CCXXXII.—*The Lupin Alkaloids. Part I.*

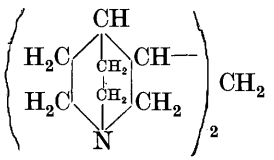
By GEORGE ROGER CLEMO and GRACE CUMMING LEITCH.

THIS group of alkaloids includes lupinine, $C_{10}H_{19}ON$, sparteine, $C_{15}H_{26}N_2$, lupanine, $C_{15}H_{24}ON_2$, and hydroxylupanine, all of which have been isolated from one or other of the different varieties of lupin seeds. Although numerous chemists have worked on these alkaloids, the present real knowledge of their structures is very scanty indeed. For instance, in spite of the fact that bridged piperidine ring systems have been postulated for these compounds, it appears that there is not a single recorded case of a monocyclic pyridine or piperidine derivative having been definitely obtained from any of them.

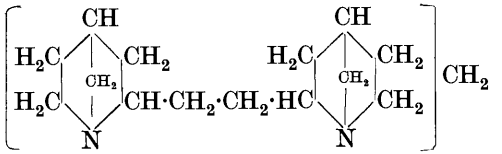
Lupinine, present in *Lupinus luteus*, was examined by Willstätter and Fourneau (*Ber.*, 1902, **35**, 1914), who concluded that it contained a primary alcoholic side chain, together with a tertiary nitrogen atom probably common to two rings as in quinuclidine. Recently, Kalle & Co. (D.R.-PP. 386,936 and 396,508) have described the production of chlorolupinine and lupinan, $C_{10}H_{19}N$; but the structural question appears to be still as left by Willstätter in 1902.

The chief workers on sparteine have been Moureu and Valeur, who advanced the β-diquinuclidylmethane formula (I) for this alkaloid (*Compt. rend.*, 1905, **141**, 117). Germain (*Gazzetta*, 1912, **42**, i, 447) oxidised sparteine with permanganate in phosphoric acid solution

and, obtaining some succinic acid, felt justified in advancing formula (II) for the alkaloid.

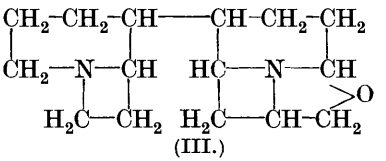


(I.)

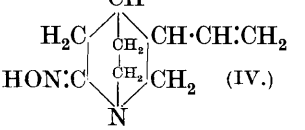


(II.)

Lupanine occurs in the dextro- and the inactive form in *L. albus* and in the dextro-form in *L. angustifolius*, and the inactive modification can be easily isolated in a pure condition from *L. termis*, which appears to be native to North Africa and Syria. The authors are greatly indebted to Dr. R. G. A. Heathcote, of the Royal School of Medicine, Cairo, for securing the necessary seed and extracting the first batch of *i*-lupanine used in this investigation. The early workers on lupanine include Schmidt (*Arch. Pharm.*, 1897, **235**, 192), who advanced the empirical formula $C_{15}H_{24}ON_2$, and Davis (*ibid.*, p. 199), who proved the absence of a reactive carbonyl or hydroxyl group. Many chemists, including Siebert (*ibid.*, 1891, **229**, 544), Callsen (*ibid.*, 1899, **237**, 577), Soldaini (*Gazzetta*, 1903, **33**, 1428), and Beckel (*Arch. Pharm.*, 1912, **250**, 691), have studied the oxidation of the alkaloid, but except oxalic acid, no oxidation product appears to have been isolated in quantity sufficient for its characterisation. Beckel (*Arch. Pharm.*, 1911, **249**, 329) concluded from titration experiments that lupanine is a monoacidic base (see p. 1813). Molander (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 265) subjected the alkaloid to drastic treatment with fuming hydrochloric acid at 210°, to fusion with caustic potash, etc., but in all cases the lupanine was recovered almost wholly unchanged. Thoms and Bergerhoff (*Arch. Pharm.*, 1925, **263**, 1) state that lupanine is recovered when its methylammonium hydroxide is distilled in a vacuum, but that when the alkaloid is distilled with zinc dust a small proportion is changed to give, together with other products, what they describe, mainly from its odour and boiling point, as α-ethylpyridine. On these grounds, they advanced the tentative formula (III) for the alkaloid.



(III.)



(IV.)

