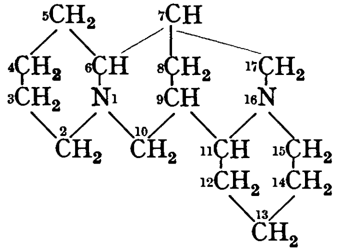
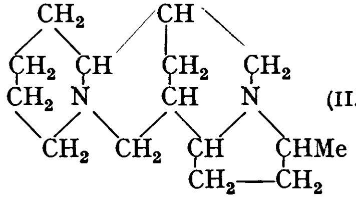
163. *The Lupin Alkaloids. Part VII. The Structure of Lupanine and Sparteine.*

By G. R. CLEMO and R. RAPER.

THROUGH the kindness of Dr. H. R. Ing we have discussed with him his new work and conclusions on anagyrine (this vol., p. 504) and now wish to submit formula (I) to represent sparteine, and its 2-keto-derivative for lupanine. The fact that tetra- and hexa-hydro-anagyrine have been shown by Ing (*loc. cit.*) to be identical with *l*-lupanine and *d*-sparteine respectively, combined with the suggested relationship of the former compounds to cytisine, indicates that cytisine and the lupin alkaloids possess structural similarity.

(I.) 

 (II.)

Adopting the formula suggested for cytisine (J., 1932, 2778), it is possible, by attaching a tetramethylene chain so as to form a new piperidine ring, to obtain structure (I) with two fused octahydropyridocoline systems.

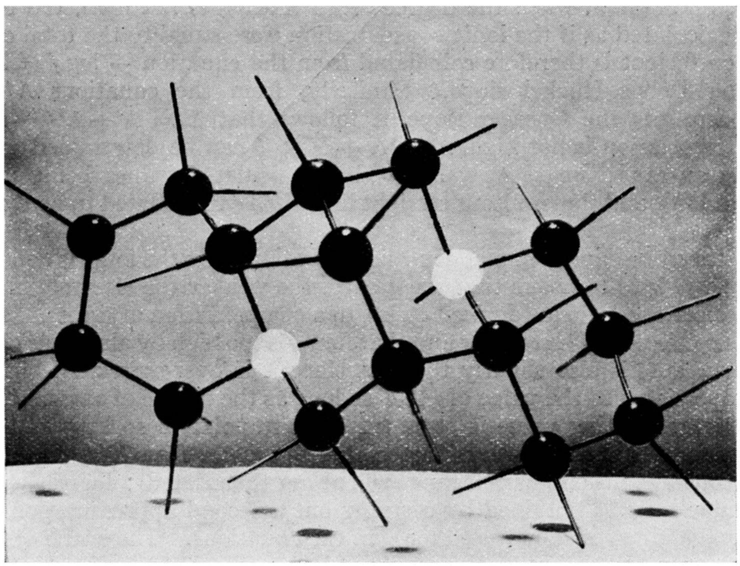
Formula (II), which contains the skeleton favoured by Ing for anagyrine, is a slight variation of this, and would clearly account for the recorded observations that decomposition products of the lupin alkaloids give pyrrole-like colour reactions. It would, moreover, indicate two structurally isomeric monomethiodides for sparteine, whereas the evidence points to their being stereoisomerides.

We have found, however, that the products of distillation of cytisine with zinc dust give pyrrole-type colour reactions, thus indicating the production of a 5-membered ring and making it unnecessary to postulate one preformed as in (II).

On the assumption, therefore, that formula (I) represents sparteine, the keto-group of lupanine is at C_2 as in cytisine, and it is then possible to account for the degradative results obtained in the study of these alkaloids.

Thus the keto-group of oxysparteine and the second keto-group of oxylupanine is probably at C_{17} rather than C_{10} or C_8. If it were at C_{10}, the baryta hydrolysis of substance "A," $C_{15}H_{22}O_3N_2$ (J., 1931, 3193), would not yield a product containing two nitrogen atoms. If it were at C_8, active ketonic properties would be expected. The fact that there is no methylene group next to this CO also receives an explanation. The further oxidation of oxylupanine to "A" results in the conversion of the hydrogen atom attached to C_6 into a tertiary hydroxyl group; the product, on baryta hydrolysis, splits out carbon atoms C_2 to C_6 as glutaric acid. The isomeric substance "B" (*loc. cit.*) would then probably be the corresponding 11-carbinol. The essential difference between formula (I) and those advanced by Karrer and co-workers for sparteine (*Helv. Chim. Acta*, 1928, **11**, 1068) lies in the attachment of C_{11} to C_9.

An examination of the model of the strain-free structure (I) leads to the striking conclusion that if, of the numerous possible arrangements, the octahydropyridocoline systems are both ***trans*** and if the C_7–C_9 bridge is ***cis*** with respect to the hydrogen atoms attached to C_6 and C_{11}, the system is locked with the nitrogen atoms so situated that steric hindrance would account for the remarkable and hitherto inexplicable fact that sparteine gives only a



monomethiodide (see photograph). This formula involves the possibility that the $CH_2{\cdot}OH$ group of lupinine may possibly be attached to C_9, whilst, if (II) were correct, lupinine might be a derivative of 2-methyloctahydropyrrocoline.

The *trans*-arrangement of rings agrees with the similar configuration claimed by other workers for natural products such as œstrin. Experimental work to confirm these conclusions is now in progress. The attachment of a *N*-methylenepiperidine complex to carbon atoms 3 and 5 leads to a possible formula for the alkaloid porphyrine, $C_{21}H_{25}O_2N_3$ (cf. Hesse, *Annalen*, *Supp*. 442).

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