129. *The Alkaloids of* Anagyris Foetida *and their Relation to the Lupin Alkaloids.*

By H. Raymond Ing.

The alkaloids of *Anagyris foetida* were first investigated by Partheil and Spasski (*Apoth.-Ztg.*, 1895, **10**, 903), who isolated cytisine and a varnish-like base which they named anagyrine. The subject was later taken up by Litterscheid (*Arch. Pharm.*, 1900, **238**, 191, 230) and Klostermann (*ibid.*, p. 227). Anagyrine was not obtained crystalline, but analysis of its salts indicated the formula $C_{15}H_{22}ON_2$. It was a ditertiary base, but formed only a monomethiodide. Like cytisine, it was readily brominated and its oxygen atom was unreactive. Litterscheid regarded it as a cytisine derivative, possibly *N*-butylcytisine, but Goessmann (*Arch. Pharm.*, 1906, **244**, 30) later threw doubt upon the accepted formula.

The chief difficulty facing the early investigators was the initial separation of anagyrine from cytisine, which it resembled closely. Klostermann effected a partial separation by precipitating anagyrine as its less soluble mercurichloride, and Litterscheid removed most of the cytisine as its phenylthiocarbamide derivative. It has now been found that anagyrine is much more readily extracted by benzene from its aqueous solution than cytisine and that its *perchlorate* is much less soluble in water than *cytisine perchlorate*. A rapid and easy separation of the two alkaloids based on these findings is described in the experimental section below.

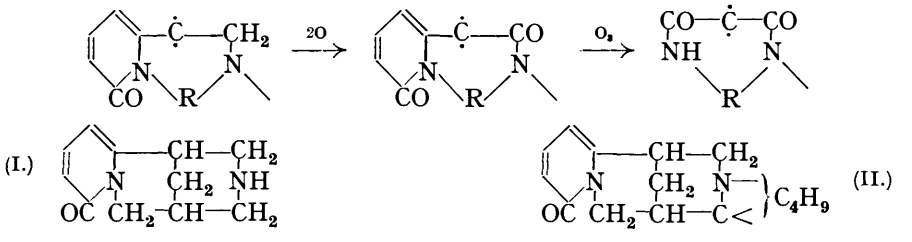
Anagyrine forms a pale yellow glass and has not been obtained crystalline. It is lævorotatory and has the composition $C_{15}H_{20}ON_2$, a formula which is supported by the analysis of its salts and simple derivatives. Consequently it differs from cytisine by C_4H_6, not C_4H_8 as found by previous workers, a result which suggests that it may be derived from cytisine by the formation of a new piperidine or methylpyrrolidine ring.

Anagyrine resembles cytisine in the following particulars : (i) It contains an unreactive oxygen atom and gives a red colour with ferric chloride. (ii) It is readily brominated to form *dibromoanagyrine*, $C_{15}H_{18}ON_2Br_2$ (isolated by Klostermann as the hydrobromide), which is readily reduced to anagyrine, but does not lose hydrobromic acid with alkali. (iii) It is reduced with difficulty, but catalytic hydrogenation above 80° yields *tetrahydroanagyrine*, $C_{15}H_{24}ON_2$. (iv) It is reduced electrolytically to *hexahydrodeoxyanagyrine*, $C_{15}H_{26}N_2$. These reduction products will be considered later (p. 506). (v) It is oxidised by barium permanganate to a crystalline substance, $C_{15}H_{18}O_2N_2$, probably identical with the " anagyrine oxide " of Litterscheid (*loc. cit.*), which it is proposed to call *anagyramide* by analogy with the *N*-methylcytisamides (Ing, J., 1932, 2778).

Anagyramide contains no hydroxyl or ketone group and does not form a methiodide. It is remarkably stable to hydrolytic agents, but on treatment with hydriodic acid and phosphorus at 240° it loses carbon dioxide and yields a new secondary base, *anagyramine*, $C_{14}H_{20}ON_2$, which was characterised by *nitroso-* and *acetyl* derivatives. On ozonisation anagyramide loses C_4H_2 and yields a new lactam, $C_{11}H_{16}O_2N_2$. The loss of C_4H_2 in this reaction is analogous to the similar loss in the ozonisation of tetrahydrohemicytiseline (Späth and Galinovsky, *Ber.*, 1932, **65**, 1526) and taken in conjunction with the bromination and reduction products of anagyrine [(i)–(iv) above] is convincing evidence that this alkaloid contains the α-pyridone ring characteristic of cytisine (Ing, J., 1931, 2195).

