479. *The Alkaloids of* Gelsemium sempervirens. *Part II.**

By Gurnos Jones and T. S. Stevens.

Experiments on the Hofmann, Emde, cyanogen bromide, and other processes for the degradation of gelsemine give no support to the formulation of the alkaloid as an allylamine derivative. The presence of an oxindole system having a free imino-group is confirmed, the second (basic) nitrogen atom being methylated. A new process for the degradation of allylamine derivatives by *N*-bromosuccinimide is described.

The recent work of Marion (*J. Amer. Chem. Soc.*, 1950, **72**, 2308; *Helv. Chim. Acta*, 1952, **35**, 638), Prelog (*ibid.*, 1951, **34**, 1139, 1962; 1952, **35**, 640), Witkop (*J. Amer. Chem. Soc.*, 1948, **70**, 1424), and their associates shows that one nitrogen atom—N(*a*)—of gelsemine is involved in a 3 : 3-disubstituted oxindole system, and throws light on the structure of the remainder of the molecule containing the basic N(*b*). We now record observations which in part cover similar ground.

While it was shown (Part I) that gelsemine gave no homogeneous product with cyanogen bromide, dihydrogelsemine yields a cyanamide which can be hydrolysed to a demethyldihydrogelsemine giving on remethylation a material not distinguishable from

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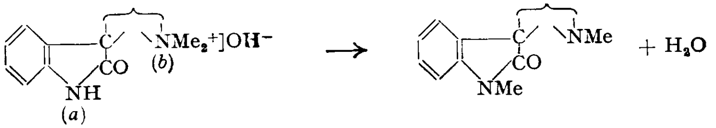
* Part I, *J.*, 1945, 579.

dihydrogelsemine methiodide. Since the cyanamide is non-basic, the alicyclic N(*b*) must have been attacked, and this atom therefore carries the methyl group of the alkaloid. The properties of the benzoyl derivative of the demethylated base discouraged any attempt to degrade it further by treatment with phosphorus pentachloride.

Pyrolysis of dihydrogelsemine methohydroxide at 190° gave dihydro-*N*(*a*)-methylgelsemine, prepared meantime under more drastic conditions by Prelog *et al.* (*loc. cit.*) :



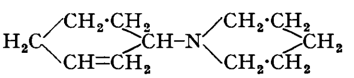
Like these authors we failed to degrade the methohydroxide of the new base. Gelsemine methohydroxide at 190° reverted to the parent alkaloid, in contrast to the transmethylation which they effected at 230—240°.

The proposal (*idem, loc. cit.*) for gelsemine of formulæ containing an allylamine system suggested the application of Emde's method. Since attempted Emde degradation of dihydrogelsemine appeared to give an organo-mercury compound (Part I), we explored the use of mercury-free reagents. Model experiments with sodium–lead alloy (compare Fichter and Stenzl, *Helv. Chim. Acta*, 1933, **16**, 571) gave favourable results with benzyltrimethylammonium iodide in alkaline solution, but with gelsemine methosulphate gave no characterisable product. Emde and Kull (*Arch. Pharm.*, 1936, **274**, 173) found that some quaternary ammonium compounds resistant to sodium amalgam could be degraded by catalytic hydrogenation. Benzyltrimethylammonium iodide was not effectively reduced by hydrogen over platinised charcoal, but the methyl sulphate in acetic acid gave moderate yields of toluene and trimethylamine; gelsemine methosulphate, however, gave no non-quaternary product. With sodium in liquid ammonia, used by Clayson (*J.*, 1949, 2016) to degrade hydrocotarnine methiodide, gelsemine methiodide gave only slightly impure gelsemine. This reagent, which Manske (*J. Amer. Chem. Soc.*, 1950, **72**, 58) found effective in the fission of resistant ethers, was also applied to dihydrogelsemine, since the second oxygen of gelsemine is believed to be ethereal; the base was unaffected.

