LVIII.—*The Lupin Alkaloids. Part III.*

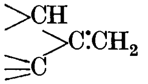
By George Roger Clemo, Richard Raper, and Charles Robert Sydney Tenniswood.

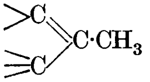
ALTHOUGH it has generally been assumed that lupanine and sparteine are structurally related, no evidence in favour of this view has hitherto been advanced. Since, however, *dl*-lupanine can be reduced to an inactive base $C_{15}H_{26}N_2$ (Clemo and Leitch, J., 1928, 1811), which is probably *dl*-sparteine, we were induced to repeat the experiment with the active lupanines.

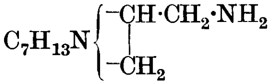
No supplies of the active alkaloids being available, experiments on the resolution of the *dl*-base were carried out. Davies (*Arch. Pharm.*, 1897, **235**, 211) gives a method for accomplishing this by mechanically separating the crystals of the thiocyanate of the base, but we were unable to repeat his work, and his statement that the thiocyanate of the *d*-base is yellow while that of the *l*-base is colourless suggests that the presence of a coloured active impurity may have facilitated the spontaneous resolution. We find, however, that the active forms of the alkaloid are readily obtained by crystallising the *camphorsulphonates* from acetone, in which the *d*-salt of the *d*-base and the *l*-salt of the *l*-base are less soluble than the alternative pair of compounds. From these, *d*- and *l*-lupanine have been obtained, showing respectively $[\alpha]_D$ + 61·4° and − 61·0°. So far the *l*-base has not been induced to crystallise, but the *d*-base solidifies on standing and then melts at 40° (Davies, *loc. cit.*, gives 44°). By mixing equal quantities of the active forms, *dl*-lupanine, m. p. 98°, is regenerated. The thiocyanates of the active bases soften at about 145° with loss of crystal water, and melt at 184° (Soldaini, *Gazzetta*, 1893, **23**, i, 145; 1895, **25**, i, 364, gives 183—184° for the *d*-thiocyanate and 123—124° for the *dl*, and Davies gives 188—189° for the active and 124° for the inactive salt).

By reducing *d*-lupanine with hydriodic acid and red phosphorus we have obtained a base which we believe to be *l*-sparteine. The picrate melts at 205—206°, alone or mixed with a specimen prepared from sparteine sulphate purchased from Messrs. Smith of Edinburgh, and the monohydriodide melts at 231°, alone or mixed with an authentic specimen prepared from the same source. The latter is especially suitable for the mixed melting-point test, as its decomposition point is much higher than the melting point. So far, however, the naturally occurring base and that obtained from lupanine show a difference of some 6° in their specific rotations. Similarly, *l*-lupanine is reduced to d-*sparteine*, whose *picrate* melts at 205—206°, but at 200° when mixed with that of *l*-sparteine.

Further evidence of the labile nature of the lupinine molecule has been obtained (compare Part II, J., 1929, 1928) by the action of alkalis on ω-bromolupinane. When this compound is heated at 170—180° with an aqueous solution of sodium acetate, lupinine is formed, but with 20% methyl-alcoholic potash on the water-bath it gives a mixture of lupinine methyl ether and *l*-ψ-anhydrolupinine. This facile formation of the lævorotatory ψ-anhydrolupinine might be explained by its having structure (I), hitherto given to anhydrolupinine, while the inactive anhydrolupinine prepared by the more drastic method of Willstätter and Fourneau (*Ber.*, 1902, **35**, 1922; compare also Schopf and Thoma, *Annalen*, 1928, **465**, 97) might be represented by structure (II). This does not accord well, however, with the formation of ψ-anhydrolupinine by the Hofmann degradation of chlorolupinane methiodide, or the fact that the ψ-base forms two stereoisomeric methiodides, and it appears necessary to envisage the possibility of radical structural changes occurring in the lupinine molecule such as, for instance, the change of bornyl chloride into camphene.


(I.)


(II.)