The loss of carbon dioxide in the hydrolysis of anagyramide by hydriodic acid suggests that the new carbonyl group is in a position β to the pyridone ring, as was found for β-*N*-methylcytisamide. Moreover the ozonisation product $C_{11}H_{16}O_2N_2$ appears to contain a malonyl residue, since the *benzenesulphonyl* derivative of the corresponding amino-acid loses carbon dioxide at its melting point.

The data so far discussed are summarised in the partial formulæ below and appear to justify the assumption that anagyrine is simply related to cytisine (I) (Ing, *locc. cit.*) :

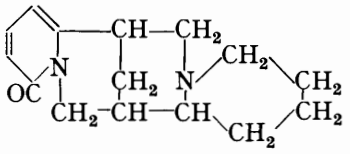


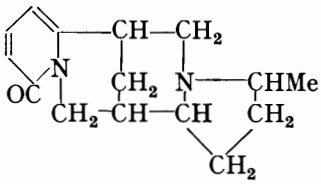
Anagyrine contains no methylimino-group and consequently (II) represents the simplest way of deriving anagyrine from cytisine, where C_4H_9 is part of a new piperidine or methylpyrrolidine ring.

In order to obtain more data bearing on formula (II) anagyrine was subjected to exhaustive methylation, followed by catalytic reduction at each stage. Anagyrine methohydroxide decomposed smoothly in boiling benzene and the product was readily hydrogenated to *dihydromethylanagyrine*. If the methohydroxide be decomposed at higher temperatures, the product probably polymerises, since it cannot then be hydrogenated. After two further degradations the end product, *hexahydroanagyryline*, $C_{15}H_{23}ON$, was obtained. It was a feebly basic oil which lost C_4H_2 on ozonisation to give a *lactam*, $C_{11}H_{21}ON$, which was hydrolysed and oxidised with elimination of the amino-group. An oily *acid*, $C_{11}H_{20}O_4$, was obtained, which was converted through its anhydride into a crystalline *imide*, $C_{11}H_{19}O_2N$. By subjecting cytisine to a similar course of degradative reactions, Späth and Galinovsky (*loc. cit.*) obtained αα′-dimethylglutaric acid, and on the basis of (II) anagyrine should yield α-methyl-α′-amylglutaric acid. The melting point of

the imide $C_{11}H_{19}O_2N$ was rather ill-defined (52—54°), but synthetic *α-methyl-α'-n-amylglutarimide* had the same melting point, alone or mixed with it. Consequently it appears legitimate to conclude that anagyrine differs from cytisine in the formation of a piperidine or α-methylpyrrolidine ring as in (III) or (IV).

(III.)



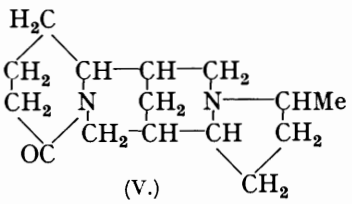


(IV.)

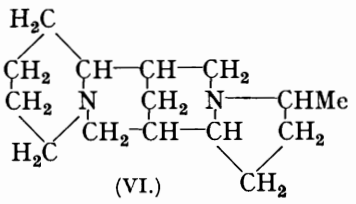
Of these formulæ, (IV) appears to be more probable for a number of reasons. For instance, oxidation of anagyrine yields only one anagyramide (80% yield), whereas methylcytisine yields two methylcytisamides, and consequently it is probable that anagyrine contains only one methylene group attached to the basic nitrogen. Moreover anagyrine, anagyramide, and anagyramine when distilled with zinc dust all yield bases which give pyrrole reactions. Dehydrogenation of dihydromethylanagyrine with selenium also yields bases giving pyrrole reactions. Pure products have not yet been isolated from these reactions, but the available evidence is in favour of (IV).

