stead behave anomalously.[2] Thus a quantity of acetate in 10 ml. of a solution of hydrogen bromide in acetic acid and acetyl bromide, calculated to produce 7.576×10^{-4} mole of 1-bromotetraacetyl glucose, assuming the disaccharide is quantitatively converted to this derivative, gave the following end rotations: β-maltose octaacetate, +17.2; gentiobiose octaacetate, +12.2; and octaacetates I and II, + 12.1 and +11.2°, respectively.

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RECEIVED AUGUST 8, 1947

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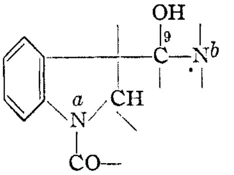
[2] Allene Jeanes and G. E. Hilbert, presented before the American Chemical Society, Sept. 11-15, 1944.

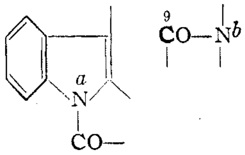
[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

THE STRUCTURE OF STRYCHNINE

Sir:

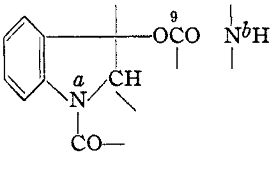
We have found that the ultraviolet absorption spectrum [$\lambda\lambda_{\max.}$ (log ϵ): 246(4.15), 270(3.92), 294(3.72)] of strychnone, the neutral product[1] of the action of acidic hydrogen peroxide on *pseudo*strychnine, resembles closely that of model N-acylindoles, and is entirely different from that of strychnine and other N-acyldihydroindoles. This observation can be accommodated on the basis of the change I → II. It is clear that in the imino-carbonyl chain tautomer of I, the oxidizing agent interpolates an oxygen atom between the (potential) carbonyl group at C.9 and the β-carbon atom of the indole nucleus, giving III. The subsequent changes are unexceptional. The new expression leads to $-\overset{|}{N}{}^{a}H \quad HOO\overset{|}{C}$ for strychnone hydrate. N^a is now part of an indole system, and in the hydrate is only very feebly basic, as required. Methoxydihydrostrychnone is simply the ester $-\overset{|\,a}{N}H \quad MeOO\overset{|}{C}$. Like other indoles and N-acylindoles, none of these substances gives, as do N-acyldihydroindoles, the characteristic Otto reaction.

I


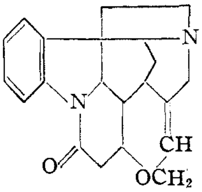


II

The importance of these considerations is twofold: (i) on the new basis, the formation of strychnone is the long-sought crucial experiment with respect to resolving the remaining dubieties concerning the mode of the linkage of N^b to the indole ring. Consequently, taken with the recent observations of Robinson[2] on the environment of the double bond in the *neo* series, and similar studies in this Laboratory on the replacement by methylene of the ketonic group of methoxymethyl-*chano*dihydrostrychnone, the new evidence completes the inferential proof for a particular expression for strychnine, IV.[3] (ii) In the formation of strychnone, the very involved tightly fused polycyclic system of strychnine has been broken into to an extent not achieved in any of the extensive earlier degradations, which have in the main led only to the destruction of the periphery of the molecule. Thus, the way is now open to build up an unequivocal degradative proof of structure for strychnine.



III



IV

CONVERSE MEMORIAL LABORATORY R. B. WOODWARD
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RECEIVED JULY 28, 1947

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[1] Leuchs, *et al.*, *Ber.*, **77**, 408 (1944).

[2] Chakravarti and Robinson, *Nature*, **160**, 18 (1947).

[3] This expression, which for some years has been considered independently in this Laboratory (*cf. J. Chem. Soc.*, 903 (1946), footnote, p. 904) and in that of Sir Robert Robinson (ref. 2), represents a slight modification of the structure regarded in 1939 by the latter (*J. Chem. Soc.*, 603 (1939)) as the culmination of the strychnine structure problem, on the basis of a long and brilliant logical sequence, much of which had been elaborated as early as 1930 (Robinson, *Proc. Roy. Soc.* (*London*), **130A**, 431 (1931).