$C_7H_{13}N\left\{\begin{array}{l}-CH\cdot CH_2\cdot NH_2\\ \quad | \\ -CH_2\end{array}\right.$
(III.)

Against formula (II) for anhydrolupinine, Karrer and Vogt (*Helv. Chim. Acta*, 1930, **13**, 1073) report that they have prepared the *l*-anhydro-base in 36% yield by treating chlorolupinane with trimethylamine and submitting the resulting ammonium salt to the Hofmann degradation. It is claimed that the properties of the *l*-base agree in all respects * with those already described for *dl*-anhydrolupinine. In view of the above results, which had been obtained before the appearance of Karrer's paper, it seemed to us possible that the activity of the so-called *l*-anhydrolupinine might be due to the presence of *l*-ψ-anhydrolupinine. On repeating the experiment we found that the resulting anhydro-base, which, as shown in the experimental part, contained some ω-dimethylaminolupinane even when the fractionation was carried out at 0·5 mm., had the properties of the ψ- rather than of the *dl*-anhydro-base : it was much more stable to air, had the characteristic odour of the ψ-base, and gave a picrate (difficult to separate from a small amount of ω-dimethylaminolupinane picrate) of $[\alpha]_D$ — 53·0°, and m. p. 152°, not depressed by admixture with ψ-anhydrolupinine picrate

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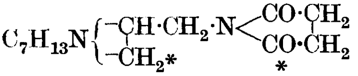
* " Die Verbindung besass alle schon von früheren Autoren beobachteten Eigenschaften und Eigentümlichkeiten. Insbesondere erwies sie sich auch wenig haltbar, indem sie sich schon nach mehrstündigem Stehen bräunte und dunkle, viscose, ölige Anteile ausschied."

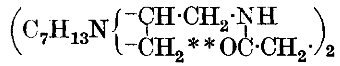
of m. p. 154° and $[\alpha]_D$ $-$ 54·8°. As, however, the two picrates do not always appear identical under the microscope, identity is not claimed at present. Further, catalytic reduction of Karrer and Vogt's *l*-anhydro-base gave a dihydro-compound with $[\alpha]_D$ $-$ 0·64°. In Part II (*loc. cit.*) we described ψ-anhydrodihydrolupinine with $[\alpha]_D$ + 21·7° in acetone, and it seems possible, therefore, that Karrer's claim to have prepared active anhydrolupinine, as called for by his lupinine formula, may be explained by his base being a mixture of ψ-anhydrolupinine with a small amount of ω-dimethylaminolupinane, which, we find, has $[\alpha]_D$ $-$ 37·7° in acetone. It is noteworthy that, although anhydrolupinine is so unstable to air, it is largely recovered after 24 hours' boiling with nitric acid (20%).

When ω-chlorolupinane (J., 1929, 1934) is heated with potassium phthalimide, and the resulting compound hydrolysed by the method of Ing and Manske (J., 1926, 2348), ω-aminolupinane (III) is formed. This reacts somewhat violently with succinic anhydride, giving a solid insoluble in alcohol which has not been examined further, but with methyl succinate it yields N(11)-*lupinylsuccinimide* (IV) and *dilupinylsuccinamide* (V). With methyl glutarate, on the other hand, the main products are *methyl* N(11)-*lupinylglutaramate* (VI) and *dilupinylglutaramide* (VII), and up to the present it has not been possible to convert (VI) into *N*(11)-lupinylglutarimide, to effect ring closure between the carbonyl and the methylene group marked *, and to eliminate methyl alcohol from the imino- and the carbomethoxy-group (†) of (VI), so as to obtain compounds isomeric, or identical, with lupanine. The two carbonyl groups in both *N*(11)-lupinylphthalimide and (IV) are converted into methylene groups by electrolytic reduction.