The only definitely established facts, however, are that lupanine possesses a very stable, fully saturated ring system with one reactive

tertiary nitrogen atom, and no reactive carbonyl, hydroxyl, or methoxyl groups.

It has now been found that lupanine forms a crystalline *dihydrochloride*. The basic nature of both nitrogen atoms is thus proved, but the result does not exclude the presence of a lactam group >N·CO–, for α-quinuclidones, if they were known, might be expected to be basic from the fact that α-oximino-β-vinylquinuclidine (IV) forms a methiodide (*Ber.*, 1908, **41**, 68). The presence of such a group, whilst explaining why lupanine is very much more soluble in water than deoxylupanine (see p. 1819) or sparteine, is yet difficult to reconcile with its ready solubility in ether and ligroin, with its great stability to acids and alkalis, and with the fact that it cannot be reduced electrolytically. The alternative is that lupanine has an ethereal oxygen atom. Notwithstanding its dibasic character the alkaloid yields only a *monomethiodide* and a *monomethosulphate*, in this respect resembling sparteine. Lupanine methiodide is a stable compound, crystallising unchanged after refluxing with methyl-alcoholic potash, and its quaternary ammonium hydroxide when vacuum-distilled gives lupanine and methyl alcohol. Again, when the methiodide is heated in a vacuum with caustic soda, lupanine is largely regained; but if a mixture of caustic potash and caustic soda is used, the distillate contains, in addition to some lupanine, two methyl-lupanines and a small proportion of simpler bases; and if caustic potash alone is used, the bulk of the distillate consists of simpler bases.

From what follows, it seems probable that the lupanine oxygen atom is in that part of the molecule containing the reactive tertiary nitrogen atom involved in these changes, and if the latter is in a quinuclidine system linked in either the α- or the β-position to the rest of the molecule (see I), more than two methyl-lupanines might be expected to result by the elimination of hydrogen iodide from lupanine methiodide. So far, however, only two methyl-lupanines have been obtained, one of which, *α-methyl-lupanine*, is, remarkably enough, a water-insoluble solid; the *β-compound*, apparently an oil, is easily soluble in water and has only been obtained pure in the form of its crystalline *methiodide*. The α-compound forms a *monohydrochloride* and a *monomethiodide*, and α-methyl-lupanine methylammonium hydroxide, when distilled in a vacuum, is largely converted into an isomeric oil, soluble both in water and in ether (*i.e.*, apparently $\overset{-CH_2}{\underset{-NMe_2}{>}}NMe_2\cdot OH \longrightarrow \overset{-CH_2\cdot OH}{-NMe_2}$), which has not yet been satisfactorily converted into a crystalline methiodide. In addition, a small proportion of α-methyl-lupanine is recovered from the distillate.

When lupanine methiodide is heated in a metal bath with caustic potash, the bulk of the distillate boils below 145°/1 mm. (b. p. of lupanine, 190°/1 mm.) and contains a mixture of bases, three of which have given crystalline derivatives: *e.g.*, a small fraction, b. p. 88—92°/1 mm. (approx.), gives mainly a *picrate* (m. p. 130°) together with a small amount of a second *picrate* which decomposes at 225°, and the fraction, b. p. 127—132°/1 mm., gives a crystalline *picrate* and a *dimethiodide*. Analytical results point to the empirical formula $C_{13}H_{22}N_2$ for the latter *base*, but the question of determining the structure of these degradation products, which are probably derivatives of quinuclidine, is rendered difficult by the fact that the literature contains few references to such compounds, and some of these, as, for instance, the observation by Koenigs (*Ber.*, 1904, **37**, 3250) that the β-ethylquinuclidine methiodide melts between 55—85°, are not very helpful for characterisation purposes. Accordingly, the detailed examination of these bases may have to be supplemented by synthetic work before their structures can be settled.