The action of *N*-bromosuccinimide on tertiary allylamines might be expected to take the course :

$$\mathrm{R{\cdot}CH{:}CH{\cdot}CH_2{\cdot}NR'_2 \longrightarrow R{\cdot}CH{:}CH{\cdot}CHBr{\cdot}NR'_2 \xrightarrow{H_2O} R{\cdot}CH{:}CH{\cdot}CHO + HBr + NHR'_2}$$

Cinnamyldimethylamine thus afforded 34% of cinnamaldehyde, and 3 : 3-diphenylallyldimethylamine, $\mathrm{CPh_2{:}CH{\cdot}CH_2{\cdot}NMe_2}$, gave 60% of diphenylacraldehyde. Attack at either carbon atom adjacent to the ethylenic system is possible with 3-piperidino- (I) and 3-morpholino-*cyclo*hexene. The reaction with bromosuccinimide did not go smoothly in either case, and no *cyclo*hexenone could be identified. The morpholine derivative gave some 1 : 2-dibromo-3-morpholino*cyclo*hexane, and a little *p*-bromophenol by a combination of bromination, dehydrobromination, and hydrolysis. Gelsemine with bromosuccinimide yielded a water-soluble and an insoluble product; with alkali the former gave a base which quickly changed into an insoluble material apparently identical with that obtained directly. This contained ionisable bromine and from its ultra-violet absorption and other properties appeared to be the bromo-*allo*gelsemine hydrobromide which Prelog *et al.* (*loc. cit.*) obtained by bromination of gelsemine. Braude and Wright (*J.*, 1952, 1120) observe that in presence of tertiary amines, and especially of ammonium salts, bromosuccinimide tends to attack the double bond rather than the "allyl position" of olefins; it is significant that a higher yield of bromo*allo*gelsemine was obtained from gelsemine hydrochloride than from the free base.



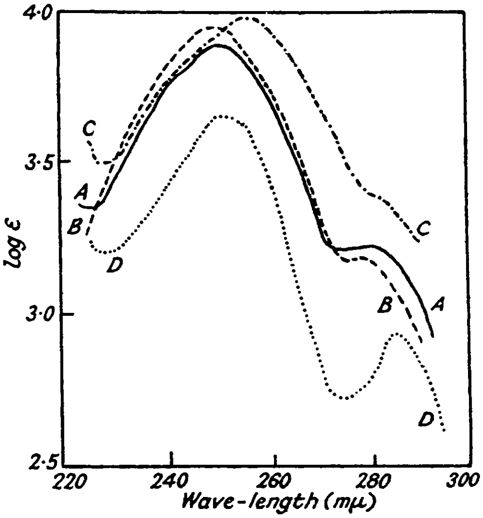
(I)

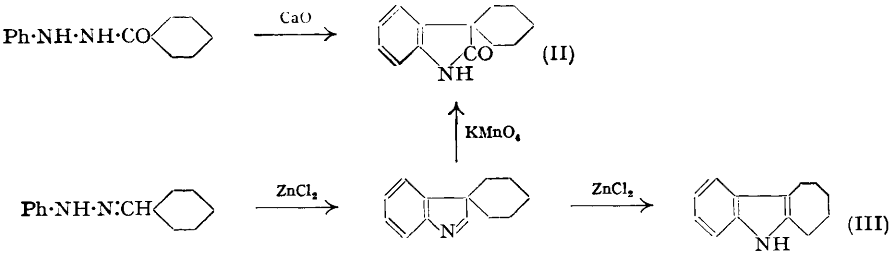
We have thus failed to produce evidence for the existence of an allylamine system in gelsemine. The fact that dihydrogelsemine is a stronger base than gelsemine, by a factor of about 2 in K_b, shows that the alkaloid is not a vinylamine derivative, since cyclic vinylamines are stronger than the corresponding saturated bases (Adams and Mahan, *J. Amer. Chem. Soc.*, 1942, **64**, 2589). Data are lacking as to the relative strengths of allylamines and bases in which the nitrogen atom is more remote from the double bond, but values for phenylated amines (*e.g.*, benzyldimethylamine, K_b 1·05 × 10^{-5}, compared with trimethylamine, 5·27 × 10^{-5}) suggest that in gelsemine more than one carbon atom separates the nitrogen atom from the ethylenic system. It is further significant that dihydrogelsemine and its *N*(*a*)-methyl derivative do not undergo Hofmann degradation, for the reduction product of an allylamine must contain at least one hydrogen atom in the β-position to nitrogen.