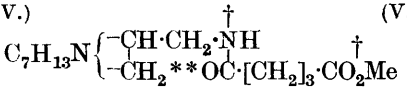
$$C_7H_{13}N\left\{\begin{matrix}-CH\cdot CH_2\cdot N\left<\begin{matrix}CO\cdot CH_2\\ \underset{*}{CO}\cdot CH_2\end{matrix}\right.\\ -CH_2*\end{matrix}\right.$$

(IV.)



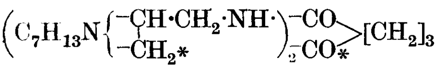
$$\left(C_7H_{13}N\left\{\begin{matrix}-CH\cdot CH_2\cdot NH\\ -CH_2**OC\cdot CH_2\cdot\end{matrix}\right.\right)_2$$

(V.)



$$C_7H_{13}N\left\{\begin{matrix}-CH\cdot CH_2\cdot \overset{\dagger}{N}H\\ -CH_2**OC\cdot[CH_2]_3\cdot \overset{\dagger}{C}O_2Me\end{matrix}\right.$$

(VI.)



$$\left(C_7H_{13}N\left\{\begin{matrix}-CH\cdot CH_2\cdot NH\cdot\\ -CH_2*\end{matrix}\right.\right)_2\begin{matrix}-CO\\ -CO*\end{matrix}>[CH_2]_3$$

(VII.)

When α-methyloxysparteine ‡ is treated with two atomic proportions of bromine in benzene or carbon disulphide solution, bromo-α-methyloxysparteine hydrobromide is formed, from which potassium carbonate liberates the base. The bromine atom in this compound is very firmly held, as the substance is not attacked by

‡ We wish to acknowledge valuable assistance in this work from Mr. H. R. Wilson, B.A.

alcoholic potash, hydrobromic acid, potassium hydroxide at 180°, or boiling pyridine.

EXPERIMENTAL.

d-*Lupanine* d-*Camphorsulphonate*.—*dl*-Lupanine (50 g.) and *d*-camphorsulphonic acid (46 g.) were dissolved in boiling acetone (100 c.c.). On cooling, 37 g. of salt separated in colourless prisms, m. p. 112—115°, $[\alpha]_D + 42{\cdot}5°$ in 5·106% aqueous solution (Found : C, 58·2; H, 8·3%). This was recrystallised three times from acetone ($[\alpha]_D$ 45·0°, 45·5°, 45·5°). The last crop (24·2 g.), m. p. 108—110°, gave C, 58·2; H, 8·6; N, 5·2 ($C_{25}H_{40}O_5N_2S,2H_2O$ requires C, 58·1; H, 8·5; N, 5·4%).

d-*Lupanine*.—When the above salt (23 g.) in water (30 c.c.) was treated with a saturated solution of potassium iodide (25 g.), d-*lupanine hydriodide* (14 g., colourless prisms, m. p. 189°, $[\alpha]_D + 45{\cdot}5°$ in water) was deposited (Found : C, 43·95; H, 7·0. $C_{15}H_{24}ON_2,HI,2H_2O$ requires C, 43·7; H, 7·0%), 13 g. of which, decomposed with potassium hydroxide and extracted five times with chloroform, gave *d*-lupanine (6·5 g., b. p. 185—186°/0·08 mm.) as an almost colourless, very viscous oil, $[\alpha]_D + 61{\cdot}4°$ in 3·495% acetone solution (Found : C, 72·6; H, 9·7. Calc. for $C_{15}H_{24}ON_2$: C, 72·6; H, 9·7%). On standing, the oil crystallised completely, and then melted at 40°. It was hygroscopic, and gradually turned brown in the air.

d-Lupanine thiocyanate is formed, when the base is treated in water with ammonium thiocyanate (1 mol.) (Davies, *loc. cit.*), as colourless prisms, softening at 143° with loss of water of crystallisation, and finally melting at 184°; $[\alpha]_D + 55{\cdot}6°$ in 1·062% aqueous solution. Davies gives 47·1°, no solvent or concentration being mentioned.