The possibility that lupanine may be an oxygen derivative of sparteine caused attention to be directed to the action of reducing agents on the base. Prolonged heating at 220° in sealed tubes with fuming hydriodic acid and red phosphorus gave *deoxylupanine*, $C_{15}H_{26}N_2$, but 25% of the lupanine was recovered unchanged. Deoxylupanine is an oil which forms a *monomethiodide* and is sparingly soluble in cold water. The question of its structural relationship to sparteine, which occurs naturally in the lævo-form, is complicated by the fact that it has not been possible to racemise the latter or resolve the former. That no ring change occurs in the preparation of deoxylupanine seems certain from the fact that sparteine can be recovered unchanged after a similar treatment. This fact indicates the presence of the quinuclidine ring system, as β-ethylquinuclidine is stable to hydriodic acid, which decomposes, for example, pyridine and coniine. Deoxylupanine and sparteine, however, differ in some respects in their chemical properties, which points to some structural dissimilarity. For instance, deoxylupanine is much more stable to air than sparteine, and it gives crystalline *mono-* and *di-picrates*, whereas sparteine only forms a crystalline dipicrate. When hydrogen sulphide is passed into an ethereal solution of deoxylupanine containing sulphur in suspension, an orange precipitate results in contrast with the dull red one given by sparteine. Both bases, however, can be readily oxidised to give iso*lupanine* and oxysparteine, respectively. *iso*Lupanine resembles lupanine in being very easily soluble in water to give an alkaline solution, and also in organic solvents. It shows no evidence of the

presence of a reactive carbonyl group, and forms only a *monomethiodide*. Neither lupanine, *iso*lupanine, nor oxysparteine gives a precipitate in the hydrogen sulphide test.

Although, as stated, numerous chemists have unsuccessfully studied the oxidation of lupanine, it has now been found that it can be easily oxidised by permanganate in acetone solution to give *oxylupanine*, $C_{15}H_{22}O_2N_2$. Curiously enough, the action always ends when five atomic proportions of oxygen have been used up, and in addition to oxylupanine a very small amount of another oxidation product and some oxalic acid are also formed. Oxylupanine is a deliquescent compound giving an aqueous solution which is neutral to litmus. It has no reactive carbonyl, methylene, or hydroxyl group, as judged by its non-reactivity with phenylhydrazine, piperonal, and benzoyl chloride, and contains no reactive tertiary nitrogen atom. It seems certain, however, that *iso*lupanine, oxylupanine, and oxysparteine are formed by the conversion of methylene into carbonyl groups. As these are all non-reactive, the case for the presence of a carbonyl group in lupanine is strengthened. These facts can be explained if the reactive tertiary nitrogen atom of lupanine is in a quinuclidine ring, which can form at least two isomeric α-quinuclidones, whose lactam carbonyl groups might be expected to be non-reactive. On this basis, oxylupanine might be the αα′-diketo-compound with the nitrogen no longer basic. Against this inference, however, must be put the fact that no oxidation results similar to the above have been observed with the quinine alkaloids, and further the lupin alkaloids differ completely in physiological action from the latter. Again, it is unlikely that α-quinuclidones would be stable to both alkalis and acids, judging from the fact that α-oximino-β-vinylquinuclidine (IV) is hydrolysed by dilute acids, presumably *via* the α-quinuclidone, to meroquinine.

It is hoped to describe the extension of the work along the aforementioned and cognate lines, and its further bearing on the structural problem presented by these alkaloids, in a future communication.

Experimental.

i-*Lupanine*.—Crude lupanine sulphate * (80 g.) was dissolved in water (60 c.c.) and made alkaline with caustic potash (160 c.c.; *d* 1·25), and the liberated base was extracted with chloroform and fractionated; 41·5 g. of a colourless viscid oil passed over at 185—195°/1 mm. and 2 g. at 195—220°/1 mm. The main fraction quickly crystallised (softened at 85°; m. p. 95°), and after recrystallising from acetone (24 c.c.) gave colourless, prismatic plates (30 g.),

* The authors are much indebted to Messrs T. and H. Smith, Ltd., of Edinburgh for carrying out the extraction of the seed on a large scale.

m. p. 98—99° (Found: C, 72·7; H, 9·8; N, 11·4. Calc. for $C_{15}H_{24}ON_2$: C, 72·6; H, 9·7; N, 11·3%). *i*-Lupanine is very easily soluble in cold water, giving a strongly alkaline solution, and in the usual organic solvents.

Lupanine Mono- and Di-hydrochlorides.—The precipitate obtained by passing hydrogen chloride into a solution of lupanine (1 g.) in dry ether (20 c.c.) was collected and dissolved in absolute alcohol (10 c.c.). On dilution with ether (15 c.c.), stout colourless prisms separated, m. p. 185° (decomp.) (Found: C, 55·7; H, 7·9; Cl, 21·6. $C_{15}H_{24}ON_2,2HCl$ requires C, 56·1; H, 8·1; Cl, 22·1%). The *dihydrochloride* is deliquescent, its aqueous solution being acid to litmus. When it is heated under 1 mm. pressure, decomposition occurs and a sublimate of the very deliquescent crystalline monohydrochloride is formed (Found: Cl, 12·0. Calc. for $C_{15}H_{24}ON_2,HCl$: Cl, 12·4%).