Several indole derivatives were prepared for comparison with gelsemine and its transformation products. Heated with lime, hexahydrobenzophenylhydrazide gives *cyclo*hexane*spiro*-3-oxindole (II), which was also obtained by permanganate oxidation of *cyclo*hexane*spiro*indolenine, the product of a cautious Fischer indole synthesis with hexahydrobenzaldehyde phenylhydrazone :

Substance	$\lambda_{max.}$, mμ	Log_{10} ε
2 : 3-Dimethylindole	* 280	3·85
1 : 2 : 3-Trimethylindole	245, 295	4·15, 3·45
*cyclo*Heptenoindole (III)	234, 284	4·05, 3·90
3 : 3-Dimethyloxindole	248, 279 †	3·97, 3·17
*cyclo*Hexane*spiro*oxindole	249, 279	3·94, 3·17 (*B* in Fig.)
Gelsemine	252, 282	3·89, 3·18 (*A* in Fig.)
Dihydrogelsemine	250, 281	3·90, 3·15
Dihydro-*N*(*a*)-methylgelsemine	258, 281 †	3·98, 3·33 (*C* in Fig.)
Cyanodemethyldihydrogelsemine	252, 287	3·65, 2·90 (*D* in Fig.)
Bromo*allo*gelsemine hydrobromide	259	3·87
3 : 3-Dimethylindolenine ‡	255	3·6
*cyclo*Hexane*spiro*indolenine	252	2·6

* Not measured below 245 mμ. † Inflection.
‡ Grammaticakis, *Compt. rend.*, 1940, **210**, 569.

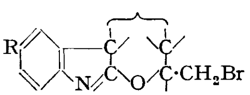




In the last process, more vigorous treatment led by Wagner–Meerwein ring-enlargement to the isomeric *cyclo*heptenoindole (III; Perkin and Plant, *J.*, 1928, 2583); Brunner

(*Monatsh.*, 1895, **16**, 849) obtained 2 : 3-dimethylindole by heating the zinc chloride complex of 3 : 3-dimethylindolenine. Data on ultra-violet absorption are summarised in the Table; the curves are similar for oxindoles and for gelsemine and all its derivatives, except bromo*allo*gelsemine which absorbs in the same region as 3 : 3-disubstituted indolenines.

Prelog *et al.* (*loc. cit.*) formulate bromo*allo*gelsemine as a cyclic 2-alkoxyindolenine with the partial formula (IV; R = H). With diazobenzenesulphonic acid it gives a yellow dye which becomes deep red in alkali, and on this formulation the normal product of coupling (IV; R = $HSO_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}$) would lack a mobile proton such as would account for the behaviour with alkali. *cyclo*Hexane*spiro*indolenine, on the other hand, does not couple.


(IV)

Hydrogenation of 3 : 3-dimethyloxindole was studied for comparison with that of the alkaloid. Over Adams's catalyst it gave a hexahydro-derivative transparent down to 230 mμ, analogous to the octahydrogelsemine similarly prepared from gelsemine or dihydrogelsemine (*idem, loc. cit.*). A sharply melting, crystalline product isolated after absorption of 2 mols. of hydrogen was a mixture or complex of the hexahydro-compound and dimethyloxindole. Attempts to open the lactam ring of dimethylhexahydro-oxindole failed : hydrochloric acid at 160° had no effect, and baryta gave a product which could not be purified.

EXPERIMENTAL

Gelsemine was isolated from *Gelsemium sempervirens* root, and from the pharmacological extract which yielded little of the thermally unstable sempervirine and no gelsemicine. *Gelsemine methosulphate,* which separated after 10 minutes' boiling of the components in acetone and crystallised from ethanol, had m. p. 298° (decomp.) (Found : N, 5·7; S, 6·3. $C_{22}H_{28}O_6N_2S,C_2H_6O$ requires N, 5·7; S, 6·5%). Hydrogenation of gelsemine over Raney nickel at 150°/100 atm. gave only the known dihydrogelsemine, m. p. 224°. The colour reactions of gelsemine and some indole derivatives were compared :

Substance	Vanillin–HCl	Ehrlich's reagent	H_2SO_4–$K_2Cr_2O_7$
Gelsemine	Pale yellow	Pale green	Red → violet → green
2 : 3-Dimethylindole ...	Yellow → orange	Deep rose → red-violet	—
1 : 2 : 3-Trimethylindole	Yellow → orange	Magenta → red-violet	—
3 : 3-Dimethyloxindole ...	Pale yellow	Pale green	Intense red

Values of pK_b for gelsemine (4·71) and dihydrogelsemine (4·41) were obtained by determining the pH of solutions of the hydrochlorides with a Cambridge pH meter.