l-*Lupanine* l-*Camphorsulphonate*.—The mother-liquors from the first crop of *d*-lupanine *d*-camphorsulphonate were evaporated as far as possible, treated with potassium iodide (25 g.) in water (30 c.c.), and boiled till free from acetone. On cooling, lupanine hydriodide (33·6 g.) crystallised, from which lupanine (18 g., b. p. 185—188°/0·08 mm.) was obtained. When this was combined with *l*-camphorsulphonic acid (16·5 g.) in acetone (35 c.c.), l-*lupanine* l-*camphorsulphonate* (20 g.), $[\alpha]_D - 41{\cdot}5°$, separated. Recrystallisation from acetone gave 16·1 g., m. p. 110—113°, $[\alpha]_D - 45{\cdot}3°$ (Found : C, 58·0; H, 8·5; N, 5·5. $C_{25}H_{40}O_5N_2S,2H_2O$ requires C, 58·1; H, 8·5; N, 5·4%).

l-*Lupanine*.—The camphorsulphonate (15 g.) in water (15 c.c.) was treated with potassium iodide (15 g.) in water (15 c.c.); l-*lupanine hydriodide* (10 g.) then crystallised in colourless prisms, m. p. 190°, $[\alpha]_D - 43{\cdot}6°$ (Found : C, 43·9; H, 6·8. $C_{15}H_{24}ON_2,HI,2H_2O$ requires C, 43·7; H, 7·0%), from 9·5 g. of which *l*-lupanine (4·7 g.,

b. p. 186—188°/1 mm., $[\alpha]_D$ − 61·0° in 3·146% acetone solution) was obtained as a very viscous oil (Found: C, 72·75; H, 10·0. Calc. for $C_{15}H_{24}ON_2$: C, 72·6; H, 9·7%). *l*-Lupanine thiocyanate, prepared from the above, melted at 183—185° after softening at 142°, and showed $[\alpha]_D$ − 55·3° in 1·25% aqueous solution.

Equal weights of the *d*- and the *l*-lupanine, mixed together, gave *dl*-lupanine, m. p. 97°, raised to 98° by recrystallisation from acetone and not depressed by admixture with *dl*-lupanine (m. p. 98°) from *Lupinus termis* seeds.

l-*Sparteine*.—Four sealed tubes, each containing *d*-lupanine (1·25 g.), red phosphorus (1·25 g.), and hydriodic acid (5 c.c., *d* 1·94), were heated for 36 hours at 220—230°. The excess of hydriodic acid was then removed at 150° under reduced pressure and the residue was treated with potassium hydroxide and extracted with chloroform. On fractionation, 0·65 g. passed over up to 150°/1 mm., and 1·25 g. above this temperature. The latter solidified on standing and was unchanged lupanine. When the first fraction was redistilled, *l*-sparteine (0·45 g., b. p. 130—135°/1 mm.) passed over (Found: C, 76·6; H, 11·2. Calc. for $C_{15}H_{26}N_2$: C, 76·9; H, 11·1%); $[\alpha]_D$ in 2·732% absolute alcoholic solution, − 11·3°. Another similar experiment gave 0·55 g. of base, b. p. 130—135°/1 mm., $[\alpha]_D$ − 10·5°. The recorded specific rotation of sparteine is − 16·4° (Willstätter and Marx, *Ber.*, 1904, **37**, 2356).

The *l*-sparteine prepared from lupanine gives the sulphur–hydrogen sulphide colour reaction of sparteine. The picrate, prepared from the base and picric acid (2 mols.), melts at 205—206°, alone or mixed with authentic *l*-sparteine picrate (Found: C, 46·5; H, 4·5. Calc. for $C_{15}H_{26}N_2,2C_6H_3O_7N_3$: C, 46·8; H, 4·6%). The monohydriodide (colourless prisms from water) has m. p. 231°, alone or mixed with authentic *l*-sparteine hydriodide (Found: C, 49·5; H, 7·7. Calc. for $C_{15}H_{26}N_2,HI$: C, 49·7; H, 7·5%).