Lupanine Monomethiodide.—When lupanine (as obtained direct by distillation; 41·5 g.), dissolved in acetone (50 c.c.), was mixed with methyl iodide (20 c.c.), the *methiodide* began to separate almost at once. The mixture was refluxed gently over-night, the crystalline precipitate collected and ground with a small volume of alcohol, and the product (62 g.; decomp. 246—250°) recrystallised from absolute alcohol, giving stout prisms (51·5 g.), m. p. 258—260° (decomp.), raised to 262—263° by a further crystallisation from alcohol (Found: C, 49·8; H, 7·1; I, 33·0. $C_{15}H_{24}ON_2,MeI$ requires C, 49·2; H, 6·9; I, 32·6%). The methiodide is very soluble in water and sparingly soluble in absolute alcohol.

Lupanine Monomethosulphate.—Methyl sulphate (1·3 g.) was added to lupanine (2·5 g.) in acetone (5 c.c.), and the solution refluxed over-night. The resulting deliquescent prisms (2·7 g.), m. p. 188°, decomp. 275°, were recrystallised from alcohol (3 c.c.) by dilution with acetone (10 c.c.); m. p. 196° (Found: C, 54·6; H, 8·0. $C_{17}H_{30}O_5N_2S$ requires C, 54·5; H, 8·0%).

Action of Alkalis on Lupanine Methiodide.—(a) *α- and β-Methyllupanines.* The powdered methiodide (2 g.), mixed with caustic potash (1·5 g.) and caustic soda (1·5 g.), was carefully heated under 1 mm. pressure with a free flame, an absorbent charcoal trap being placed between the receiver and the pump. Five such experiments, after the recovery of a small quantity from the trap, gave 5·7 g. of distillate, which set to a buttery mass and on fractionation gave 0·2 g., b. p. up to 145°/1 mm., 1·4 g., b. p. 145—180°/1 mm., and 3·9 g., b. p. 180—190°/1 mm. The last fraction while still an oil was stirred with cold water (25 c.c.), and the resulting colourless solid was collected—filtrate X—washed with a little water, dried on the water-bath, and crystallised (1·5 g.) from a small volume of ligroin (b. p.

60—80°); well-defined, colourless prisms then separated, m. p. 123° (Found : C, 73·7, 73·2; H, 9·7, 9·9; N, 10·2; OMe, 0; *M*, cryoscopic in benzene, 274. $C_{16}H_{26}ON_2$ requires C, 73·3; H, 9·9; N, 10·7%; *M*, 262). *α-Methyl-lupanine* is readily soluble in the usual organic solvents, but insoluble in water, and its cold acetone solution rapidly decolorises potassium permanganate. From a solution of the base in ether, hydrogen chloride precipitates the *monohydrochloride*, which crystallises from alcohol–ether in flat prisms, m. p. 209° (decomp.) (Found : Cl, 11·2. $C_{16}H_{26}ON_2$,HCl requires Cl, 11·9%).

α-Methyl-lupanine methiodide. The base (3·3 g.) was heated overnight in a sealed tube in the water-bath with methyl alcohol (4 c.c.) and methyl iodide (4 c.c.); the crystalline deposit (4·3 g.), when recrystallised from alcohol, formed stout colourless prisms, m. p. 258° (decomp.) (Found : C, 51·0; H, 7·3; N, 6·9; I, 31·4. $C_{16}H_{26}ON_2$,MeI requires C, 50·5; H, 7·2; N, 6·9; I, 31·4%). The compound was very soluble in cold water, and when distilled with caustic potash in a vacuum gave a mixture of bases apparently similar to those described under (b) below. When, however, the methyllupanine methylammonium hydroxide from this methiodide (4·3 g.) was distilled in a vacuum, 2·8 g. of a colourless viscid oil passed over at 190—215°/1 mm., from which 0·3 g. of α-methyl-lupanine was recovered by stirring with water. On fractionating the aqueous filtrate, 2·2 g. of oil passed over at 210—215°/1 mm. (Found : C, 69·9; H, 10·4. $C_{17}H_{30}O_2N_2$ requires C, 69·4; H, 10·2%); this *base* was readily soluble in water and in ether.

