

When sulphur dioxide was passed for some time through an aqueous solution of "A," the liquid boiled and evaporated to dryness, and the residue dissolved in acetone and concentrated to small bulk, prisms, m. p. 144°, not raised by a second recrystallisation from acetone, resulted (Found: C, 64·8; H, 7·9%). A further crystallisation from acetone then raised the m. p. to 157°, not depressed by admixture with "A" (Found: C, 64·7; H, 7·9%).

The Hydrolysis of "A" with Barium Hydroxide.—"A" (1 g.), recrystallised barium hydroxide (5 g.), and water (30 c.c.) were heated in a sealed tube for 6 hours at 270°. The contents were steam-distilled. The distillate (150 c.c.) was acidified with hydrochloric acid and evaporated to dryness, the small residue extracted with alcohol, and the filtered extract treated with alcoholic picric acid. After concentration, brown lozenge-shaped crystals, decomp. 290°, slowly separated in amount too small for identification. The residue in the steam distillation flask was filtered and treated with saturated copper sulphate solution as long as a precipitate was produced. This was filtered off (filtrate "F"), suspended in boiling water, and decomposed with hydrogen sulphide. The filtrate from the copper sulphide was vaporated to dryness, and the residue extracted with dry ether; removal of this solvent left a solid (0·3 g.) which, recrystallised from ether–light petroleum, gave glutaric acid (0·2 g.), m. p. and mixed m. p. 97—98° (Found: C, 45·8; H, 5·8. Calc.: C, 45·5; H, 6·1%).

The filtrate "F" from the copper precipitate was saturated with hydrogen sulphide, filtered, and evaporated to dryness; the residue was dissolved in alcohol, and the filtered solution evaporated,

leaving a yellow gum, which began to crystallise on standing. Boiling with light petroleum hastened the process without extracting anything. From the residue, acetone extracted a non-solidifying gum, which, dissolved in alcohol and treated with alcoholic picric acid (0·1 g.), gave, on addition of ether and long standing, a dark brown, crystalline *product*, m. p. 231° (Found : C, 47·5; H, 5·4; N, 16·6, 16·8%). The residue from the acetone extraction, crystallised twice from alcohol, gave colourless irregular crystals (0·15 g), m. p. 248° (Found : C, 51·4; H, 8·8. $C_{10}H_{20}O_4N_2$ requires C, 51·7; H, 8·6%).

Repetition of the hydrolytic experiment with " A " (0·3 g.) at 200° gave glutaric acid (0·02 g.), m. p. 97° (alone or mixed with an authentic specimen), and also the substance of m. p. 248°. Oxylupanine (1 g.), hydrolysed in the same way at 270°, gave glutaric acid (0·1 g.), m. p. 96—97° (alone or mixed with an authentic specimen), the picric acid product, m. p. 231° (alone or mixed with the specimen from " A ") (Found : C, 47·9; H, 5·8; N, 16·95, 17·4%), and the product of m. p. 248° (0·2 g.) (Found : C, 51·8; H, 8·25; N, 12·2, 12·7. $C_{10}H_{20}O_4N_2$ requires C, 51·7; H, 8·6; N, 12·0%).

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