d-*Sparteine* (0·6 g.) was similarly obtained from *l*-lupanine (3·75 g.) and is a colourless oil, b. p. 133—135°/1 mm., $[\alpha]_D$ + 15·9° (Found: C, 76·9; H, 11·2. $C_{15}H_{26}N_2$ requires C, 76·9; H, 11·1%). The *picrate* melts at 205—206° (Found: C, 47·0; H, 4·3. $C_{15}H_{26}N_2,2C_6H_3O_7N_3$ requires C, 46·8; H, 4·6%), and the *monohydriodide* at 229° alone, but, mixed with *l*-sparteine hydriodide, at 194—198° (Found: C, 49·5; H, 7·6. $C_{15}H_{26}N_2,HI$ requires C, 49·7; H, 7·5%).

Bromolupinane.—A mixture of phosphorus pentabromide (4·3 g.) and lupinine (1·65 g.) in dry benzene (10 c.c.) was heated for an hour on the water-bath and cooled and a little ice and then potassium hydroxide (25 c.c., *d* 1·25) were added. The benzene layer was separated, the alkaline solution again extracted with benzene, and the combined benzene extracts dried and fractionated, giving bromolupinane as a colourless oil (1·8 g.), b. p. 103°/1 mm., which formed a *methiodide*, colourless prisms, m. p. 226—228° (decomp.), from ethyl alcohol (Found : C, 35·7 ; H, 5·8. $C_{10}H_{18}NBr,MeI$ requires C, 35·3 ; H, 5·6%).

The action of methyl-alcoholic potash on bromolupinane. Bromolupinane (5 g.) and methyl-alcoholic potash (10 c.c. of 20%) were refluxed on the water-bath for 16 hours, the alcohol was removed, and the residue extracted twice with ether and fractionated, giving " A " (1·6 g.) up to 75°/1 mm. and " B " (1·6 g.) from 80—85°/1 mm. The " A " fraction, when redistilled, almost all passed over at 61—63°/0·5 mm.; it gave a picrate, yellow plates from alcohol, m. p. 154°, not depressed by admixture with ψ-anhydrolupinine picrate (Found : C, 50·9 ; H, 5·6. Calc. for $C_{10}H_{17}N,C_6H_3O_7N_3$: C, 50·5 ; H, 5·3%). The " B " fraction redistilled almost wholly at 84—85°/1 mm., giving lupinine methyl ether; this formed a *methiodide*, colourless plates, m. p. 177—178°, from acetone (Found : C, 44·7 ; H, 7·4. $C_{12}H_{24}ONI$ requires C, 44·3 ; H, 7·4%), and a *picrate*, bright yellow prisms, m. p. 81—82°, from ethyl alcohol (Found : C, 49·7 ; H, 6·0. $C_{11}H_{21}ON,C_6H_3O_7N_3$ requires C, 49·5 ; H, 5·8%).

The Action of Heat on ω-Lupinyltrimethylammonium Chloride.—This compound (3·5 g.) was prepared and treated with silver oxide as described by Karrer and Vogt (*loc. cit.*), giving 1·2 g. of a damp oil which, after being dried in ether and fractionated, gave 0·8 g., b. p. 63—65°/0·5 mm., and 0·2 g. up to 90°/0·5 mm. (approx.). A portion (0·2 g.) of the main fraction, when treated in alcohol–ether with picric acid (0·3 g.), gave 0·45 g. of crystalline picrate, m. p. 150—153°; this was freed from most of the admixed ω-dimethylaminolupinane picrate (for methiodide, see below) by recrystallisation from ethyl alcohol–ethyl acetate; it then melted at 152—153°, alone or mixed with ψ-anhydrolupinine picrate of m. p. 154°. The 152° picrate gave $[\alpha]_D$ — 53° in ethyl acetate, and ψ-anhydrolupinine picrate $[\alpha]_D$ — 54·8° in the same solvent.