The aqueous filtrate X on fractionation gave 2·1 g., b. p. 180—195°/1 mm. This was combined with similar material to give 11 g., and then fractionated into equal first and last fractions. The former slowly set to a buttery mass of lupanine. The latter also deposited a small amount of this base, which was filtered off and the filtrate was refractionated, giving 0·8 g., b. p. up to 188°/1 mm., 2·2 g., b. p. 188°/1 mm., and 1 g., b. p. 188—190°/1 mm. The middle and last fractions were treated in acetone with methyl iodide over-night and the crystalline deposit was then collected and dissolved in absolute alcohol. On cooling, some finely divided, crystalline lupanine methiodide quickly separated. This was removed, and large compact prisms separated from the filtrate over-night. These, after recrystallisation from alcohol, had m. p. 272° (decomp). alone and m. p. below 250° (decomp.) when mixed with lupanine methiodide (Found : C, 51·9; H, 7·2; N, 6·6; I, 31·7. $C_{16}H_{26}ON_2$,MeI requires C, 50·5; H, 7·2; N, 6·9; I, 31·4%). *β-Methyl-lupanine methiodide* is very soluble in water, and more soluble in alcohol than lupanine methiodide.

(b) *The base* $C_{13}H_{22}N_2$. Lupanine methiodide (2 g.), well mixed with caustic potash (3 g.) and heated under 1 mm. pressure at 260°, decomposed, giving a solid mass. The heating at 260° was continued for 15 minutes and the temperature of the bath was then raised to 300°; an oil distilled during the next 5 to 10 minutes. The combined distillates from twelve such experiments (11 g.) were divided into the following fractions: (i) 1·2 g., b. p. 85—112°/1 mm.; (ii) 7·5 g., b. p. 112—132°/1 mm.; (iii) 0·6 g., b. p. 132—150°/1 mm.; (iv) 1·7 g., b. p. up to 170°/1 mm.

When fraction (i) was redistilled, half of it passed over at 88—92°/1 mm. (Found: C, 79·4; H, 10·5; N, 10·8%). This oily *base* was slightly soluble in cold water, giving an alkaline solution, and its cold acetone solution slowly decolorised potassium permanganate. The base (0·5 g.) was boiled with picric acid (0·9 g.) in alcohol (20 c.c.) for 1 minute; the solution was then cooled and decanted from 0·1 g. of a *product* which crystallised from acetic acid in yellow prisms, decomp. 225° after darkening at 215°. The decanted alcoholic solution was partly evaporated, and ether added; lemon-yellow plates then separated, m. p. 130—131° (Found: C, 52·7, 53·0: H, 5·0, 5·2. $C_{18}H_{20}O_7N_4$ requires C, 53·4; H, 4·9%. $C_{17}H_{18}O_7N_4$ requires C, 52·3; H, 4·6%).

When fraction (ii) was redistilled, a large proportion passed over at 127—132°/1 mm.; the portion, b. p. 130°/1 mm., was analysed (Found: C, 76·5; H, 10·4; N, 13·4. $C_{13}H_{22}N_2$ requires C, 75·7; H, 10·7; N, 13·6%). The oil is sparingly soluble in water, and its cold acetone solution decolorises potassium permanganate.

Picrate of the base $C_{13}H_{22}N_2$. An alcoholic solution of the fraction, b. p. 127—132°/1 mm. (1 g.) and picric acid (1·25 g.) was boiled for 1 minute, cooled, and decanted from a small quantity of gum; the *picrate* (1·4 g.) slowly separated in yellow prisms, and melted at 137° after recrystallisation from alcohol (Found: C, 52·3, 52·5; H, 5·8, 6·1. $C_{13}H_{22}N_2,C_6H_3O_7N_3$ requires C, 52·4; H, 5·8%).

Dimethiodide of the base $C_{13}H_{22}N_2$. When the fraction, b. p. 127—132°/1 mm. (1 g.), acetone (3 c.c.), and methyl iodide (1 c.c.) were mixed together, much heat was evolved and an oil separated. After 12 hours, the crystals that had formed were collected, and recrystallised from a solution in alcohol by dilution with acetone, giving almost colourless, compact prisms, m. p. 202°, decomp. 280° (Found: C, 37·3; H, 5·9. $C_{13}H_{22}N_2,2MeI$ requires C, 36·9; H, 5·7%).