Cyanogen Bromide and Dihydrogelsemine.—Mixed dry ethereal solutions of the base (400 mg.) and cyanogen bromide (200 mg.) were boiled for a short time. After some hours the separated solid was crystallised from ethanol, giving N-*cyanodemethyldihydrogelsemine* (320 mg.), m. p. 269° (Found : C, 71·4; H, 6·1. $C_{20}H_{21}O_2N_3$ requires C, 71·6; H, 6·3%). It neither dissolved in dilute mineral acids nor reacted with methyl iodide. Hydrolysis required vigorous conditions : the cyanamide (240 mg.) in concentrated hydrochloric acid (10 c.c.) was heated for 8 hr. at 160°. Basification of the deep red solution with ammonia and extraction with ether gave a white solid which became ether-insoluble on exposure to air (? carbonate formation), and with ethereal picric acid gave *demethyldihydrogelsemine picrate,* prisms (from ethanol), m. p. 281—282° (decomp.) (Found : C, 56·3; H, 4·1. $C_{25}H_{25}O_9N_5$ requires C, 55·7; H, 4·6%). With methyl iodide in acetone, demethyldihydrogelsemine gave needles which, crystallised from ethanol, melted at 300—302° (decomp.), alone or mixed with dihydrogelsemine methiodide. *X*-Ray powder photographs of the two materials (for which we are indebted to Dr. P. Woodward of this Department) seemed identical but could not be distinguished with certainty from that of gelsemine methiodide. Schotten–Baumann benzoylation of demethyldihydrogelsemine gave an uncrystallisable product.

Attempted Hofmann Degradation.—Dihydrogelsemine methiodide (300 mg.) in aqueous solution was shaken with freshly precipitated silver oxide (300 mg.), and the solution boiled, filtered, and evaporated to dryness. The residue, heated for 30 min. at 190°/0·1 mm., gave a colourless sublimate; extraction of the whole with ether, passage through a column of unactivated alumina, and evaporation gave a colourless solid, crystallising from ligroin in prisms, m. p. 163—165°. The methiodide, prepared in acetone and crystallised from ethanol, had m. p. 289°. Prelog *et al.* (*loc. cit.*) give m. p.s (corr.) 165—166° and 299° for dihydro-*N*(*a*)-methylgelsemine and its methiodide. Prepared in ethanol, the *picrate* had m. p. 216—218° (Found : C, 57·0; H, 5·0; N, 12·4. $C_{27}H_{29}O_9N_5$ requires C, 57·1; H, 5·2; N, 12·3%). The base was unaffected by attempted reduction over Adams's platinum oxide catalyst, and oxidation with potassium permanganate in acetone gave no definable product.

Reductions with Sodium–Lead Alloy.—Benzyltrimethylammonium methyl sulphate (from benzyldimethylamine and methyl sulphate in ether; hygroscopic; 0·7 g.) in water (30 c.c.) was stirred at 3° in a slow current of hydrogen in a flask fitted with a dropping funnel, means of adding sodium–lead alloy, a condenser, and an absorption tube charged with standard acid. The alloy (Goldach, *Helv. Chim. Acta*, 1931, **14**, 1436) (8 g.), and sulphuric acid when used, were added gradually, the mixture was made alkaline and distilled, and the trimethylamine determined by back-titration of the receiver contents:

Solvent	H_2O 30 c.c.	H_2O 30 c.c.	EtOH 30 c.c.	Na, 1 g., in EtOH, 30 c.c.
Acid added	10N 20 c.c.	2N 50 c.c.	—	—
Yield, %	25	28·5	41·2	59