The same basic fraction (0·1 g.) in acetone gave, with methyl iodide, a crystalline solid which on extraction with acetone left a residue, m. p. 290—295°. This crystallised from aqueous ethyl alcohol (1 : 9) in long colourless prisms, m. p. 308°, not depressed by admixture with the dimethiodide of ω-dimethylaminolupinane (see below). On concentration of the acetone extract a crystalline deposit was obtained which melted at 198—210°, a behaviour characteristic of the mixture of α- and β-ψ-anhydrolupinine methiodides.

ω-*Dimethylaminolupinane* was prepared from ω-chlorolupinane and dimethylamine and obtained as a colourless oil, b. p. 95°/0·5 mm., $[\alpha]_D$ −37·7° in acetone (Found: C, 73·6; H, 12·2. $C_{12}H_{24}N_2$ requires C, 73·4; H, 12·2%). The *dimethiodide* formed long colourless prisms, m. p. 308°, from dilute alcohol (90%) (Found: C, 35·1; H, 6·4. $C_{14}H_{30}N_2I_2$ requires C, 35·0; H, 6·3%).

11-*Aminolupinane.*—Chlorolupinane (25·3 g.), potassium phthalimide (28 g.), and a trace of copper powder were heated for 72 hours at 210—220°. The reaction mixture was ground with dilute sodium hydroxide solution, washed with water, and dried. The product (32—33 g., m. p. 160—162°) was vacuum-distilled in portions, giving 31 g. of m. p. 164—165°, and then crystallised from light petroleum (b. p. 80—100°), giving N(11)-*lupinylphthalimide* as long colourless prisms, m. p. 165° (Found: N, 9·3. $C_{18}H_{22}O_2N_2$ requires N, 9·4%). The compound was unchanged in concentrated sulphuric acid after 24 hours.

The electrolytic reduction of the above phthalimide (2 g.) in 20% sulphuric acid gave N-*lupinyldihydro*iso*indole,* which formed long colourless prisms, m. p. 88°, from ligroin (b. p. 40—60°) (Found: C, 80·1; H, 9·8; N, 9·9. $C_{18}H_{26}N_2$ requires C, 80·0; H, 9·6; N, 10·4%).

The hydrolysis of lupinylphthalimide was effected by dissolving the crude material (9 g.) in ethyl alcohol (90 c.c.), adding hydrazine hydrate (3 c.c. of 90—95%), and refluxing the mixture for 45 minutes. Hydrochloric acid (15 c.c.; 1 : 3) was then added and after some time the phthalylhydrazide was filtered off, the filtrate evaporated to dryness on the water-bath under reduced pressure, potassium hydroxide solution (75 c.c., *d* 1·25) added, and the liberated base extracted with ether. After it had been dried over potassium carbonate, fractionation gave 11-aminolupinane (4·4 g.), b. p. 98°/1 mm. The compound rapidly absorbed carbon dioxide from the air and it formed a *benzoyl* derivative, which crystallised from light petroleum (b. p. 80—100°) in thin colourless prisms, m. p. 131—132° (Found: C, 74·5; H, 8·7. $C_{17}H_{24}ON_2$ requires C, 75·0; H, 8·8%).

N(11)-*Lupinylsuccinimide* (IV) *and Dilupinylsuccinamide* (V).—Aminolupinane (4·4 g.) and methyl succinate (4·5 g.) were heated to 160° in 5 minutes and then slowly to 190° during an hour. The product was cooled somewhat, benzene (12 c.c.) added, and the mixture kept for a time and then warmed on the water-bath. The colourless crystals (1·55 g.) of *dilupinylsuccinamide* obtained formed thin rectangular prisms, m. p. 225—226°, on recrystallisation from alcohol or benzene (Found: C, 69·0; H, 9·9. $C_{24}H_{42}O_2N_2$ requires C, 68·9; H, 10·05%).

