282. *Strychnine and Brucine. Part XL. A Note on the Hofmann Degradation of Dimethyl*des*brucidine.*

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The known dimethyl*des*brucidine has been submitted to another stage of exhaustive methylation with the production of desaza*brucidine* and trimethylamine. Like the *desaza*strychnidines, this feeble base contains three double bonds.

IN Part XXXV (Achmatowicz, Lewi, and Robinson, J., 1935, 1685) it was shown that methyl*des*dihydrobrucidine-a gives with methyl iodide two isomeric dimethiodides, the normal dimethiodide and the *allo*-dimethiodide. The latter was considered a structural isomeride, and it was shown that the corresponding dimethochloride, treated with sodium methoxide, suffers a Hofmann elimination, yielding a new *des*-base which was termed dimethyl*des*brucidine. We have now found that this base contains two double bonds; when it is hydrogenated in dilute acetic acid solution in presence of palladised charcoal, four atoms of hydrogen are taken up and the *tetrahydro*-derivative, m. p. 135—136°, is formed. This experiment definitely proves that dimethyl*des*brucidine is a normal product of the second stage of Hofmann degradation.

Dimethyl*des*brucidine, on prolonged heating with methyl sulphate, gives a dimetho-sulphate (semicrystalline), as proved by conversion into the corresponding *dimethiodide*, m. p. 251—253°. The related dimethochloride was submitted to Hofmann elimination and two degradation products were obtained together with trimethylamine. These were (a) a base, $C_{25}H_{34}O_3N_2$, m. p. 155—156°, identified with dimethyl*des*brucidine, and (b) a base, $C_{23}H_{27}O_3N$, m. p. 133—134°, termed desaza*brucidine*.

*desaza*Brucidine is a very feeble base; it contains three unsaturated linkages and exhibits brucidine-type colour reactions. It is very unlikely that it is an analogue of *desaza*strychnidine-a or -b, since, as stated above, it is derived from the *allo*-dimethiodide. It might possess a different arrangement of the ethylenic linkages or even a different skeleton and it is obvious that speculation as to its structure is useless at this stage.

EXPERIMENTAL.

Catalytic Hydrogenation of N(b)N(b)-*Dimethyl*des*brucidine. Formation of Tetrahydro*-N(b)N(b)-*dimethyl*des*brucidine*.—Dimethyl*des*brucidine (0·5 g.) was dissolved in 50% acetic acid (5 c.c.) and hydrogenated at 17° in presence of palladised charcoal (0·1 g. of palladous chloride, 1 g. of charcoal, previously heated to redness, and 30 c.c. of water). Absorption ceased after 50 minutes, 59 c.c. (at N.T.P.) having been taken up (calc. for 4H, 54 c.c.). The filtered solution was basified with ammonia and the grey caseous precipitate was washed with water, dried in a vacuum, and twice crystallised from methyl alcohol. *Tetrahydrodimethyl*des*brucidine* (0·5 g.) formed colourless silky needles, m. p. 135—136° (Found in material dried at 100°: C, 72·9, 72·7; H, 9·4, 9·5. $C_{25}H_{38}O_3N_2$ requires C, 72·7; H, 9·2%), moderately readily soluble in methyl alcohol or acetone and readily in chloroform or benzene.

The *methiodide* was formed when a suspension of the base was warmed for a few minutes with methyl iodide; recrystallised from methyl alcohol, it formed colourless leaflets, m. p. 282—284°, becoming reddish on standing in the air (Found in a specimen dried at 104°: C, 56·3, 56·4; H, 7·5, 7·6. $C_{26}H_{41}O_3N_2I$ requires C, 56·1; H, 7·2%). It is moderately soluble in methyl alcohol and readily soluble in water.

N(b)N(b)-*Dimethyl*des*brucidine Dimethiodide*.—A solution of dimethyl*des*brucidine (7 g.) in dry benzene (80 c.c. at 40°) was refluxed with methyl sulphate (7 c.c.) for 12 hours on a water-bath. The semicrystalline brown product was dissolved in water (20 c.c.), and the solution basified with ammonia (no precipitate), filtered, and mixed with aqueous sodium iodide (10 g. in 15 c.c. of water). The yellow oily precipitate which was then formed crystallised after 12 hours; the solid was collected, washed with water, and twice recrystallised from this solvent. The *dimethiodide* (10·3 g.) formed minute colourless plates, m. p. 251—253°, containing $2H_2O$ which are lost at 104° (Found in air-dried material: loss at 104°, 5·4, 5·2. $C_{27}H_{40}O_3N_2I_2,2H_2O$ requires $2H_2O$, 5·1%. Found in material dried at 104°: C, 48·6, 48·5; H, 6·3, 6·2; I, 37·9. $C_{27}H_{40}O_3N_2I_2$ requires C, 48·8; H, 6·0; I, 38·3%). The derivative is sparingly soluble in cold water or methyl alcohol, but dissolves readily on boiling.

The dimethochloride, prepared by means of silver chloride, separated from a concentrated aqueous solution as a mass of colourless needles, m. p. 214—215° after drying at 104°.

The Action of Sodium Methoxide on N(b)N(b)-*Dimethyl*des*brucidine Dimethochloride. Elimination of Trimethylamine and Formation of* desaza*Brucidine*.—The dimethochloride (5 g., previously dried at 104° in a vacuum) was dissolved in methyl alcohol (10 c.c.), mixed with methyl-alcoholic sodium methoxide (25 c.c. of 25%), and heated on a sand-bath in a flask fitted with a condenser; the distillate was collected in 5% hydrochloric acid. Evolution of trimethylamine began at about 110° (trimethylamine was identified by conversion into the hydrochloride, m. p. 271—273°, and the platinichloride, m. p. 240—242°), and when the temperature of the melt reached 145°, the heating was discontinued. The yellow oily product was allowed to cool, washed with water, dried in a vacuum (3·6 g.), and crystallised from acetone. The first crop consisted of dimethyl*des*brucidine (total yield, 2·1 g.), which, after being recrystallised from methyl alcohol, was identified by m. p. and by mixed m. p. (154—156° in both cases). The acetone mother-liquor was evaporated to dryness in a vacuum and the residue (1·2 g.) was repeatedly crystallised from light petroleum (b. p. 40—45°) -ethyl acetate. This crystallisation furnished a little dimethyl*des*brucidine and mainly desaza*brucidine*, which formed slightly yellow, prismatic plates, m. p. 133—134° (Found: C, 75·5, 75·7; H, 7·5, 7·5; N, 4·0, 4·1; OMe, 17·2, 17·3; Me as NMe, 0. $C_{23}H_{27}O_3N$ requires C, 75·6; H, 7·3; N, 3·8; 2OMe, 17·0%). It is very readily soluble in the simple alcohols, acetone, chloroform or benzene, moderately soluble in light petroleum, and sparingly in ethyl acetate. *desaza*Brucidine is sparingly soluble in dilute acids, and solutions in more concentrated acids are hydrolysed on dilution with water. A solution of the base in dilute hydrochloric acid gives a faint green coloration on addition of a few drops of ferric chloride solution. When *desaza*brucidine was hydrogenated in presence of platinum-black at room temperature, three molecules of hydrogen were taken up; the hexahydro-derivative has not yet been prepared in a crystalline state.

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