Anagyrine is structurally related not only to cytisine, but also to the lupin alkaloids. For instance, tetrahydroanagyrine has been found to be identical with *l*-lupanine. Its specific rotation and the melting points and rotations of its hydriodide and thiocyanate leave no doubt of this identity. These salts have also been compared with those of natural *l*-lupanine, specimens of which were kindly given me by Prof. G. R. Clemo. Hexahydrodeoxyanagyrine similarly appears to be identical with *d*-sparteine, although its specific rotation was some 5° low. The melting points of its salts, however, and direct comparison of its picrate with Prof. Clemo's *d*-sparteine picrate leave little doubt of its identity with *d*-sparteine. The close relation between lupanine and sparteine has already been demonstrated by Clemo, Raper, and Tenniswood (J., 1931, 429), who converted *d*- and *l*-lupanine directly into *l*- and *d*-sparteine respectively, and the structural relation of these alkaloids to anagyrine and to cytisine is particularly interesting in view of the wide occurrence of the latter in the *Leguminosæ*.

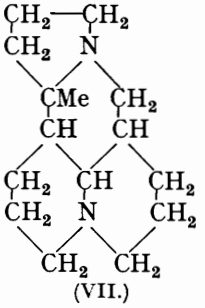
If the arguments in favour of (IV) for anagyrine are well founded, lupanine and sparteine must now be represented by (V) and (VI) respectively.



(V.)



(VI.)



(VII.)

Formula (VI) readily accounts for the formation of two sparteine monomethiodides whatever arrangements of the valencies round the nitrogen and asymmetric carbon atoms be assumed. This would not be true of a sparteine formula derived from (III) for anagyrine, since it could assume a symmetrical form.

These new formulæ for lupanine and sparteine appear to agree with the well-established facts about these alkaloids as well as any formulæ previously suggested. It is established that lupinine contains the octahydropyridocoline ring (Clemo, Ramage, and Raper, J., 1932, 2959; Winterfeld and Holschneider, *Annalen*, 1932, **499**, 109) and Karrer, Canal, Zohner, and Widmer (*Helv. Chim. Acta*, 1928, **11**, 1062) suggested that sparteine was a condensation product of lupinine and piperidine. It may be noted that (VI) differs

from one (VII) of the sparteine formulæ of Winterfeld and Kneuer (*Ber.*, 1931, **64**, 150) only in the carbon–carbon point of attachment of the α-methylpyrrolidine ring. The pentadecane obtained by Karrer and co-workers (*Helv. Chim. Acta*, 1930, **13**, 1292) from sparteine should be on the basis of (VI) a mixture of the *cis*- and *trans*-6 : 8-dimethyltridecanes.

In view of the evidence recently published by Clemo and co-workers (*loc. cit.*) that fully hydrogenated pyridocoline and pyrrocoline can exist in *cis*- and *trans*-forms, formulæ (V) and (VI) indicate the possibility of stereoisomeric lupanines and sparteines. The reduction of anagyrine to lupanine and to sparteine involves the saturation of a tetrahydropyridocolone nucleus, but no evidence was obtained of more than one reduction product in each reaction.

Experimental.

Extraction of Alkaloids.—The alkaloidal content of *Anagyris foetida* seed was kindly extracted for me by Messrs. T. & H. Smith Limited, Edinburgh. The powdered seed was mixed with 10% of its wt. of $Ca(OH)_2$, damped, and percolated with 90% EtOH until exhausted The EtOH was recovered and the alkaloids were shaken out with $CHCl_3$. Most of the $CHCl_3$ was recovered and the alkaloids were supplied as a 50% aq. solution of their mixed hydrochlorides. All evaporation of solvents was effected at a low temp. in a vac. The alkaloid content of the seed was about 3—4% by wt.

Separation of Cytisine and Anagyrine.—The solution of the mixed hydrochlorides (500 c.c.) was treated with NH_3 aq. (*d* 0·880; 150 c.c.) and extracted 5 times with C_6H_6 (150 c.c.). The aq. mother-liquor was then extracted 5 times with $CHCl_3$ (150 c.c.). The C_6H_6 extract was evaporated, and the residue taken up in H_2O and neutralised with $HClO_4$ (*d* 1·12). Most of the anagyrine crystallised as its perchlorate and a second crop was obtained by evaporation of the mother-liquor. The crude perchlorate, recryst. from boiling H_2O (charcoal), formed colourless needles, decomp. about 270° without melting. *Anagyrine perchlorate* is sparingly sol. in cold and readily sol. in boiling H_2O (Found : C, 52·1; H, 5·9; N, 8·0. $C_{15}H_{20}ON_2,HClO_4$ requires C, 52·3; H, 6·1; N, 8·1%).