Hydrohydrastinine methosulphate, prepared in acetone and crystallised from ethanol, had m. p. 188° (Found : S, 10·0. $C_{13}H_{19}O_6NS$ requires S, 10·1%). Reduced as above in alcohol with a little water, it yielded a brown oil giving NN-*dimethyl*-4 : 5-*methylenedioxy*-2-*vinylbenzylamine picrate*, m. p. 181° (Found : C, 50·2; H, 4·0. $C_{18}H_{18}O_9N_4$ requires C, 49·9; H, 4·2%); the same unsaturated base is produced by heating the methosulphate with dilute aqueous sodium hydroxide as the normal product of Hofmann degradation. When the reaction mixture was acidified before evaporation, no non-quaternary base was obtained. Gelsemine methosulphate was treated in the same way, in ethanol.

Other Reductions of Quaternary Salts.—Benzyltrimethylammonium methyl sulphate (346 mg.) absorbed 77·3 c.c. of hydrogen at 23°/758 mm. in acetic acid over platinised charcoal, affording toluene (34%), and trimethylamine (36%; distilled into hydrochloric acid and weighed as hydrochloride). Reduction of 35% of the cation to toluene and trimethylammonium, and the remainder to hexahydrobenzyltrimethylammonium requires absorption of 74·1 c.c. Little hydrogen was absorbed in a parallel experiment on benzyltrimethylammonium iodide in water.

Cinnamyldimethylamine and N-*Bromosuccinimide.*—Cinnamyl bromide (10 g.) and dimethylamine (6 g.) in nitromethane were mixed at −10°, and after 1 hr. the solvent was removed in a vacuum. The basic product of the reaction distilled at 107°/12 mm. (3·9 g.) and the derived cinnamyldimethylamine picrate had m. p. 123—124° (cf. King and Holmes, *J.*, 1947, 164). An oil (2 g.) was also formed, soluble in chloroform but not in ether, and presumed to be impure dicinnamyldimethylammonium bromide. This, heated with concentrated potassium hydroxide solution at 200°, gave equal weights of cinnamyldimethylamine and dicinnamylmethylamine, b. p. 180—182°/0·5 mm. The latter base, for which Blicke and Zienty (*J. Amer. Chem. Soc.*, 1939, **61**, 774) record b. p. 180—185°/5 mm., yielded with methyl iodide in acetone feathery plates of *dicinnamyldimethylammonium iodide*, m. p. 170—170·5° (Found : C, 58·8; H, 6·1. $C_{20}H_{24}NI$ requires C, 59·3; H, 6·0%). To cinnamyldimethylamine (2·19 g.) in dry carbon tetrachloride, *N*-bromosuccinimide (4·38 g.) was added and the mixture boiled for 30 min. When cool, the liquid was filtered from the red gum, shaken with hydrochloric acid which removed cinnamyldimethylamine (0·33 g.), and evaporated, giving more gum which was united with the other and steam-distilled. The distillate afforded cinnamaldehyde (0·52 g.) (oxime, m. p. and mixed m. p. 140°; 2 : 4-dinitrophenylhydrazone, m. p. 242°).

3 : 3-*Diphenylallyldimethylamine and* N-*Bromosuccinimide.*—3 : 3-Diphenylallyl bromide (Masson, *Compt. rend.*, 1902, **135**, 533; Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80) (6 g.) gave, with dimethylamine in nitromethane as above, diphenylallyldimethylamine, b. p. 124°/0·3 mm. (2 g.); Adamson (*J.*, 1949, S 144) gives b. p. 192—193°/18 mm. Treated as before with *N*-bromosuccinimide (0·8 g.), it (0·9 g.) gave unchanged material (40 mg.) and a gum which was boiled with water for 10 min., whereafter extraction with ether gave diphenylacraldehyde (0·47 g.). The semicarbazone melted at 219—221° (Found : N, 15·5. Calc. for $C_{16}H_{15}ON_3$: N, 15·8%); Wittig and Kethur (*Ber.*, 1936, **69**, 2085) give m. p. 217—219°. The 2 : 4-dinitrophenylhydrazone had m. p. 193·5°; Lorenz and Wizinger (*Helv. Chim. Acta*, 1945, **28**, 600) give m. p. 195—196°.