The original filtrate was fractionated, and after recovery of some methyl succinate 4·4 g. of oil passed over at 210—220°/1 mm. and at once solidified. By crystallisation from light petroleum (b. p. 80—100°), *lupinylsuccinimide* (IV) was obtained in long colourless prisms (4 g.), m. p. 137° [Found: C, 67·3; H, 8·7; N, 11·2; *M* (Rast), 244, 250, 245. $C_{14}H_{22}O_2N_2$ requires C, 67·2; H, 8·8; N, 11·2%; *M*, 250]. It is readily soluble in most organic solvents, in cold water, giving a strongly alkaline solution, and in dilute acids, and forms a *methiodide* which separates from 90% alcohol in thin colourless plates, m. p. 290; on standing in contact with the solvent, these change to stout prisms, m. p. 293—294° (Found: C, 46·0; H, 6·5. $C_{15}H_{25}O_2N_2I$ requires C, 45·9; H, 6·37%).

N(11)-*Lupinylpyrrolidine*.—Through a solution of the above base (IV) (2·2 g.) in 20% sulphuric acid (30 c.c.), a current of 3 amps. was passed for 12 hours (compare J., 1918, **113**, 764). From the reaction mixture, made strongly alkaline with sodium hydroxide, ether extracted a colourless oil (1 g.), b. p. 155°/1 mm.; this gave a *dimethiodide* which crystallised from 90% ethyl alcohol as thin colourless prisms, changing to stout prisms, m. p. 302° (decomp.) (Found: C, 37·9; H, 6·3. $C_{14}H_{16}N_2$,2MeI requires C, 37·9; H, 6·3%).

The compound (V) is not reduced under the above conditions.

Methyl N(11)-*Lupinylglutaramate* (VI) *and Dilupinylglutaramide* (VII).—A mixture of aminolupinane (3·2 g.) and methyl glutarate (3·2 g.) was heated at 180° for 75 minutes and cooled somewhat and benzene (5 c.c.) and then light petroleum (15 c.c., b. p. 80—100°) were added. The resulting gelatinous mixture was heated for a time on the water-bath and 1·6 g. of (VII) were then separated by filtration. The filtrate on fractionation gave methyl glutarate (1·9 g.) and (VI) (2·65 g.), b. p. 210—225°/1 mm., which solidified and then crystallised from benzene–light petroleum (1 : 9) in colourless plates, m. p. 75—76° (Found: C, 64·7; H, 9·6; *M*, 302, 286. $C_{16}H_{28}O_3N_2$ requires C, 64·8; H, 9·5%; *M*, 296); the mother-liquor gave thin colourless prisms, m. p. 103°, in amount insufficient for a full examination. *Methyl* N(11)-*lupinylglutaramate* distils unchanged after being heated for 2 hours at 180—190°/1 mm.

Dilupinylglutaramide (1·6 g.) crystallised slowly from ethyl alcohol in irregular prisms, m. p. 193—195° (Found: C, 69·4; H, 10·5. $C_{25}H_{44}O_2N_4$ requires C, 69·5; H, 10·2%).

Bromo-α-methyloxysparteine.—Bromine (5·9 g.) in benzene (100 c.c.) was slowly added to α-methyloxysparteine (10 g.) in benzene (100 c.c.) with shaking and cooling in running water. A bulky, pale yellow precipitate (13·6 g.), m. p. 185°, was formed, which, on crystallisation from absolute ethyl alcohol (4·5 c.c. per g.) gave *bromo-α-methyloxysparteine hydrobromide* (6·5 g.), m. p. 214° (Found: Br, 37·9. $C_{16}H_{25}ON_2Br$,HBr requires Br, 38·05%). This salt (3·6 g.) was heated for 5 hours with anhydrous potassium carbonate (3·6 g.) in alcohol (10 c.c.), and hot water was added to the filtered solution until a faint permanent turbidity appeared. On cooling, *bromo-α-methyloxysparteine* separated in colourless prisms, m. p. 142° (yield, almost theoretical) (Found: C, 56·3; H, 7·3; Br, 23·65. $C_{16}H_{25}ON_2Br$ requires C, 56·4; H, 7·4; Br, 23·4%).

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