The $CHCl_3$ extract was dried with Na_2SO_4 and evaporated. The semi-solid residue was extracted with hot EtOAc, leaving an insol. black tar. Crude cytisine crystallised on concn. of the solution and was purified by distillation in vac. and crystn. from acetone. A small amount of anagyrine perchlorate was obtained by neutralising the EtOAc mother-liquors with $HClO_4$. *Cytisine perchlorate* forms colourless needles readily sol. in cold H_2O (Found : N, 10·0. $C_{11}H_{14}ON_2,HClO_4$ requires N, 9·6%).

The ultimate mother-liquors from anagyrine perchlorate have been left for future examination.

Anagyrine, obtained from the perchlorate by treatment with NH_3 aq. and extraction with $CHCl_3$, was purified by distillation (210—215°/4 mm.). It formed a pale yellow glass which darkened in light, was deliquescent, and was not obtained cryst. (Found : C, 73·6; H, 8·1; N, 11·45. Calc. for $C_{15}H_{20}ON_2$: C, 73·8; H, 8·2; N, 11·5. Calc. for $C_{15}H_{22}ON_2$: C, 73·2; H, 8·9; N, 11·4%). In alc. solution (1·796%) it had $[\alpha]_D^{20°}$ − 165·3°. Anagyrine is less sol. in hot than in cold H_2O, readily sol. in EtOH, C_6H_6, Et_2O, and $CHCl_3$, and insol. in ligroin. Like cytisine, it gives a red colour with $FeCl_3$ aq. The hydrochloride forms colourless needles (Found : C, 60·5; H, 7·4; N, 9·8. Calc. for $C_{15}H_{20}ON_2,HCl,H_2O$: C, 60·3; H, 7·4; N, 9·4%). The hydriodide crystallises in anhyd. colourless needles from EtOH (Found : C, 47·9; H, 5·7; NMe, 0. Calc. for $C_{15}H_{20}ON_2,HI$: C, 48·4; H, 5·6%).

Dibromoanagyrine (cf. Klostermann, *loc. cit.*) forms colourless leaflets from EtOH, m. p. 202—203° (Found : C, 45·0; H, 4·6; Br, 39·4. $C_{15}H_{18}ON_2Br_2$ requires C, 44·8; H, 4·5; Br, 39·8%). On reduction with Zn dust and AcOH it gave anagyrine. It was recovered unchanged after boiling with alc. KOH.

Anagyramide.—Anagyrine (24·4 g.), dissolved in H_2O (200 c.c.), was treated gradually with 10% aq. barium permanganate (about 340 c.c., *i.e.*, 2—3 oxygen atoms/mol. of anagyrine) below 10° until the solution remained faintly pink for 5 min. The filtrate and washings from the MnO_2 were evaporated to small bulk in vac., made alkaline, and extracted with $CHCl_3$. The $CHCl_3$ solution was dried with Na_2SO_4 and evaporated. The residue solidified and was crystallised by solution in cold $CHCl_3$ (1 vol.) and addition of light petroleum (4 vols.). The product softened at 195° and melted at 201°. Yield, 21 g. (*i.e.*, approx. 80% of theo.). Final purification was effected by extraction with hot abs. Et_2O and concn. of the ethereal solution.

Anagyramide crystallised in colourless needles, m. p. 201—202°. Litterscheid's "anagyrine oxide" had m. p. 195° (Found: C, 69·9; H, 7·0; N, 10·7. Calc. for $C_{15}H_{18}O_2N_2$: C, 69·8; H, 7·0; N, 10·8%).

Anagyramide is a feebly basic substance which forms no methiodide. It is remarkably stable to acidic and alkaline hydrolysis. 2·5 G. were heated with HI aq. (5 c.c., *d* 1·7) and red P (0·5 g.) at 235—240° for 4 hr. The diluted product was made alkaline and extracted with Et_2O. Removal of the ether left an oil which, after solidifying, was crystallised from light petroleum and finally from hexane. *Anagyramine* melted at 98—99° with softening at 96° (Found: C, 72·7; H, 8·5; N, 12·5. $C_{14}H_{20}ON_2$ requires C, 72·4; H, 8·6; N, 12·1%). Anagyramine formed an *acetyl* derivative which, cryst. from EtOAc, had m. p. 134—135° (Found: C, 70·3; H, 8·1; N, 10·1. $C_{16}H_{22}O_2N_2$ requires C, 70·7; H, 8·0; N, 10·2%), and resisted hydrolysis by boiling with conc. HCl for 2 hr. A *nitroso*-derivative was also obtained in plates, m. p. 127—128°, from Et_2O (Found: C, 64·5; H, 7·2; N, 16·1. $C_{14}H_{19}O_2N_3$ requires C, 64·4; N, 7·3; N, 16·1%).