3-*Piperidino*cyclo*hexene and* N-*Bromosuccinimide.*—Piperidino*cyclo*hexene picrate had m. p. 108·5° (Found : C, 51·8; H, 5·8. Calc. for $C_{17}H_{22}O_7N_4$: C, 51·8; H, 5·6%); Bamford and

Stevens (*J.*, 1952, 4735) give m. p. 109—111°. The free base, b. p. 106—108°/15 mm. (3·3 g.), in dry carbon tetrachloride was treated with bromosuccinimide (3·5 g.). The very vigorous reaction produced a red gum which was distilled in steam, but no *cyclo*hexenone could be recognised; the only substance identified was a little unchanged base.

3-*Morpholino*cyclo*hexene and* N-*Bromosuccinimide*.—1 : 2-Dibromo*cyclo*hexane (23 g.) and morpholine (27 g.) were heated at 100° for 2 hr. The mixture was shaken with water and ligroin, and the upper layer washed thoroughly with water, dried, and distilled; 3-morpholino*cyclo*hexene (13·3 g.) boiled at 110—115°/16 mm.; the *picrate*, needles from ethanol, had m. p. 148—149° (Found : C, 48·9; H, 5·1. $C_{16}H_{20}O_8N_4$ requires C, 48·5; H, 5·1%). A solution of the base (3·34 g.) in carbon tetrachloride became warm on addition of bromosuccinimide (3·56 g.) and deposited a red gum. The filtrate afforded only unchanged base (1·5 g.). Distilled in steam, the gum gave *p*-bromophenol (50 mg.) (benzoyl derivative, m. p. 103—104°); basification of the residual aqueous solution yielded an oil which with ethanolic picric acid gave yellow, halogen-containing needles, m. p. 174—175°, of 1 : 2-*dibromo*-3-*morpholino*cyclo*hexane picrate* (Found : C, 34·9; H, 3·7. $C_{16}H_{20}O_8N_4Br_2$ requires C, 34·5; H, 3·6%).

Gelsemine and N-*Bromosuccinimide*.—Acetone-free gelsemine (250 mg.) was boiled in carbon tetrachloride with bromosuccinimide (275 mg.) for several hours, giving a cream-coloured precipitate which was filtered off after cooling; nothing was obtained from the filtrate. Part of the solid dissolved in boiling water; the solution on basification gave a flocculent precipitate soluble in ether and acetone, which could not be crystallised and passed on evaporation into a product insoluble in ether, apparently identical with the original water-insoluble fraction. This was purified by repeated precipitation from chloroform by ether, giving a very pale yellow powder which decomposed at 310° and had ultra-violet absorption similar to that of bromo*allo*gelsemine (Found : N, 5·5. Calc. for $C_{20}H_{22}O_2N_2Br_2$: N, 5·8%). With diazobenzene-*p*-sulphonic acid it produced a yellow precipitate giving a deep orange colour with alkali.

3 : 3-*Dimethyloxindole*.—Prepared by Brunner's method (*Monatsh.*, 1897, **18**, 98), crystallised from ethyl acetate, and sublimed (12 mm.), this melted at 154—154·5° (Found : C, 74·1; H, 6·7; N, 9·0. Calc. for $C_{10}H_{11}ON$: C, 74·5; H, 6·9; N, 8·7%). Dimethyloxindole in acetic acid (distilled over chromium trioxide) absorbed 2·96 mols. of hydrogen at 19°/1 atm. over Adams's catalyst. *Hexahydro*-3 : 3-*dimethyloxindole* crystallised from ligroin in prisms, m. p. 126—127° (Found : C, 72·4; H, 9·9; N, 8·4. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2; N, 8·4%). One experiment was interrupted when 2·0 mols. of hydrogen had been absorbed, and the product, crystallised from ligroin or ethyl acetate, had the sharp and reproducible m. p. 99°; but, treated with aqueous solvents it gave dimethyloxindole (mixed m. p.). An equimolecular mixture of dimethyloxindole and the hexahydro-compound gave similar crystals from ligroin, m. p. and mixed m. p. 98—99°, and the 99° product showed ultra-violet absorption similar to that of dimethyloxindole.