Deoxylupanine.—Four sealed glass tubes, each containing lupanine (1·25 g.), hydriodic acid (5 c.c.; *d* 2), and red phosphorus (1·25 g.), were heated for 36 hours at 220°, much pressure being developed. The viscid product was heated at 150° under diminished pressure to

remove the excess of hydriodic acid, the residue treated with caustic potash solution (100 c.c.; *d* 1·25), and the liberated oil extracted with chloroform and fractionated; 1·7 g. passed over at 140—170°/1 mm., followed at 170—190° by 0·8 g. which set to a soft crystalline mass of lupanine. The first fraction was seeded with lupanine and left for some days in an ice-chest, the separated lupanine was filtered off, and the filtrate fractionated; the bulk passed over at 145°/1 mm., leaving a small residue of lupanine (Found: C, 77·4; H, 11·2; N, 11·6. $C_{15}H_{26}N_2$ requires C, 76·9; H, 11·1; N, 11·9%). *Deoxylupanine* is sparingly soluble in water, giving an alkaline solution. A deliquescent *dihydrochloride* is formed when hydrogen chloride is passed into an ethereal solution of the base and can be crystallised by slowly diluting its cold alcoholic solution with ether (Found: Cl, 23·0. $C_{15}H_{26}N_2,2HCl$ requires Cl, 23·1%).

Mono- and di-picrates of deoxylupanine. When ethereal solutions containing equal weights of the base and picric acid were mixed, a yellow precipitate of the *monopicrate* was formed, which crystallised from alcohol in well-formed, yellow, hexagonal prisms, m. p. 135° (Found: C, 54·9; H, 6·3. $C_{15}H_{26}N_2,C_6H_3O_7N_3$ requires C, 54·4; H, 6·3%).

The precipitate of the *dipicrate* formed when alcoholic solutions of deoxylupanine (0·25 g.) and picric acid (0·5 g.) were mixed crystallised from alcohol in lemon-yellow needles, m. p. 206—207° (Found: C, 46·7; H, 5·1. $C_{15}H_{26}N_2,2C_6H_3O_7N_3$ requires C, 46·8; H, 4·6%). A mixture with sparteine dipicrate (m. p. 208°) melted at 198—200°.

Deoxylupanine methiodide. The base (1·3 g.) was added to acetone (2 c.c.) and methyl iodide (1 c.c.); after 12 hours, 1·8 g. of the *methiodide* had separated, which crystallised from acetone in colourless plates, m. p. 226° (Found: C, 51·5; H, 7·9. $C_{15}H_{26}N_2,MeI$ requires C, 51·1; H, 7·7%).

iso*Lupanine*.—Deoxylupanine (1·2 g.) on oxidation * gave 0·9 g. of a distillate which crystallised; on recrystallisation from ligroin (b. p. 40—60°) colourless plates, m. p. 113°, were obtained (Found: C, 72·6; H, 9·7. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7%). Mixed with lupanine, the substance melted at 78—80°. When heated in a sealed tube with methyl alcohol and methyl iodide, iso*lupanine* gave a crystalline *monomethiodide*, which separated from alcohol–acetone (1 : 2) in colourless plates, m. p. 208°.

Oxylupanine.—Lupanine (2·5 g.) was dissolved in acetone (30 c.c.), and powdered potassium permanganate (5·3 g.) added during about 4 hours with stirring and cooling in an ice-bath. After being left overnight, the mixture was stirred for ½ hour and filtered, and the sludge extracted with acetone. The solvent was then removed from the

* Details of the method will be published shortly.

filtrate, and the residue* distilled; at about 210°/1 mm., 1·4 g. passed over, which crystallised from acetone in stout colourless prisms, m. p. 123° (Found: C, 69·1; H, 8·3; N, 10·5; *M*, cryoscopic in benzene, 266, 275. $C_{15}H_{22}O_2N_2$ requires C, 68·7; H, 8·4; N, 10·7%; *M*, 262). *Oxylupanine* forms a *chloroplatinate* which crystallises from alcohol in brown prisms, m. p. 232° (decomp.). By means of this salt the value 266 was obtained for the molecular weight of oxylupanine. After being refluxed in alcoholic or acetic acid solution with phenylhydrazine for 24 hours, or in ethereal solution containing benzoyl chloride with sodium bicarbonate in suspension, oxylupanine was recovered unchanged. It could not be condensed with piperonal, and it was also recovered after being heated in acetic acid solution, saturated with hydrogen chloride, for 24 hours at 240°.

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