Anagyramide (5 g.) in $CHCl_3$ (100 c.c.) was treated with ozonised oxygen (1·85 g. O_3). H_2O was added, and the $CHCl_3$ evaporated. The aq. solution was treated with $NaHSO_3$, made alkaline with NH_3 aq., and extracted with $CHCl_3$. Evaporation of the $CHCl_3$ solution left a solid residue (1·2 g.), which was crystallised by solution in abs. EtOH and addition of Et_2O. The new *lactam* had m. p. 258° after sintering at 250° (Found: C, 63·7; H, 7·6; N, 13·7. $C_{11}H_{16}O_2N_2$ requires C, 63·5; H, 7·7; N, 13·5%). The substance was dissolved in 20% KOH aq. by warming and shaken with $Ph{\cdot}SO_2Cl$ (excess). A *benzenesulphonyl* derivative was pptd. by acid and was purified by solution in $NaHCO_3$ aq. and repptn. The ppt. crystallised slowly and melted at 141° (efferv.) (Found: C, 55·6; H, 6·4. $C_{17}H_{22}O_5N_2S$ requires C, 55·7; H, 6·0%).

Exhaustive Methylation of Anagyrine.—Anagyrine methiodide was prepared by refluxing anagyrine for many hours with MeI in acetone solution. It separated slowly and was collected at intervals and crystallised from MeOH. It is sparingly sol. in cold MeOH, hot EtOH, and acetone; m. p. 264° (decomp.) (Found: C, 50·3; H, 5·95. Calc. for $C_{16}H_{23}ON_2I$: C, 49·7; H, 5·95%).

The methiodide (19·5 g.) in methyl-alc. suspension (250 c.c.) was shaken with Ag_2O (6 g.). The filtered solution was evaporated in vac. until the cryst. methohydroxide separated. C_6H_6 (100 c.c.) was added and 50—60 c.c. were distilled off. This method ensures the decomp. of the hydroxide without polymerisation of the resultant base. The C_6H_6 solution was filtered to remove amorphous material and extracted with 10% aq. AcOH (50 c.c.). Palladised charcoal (1 g.) was added to the acid extract, which was then freed from traces of C_6H_6 in vac. and hydrogenated; 84—85% of the theo. amount of H was taken up in 2 hr., and absorption then ceased. The solution was filtered, basified with NH_3 aq., and extracted with $CHCl_3$. *Dihydromethylanagyrine* was purified by distillation, b. p. 180—190°/1 mm., and formed a very thick oil (Found: C, 73·6; H, 8·9. $C_{16}H_{24}ON_2$ requires C, 73·8; H, 9·2%).

Dihydromethylanagyrine (18 g.) was refluxed in acetone with MeI. An amorphous methiodide separated and, when the reaction was complete, dry Et_2O was added and the supernatant liquid decanted. The methiodide was washed with Et_2O, dissolved in MeOH, and shaken with Ag_2O. The filtered solution was evaporated, and the residual hydroxide decomposed by heating at 120°/10 mm. The residue was distilled, and the fraction with b. p. 200—210°/4 mm. dissolved in AcOH (10%) and hydrogenated. Hydrogen absorption was slow, 11 g. of the base with palladised charcoal (2 g.) taking up only 70% of the theo. vol. of H in 5—6 hr., and consequently the base probably contained dihydromethylanagyrine. The reduction product was worked up as before but not analysed.