cyclo*Hexane*spiro-3-*oxindole*.—Hexahydrobenzoic acid (3 g.) was heated with phenylhydrazine (3 g.) at 140° for 2 hr. and the product crystallised from ethanol and from benzene, giving plates, m. p. 171° (Found : N, 12·8. Calc. for $C_{13}H_{18}ON_2$: N, 12·8%). Hexahydrobenzophenylhydrazide was also prepared by the method of Rupe and Metz (*Ber.*, 1903, **36**, 1095), who give m. p. 164°. The hydrazide (2 g.) was heated with freshly ignited calcium oxide (8 g.) at 195° for 6 hr., the reaction being followed by titrating the evolved ammonia. The product was boiled for 1 hr. with concentrated hydrochloric acid, then filtered after cooling, and the solid residue continuously extracted with boiling ether. The brown, gummy extract was crystallised from ligroin and sublimed (130°; high vacuum), giving *cyclo*hexane*spiro*-3-oxindole, m. p. 121—122° (Found : C, 77·8; H, 7·6; N, 6·8. Calc. for $C_{13}H_{15}ON$: C, 77·6; H, 7·5; N, 7·0%). Moore and Plant (*J.*, 1951, 3477) give m. p. 124°. The same product was obtained (mixed m. p.) on oxidation of the zinc chloride complex of *cyclo*hexane*spiro*-3-indolenine (400 mg.) with potassium permanganate (500 mg.) in water (50 c.c.) containing potassium hydroxide (150 mg.) at 10°. After 6 hr. at 8—10° and 20 hr. at room temperature a little ethanol was added and the mixture boiled and filtered hot. The filtrate, saturated with carbon dioxide, was extracted with ether, yielding *cyclo*hexane*spiro*-3-oxindole (25 mg.) which was crystallised from ligroin.

2 : 3-cyclo*Heptenoindole*.—Hexahydrobenzaldehyde (Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 344) (3·7 g.) and pure phenylhydrazine (3·3 g.) were heated until reaction was complete and the red gum was dried in a vacuum. When this was heated with powdered zinc chloride (4 g.) a violent reaction occurred, and the product was steam-distilled with excess of sodium hydroxide solution. The volatile, pale yellow solid, sublimed and repeatedly crystallised from ligroin, formed colourless leaflets, m. p. 143—145°, alone or mixed with authentic 2 : 3-*cyclo*-

heptenoindole kindly supplied by Dr. S. G. P. Plant (Found: C, 84·3; H, 8·1; N, 7·6. Calc. for $C_{13}H_{15}N$: C, 84·2; H, 8·2; N, 7·6%). In acetic acid the *cyclo*heptenoindole gave with diazobenzenesulphonic acid a deep red azo-dye, changed to orange by alkali.

cyclo*Hexane*spiro-3-*indolenine*.—Hexahydrobenzaldehyde phenylhydrazone (2·5 g.) in a little ethanol was added to ethanol (5 c.c.) containing zinc chloride (7·5 g.) and refluxed in nitrogen for 3 hr. Addition of 2N-hydrochloric acid (15 c.c.) with ice (5 g.) gave, on shaking, a colourless solution over a sticky red gum. The dried gum was crystallised from ethanol, giving colourless plates of the zinc chloride *complex* of *cyclo*hexane*spiro*indolenine, m. p. 205·5° (previous softening) (Found: C, 61·8; H, 6·2. $C_{26}H_{30}N_2Cl_2Zn$ requires C, 61·6; H, 6·0%). The fragrant-smelling free base, liberated by potassium hydroxide and distilled in steam, boiled at 85°/20 mm. and gave no colour or precipitate with diazobenzenesulphonic acid.

The ultra-violet absorptions were determined with a Beckman spectrophotometer, on ethanolic solutions except in the case of bromo*allo*gelsemine hydrobromide which was dissolved in ethanol–water (2 : 3).

The authors thank the Department of Scientific and Industrial Research for a Maintenance Allowance (to G. J.).

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[*Received, March* 12*th*, 1953.]