The crude tetrahydrodimethylanagyrine, probably mixed with dihydromethylanagyrine, was converted into the methiodide by refluxing in acetone solution with excess of MeI. The methiodide was pptd. completely with Et_2O, washed with Et_2O, and converted into the hydroxide in methyl-alc. solution. The hydroxide after removal of MeOH was decomposed by heating at 120—130°/10 mm. until no more NMe_3 was evolved. The residue was distilled at 4 mm., and the distillate shaken with dil. AcOH aq. The major part was insol. and was extracted with C_6H_6. After removal of the C_6H_6 the residue was hydrogenated in alc. solution with palladised charcoal. Absorption of H was very rapid and at its cessation the solution was filtered, the alcohol evaporated, and the residue distilled. *Hexahydroanagyryline* formed a pale yellow oil, b. p. 155—160°/4 mm. (Found: C, 76·4; H, 9·8. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9%).

Hexahydroanagyryline (3·3 g.) was treated with a slight excess of ozone in $CHCl_3$ solution

at 0°. H_2O was added, and the $CHCl_3$ distilled off. The oily residue was collected in $CHCl_3$, dried, and distilled; 1·6 g. of a yellow *oil*, b. p. 140—150°/4 mm., were obtained (Found: C, 71·9; H, 11·4. $C_{11}H_{21}ON$ requires C, 72·1; H, 11·5%).

The compound $C_{11}H_{21}ON$ (1·6 g.) was heated with fuming HCl aq. (10 c.c.) at 100° for 2 hr. The acid solution was evaporated completely, the residue taken up with H_2O, filtered, made alkaline with KOH, and treated with 1% aq. $KMnO_4$ on the water-bath until a permanent pink colour was obtained. The solution was filtered, evaporated to small bulk, and acidified. An oily acid was pptd., which was extracted with Et_2O and, after drying with $CaCl_2$, distilled. An *acid* (0·6 g.), b. p. 180—200°/4 mm. (metal-bath temp.), was obtained (Found: C, 61·5; H, 9·3. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%).

The oily acid showed no sign of crystn. It was refluxed with AcCl until all evolution of HCl ceased. The excess of AcCl was removed in vac., and the residue heated with urea (0·2 g.) at 200—220° until efferv. ceased. The product was extracted with dry Et_2O, the ethereal solution filtered and evaporated, and the residual oil distilled at 4 mm. The distillate crystallised slowly to a wax-like solid. The crystals were drained, and recrystallised by allowing the ethereal solution to evaporate. The product formed white waxy crystals very sol. in all solvents except H_2O. It softened at 50° and melted at 52—54°, and its mixture with synthetic α-methyl-α′-*n*-amylglutarimide had the same characteristic m. p.

α-*Methyl*-α′-n-*amylglutaric Acid.*—*n*-Amyl bromide (b. p. 129—130°) was condensed with ethyl sodiomalonate in alc. solution with addition of NaI, and the ethyl *n*-amylmalonate (b. p. 99—100°/5 mm.) converted into its sodio-derivative in abs. EtOH and refluxed with ethyl α-bromo*iso*butyrate. Ethyl α′-carbethoxy-α-methyl-α′-*n*-amylglutarate (b. p. 120—130°/4 mm.) so obtained was hydrolysed by boiling with aq.-alc. KOH. The acid liberated by acidification of the alcohol-free hydrolysate was an oil, which was extracted with Et_2O and distilled. It lost CO_2 at 140—160° and came over between 180° and 200°/4 mm. α-*Methyl*-α′-n-*amylglutaric acid* was an oil (Found: C, 61·5; H, 9·3. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%), which was converted into the imide as described above for the acid derived from anagyrine. α-*Methyl*-α′-n-*amylglutarimide* was insol. in H_2O, but so sol. in all other solvents that it could only be crystallised by allowing its ethereal solution to evaporate. It softened at 50° and melted at 53—54° (Found: C, 67·0; H, 9·6. $C_{11}H_{19}O_2N$ requires C, 67·0; H, 9·6%). One of the two possible stereoisomeric α-methyl-α′-*n*-amylglutaric acids eventually crystallised and was separated and recrystallised from light petroleum. It formed leaflets, m. p. 76—78°.

Tetrahydroanagyrine.—Anagyrine hydrochloride (6 g.), dissolved in AcOH (50 c.c.), was shaken in H with 20% palladised charcoal (1 g.). No absorption of H occurred at room temp., but at 80—90° 1010 c.c. (theo., 990 c.c.) were taken up in 8 hr. The catalyst was removed and washed with H_2O and EtOH, the filtrate evaporated to small bulk, basified, and extracted with $CHCl_3$, and the product fractionated twice. *Tetrahydroanagyrine* distilled at 186—190°/1 mm. and had $[\alpha]_D^{20°}$ − 61·45° in 1·028% solution in acetone (Found: C, 72·5; H, 9·8. $C_{15}H_{24}ON_2$ requires C, 72·6; H, 9·7%). Tetrahydroanagyrine was proved to be identical with *l*-lupanine (for which Clemo, Raper, and Tenniswood, *loc. cit.*, record b. p. 186—188°/1 mm., and $[\alpha]_D$ − 61·0° in acetone) by examination of the following salts, the figures in square brackets being those recorded by Clemo and co-workers for *l*-lupanine: Hydriodide, prisms from H_2O, m. p. 190° with softening at 186° [190°]; $[\alpha]_D^{20°}$ − 44·0° in 0·832% aq. solution [− 43·6°]; mixed m. p. with *l*-lupanine hydriodide, 190° (Found: C, 43·7; H, 7·0. Calc. for $C_{15}H_{24}ON_2,HI,2H_2O$: C, 43·7; H, 7·0%). Thiocyanate, softened and lost H_2O at 143—145° [142°], melted finally at 183—185° [183—185°]; mixed m. p. with *l*-lupanine thiocyanate, 183—185°; $[\alpha]_D^{20°}$ − 55·4° in 0·476% aq. solution [− 55·3°]. The *perchlorate* formed prisms from EtOH, m. p. 210°, with softening at 195° (Found: C, 49·5; H, 7·4; N, 7·4. $C_{15}H_{24}ON_2,HClO_4,H_2O$ requires C, 49·1; H, 7·4; N, 7·6%).

Hexahydrodeoxyanagyrine.—Anagyrine (32 g.), dissolved in 50% H_2SO_4 aq. (200 c.c.), was electrolysed between pure lead electrodes. The cathode had an area of 1·6 sq. dm., and a current of 40 amp. and 6·8 volts was used. The anode chamber was a porous pot containing 50% H_2SO_4 aq. and was cooled by a cold water coil. The cathode chamber was maintained at 40—45° by an ice-water jacket. The electrolysis was continued for 6 hr.; the electrolyte was then made strongly alkaline and steam-distilled, and the distillate neutralised with HCl aq., evaporated to small bulk, basified, and extracted with Et_2O. The ethereal solution was dried with KOH, and the product fractionated twice. *Hexahydrodeoxyanagyrine* had b. p. 130—135°/1 mm.; $[\alpha]_D^{19°}$ + 10·9° in 2·952% abs. alc. solution [*d*-sparteine, b. p. 133—135°/1 mm.; $[\alpha]_D$ + 15·9°] (Found: C, 76·8; H, 11·0. $C_{15}H_{26}N_2$ requires C, 76·9; H, 11·1%).

Hexahydrodeoxyanagyrine gave the sulphur–hydrogen sulphide reaction of sparteine, and was proved to be *d*-sparteine by examination of its salts: Monohydriodide, m. p. 230—231° [229°]; $[\alpha]_D^{20°}$ − 8·9° in 0·716% abs. alc. solution (Found: C, 49·6; H, 7·6. Calc. for $C_{15}H_{26}N_2,HI$: C, 49·7; H, 7·5%). Dipicrate, m. p. 205—206° [205—206°] (Found: picric acid, 66·8. Calc. for $C_{15}H_{26}N_2,2C_6H_3O_7N_3$: picric acid, 66·2%). Mixed m. p. with *d*-sparteine picrate, 205—206°. The *monoperchlorate* crystallised from EtOH in plates, m. p. 169—170° without decomp. (Found: C, 53·9; H, 8·0; N, 8·1. $C_{15}H_{26}N_2,HClO_4$ requires C, 53·8; H, 8·1; N, 8·4%). This salt is readily sol. in cold $CHCl_3$ and sparingly sol. in cold H_2O and EtOH. l-*Sparteine monoperchlorate* had similar properties and m. p. 171—172°, and a mixture of α-hexahydrodeoxyanagyrine perchlorate with it melted at 135—140° (Found: C, 53·8; H, 8·0. $C_{15}H_{26}N_2,HClO_4$ requires C, 53·8; H, 8·0%).

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