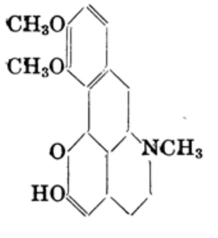
SINOMENINE AND DISINOMENINE. PART VIII.⑴ ON COLOUR REACTIONS OF SINOMENINE AND SINOMENOL.

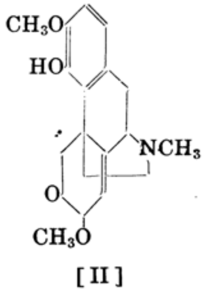
By Kakuji GOTO.

Received March 25, 1929. Published April 28, 1929.

At the time when I proposed the provisional formula for sinomenine (I), the materials to determine the position of hydroxyl, methoxyl and ketone groups were very scanty. The relative position of these groups were assumed mainly from the colour reaction of sinomenine.⑵



[I]



[II]

Sinomenine gives a purple colour with alkaline potassium ferricyanide solution, which is taken up by chloroform. This reaction reminds one of that of apomorphine. And the sinomenol, which is the decomposition product of sinomenine by potash fusion, and is determined to be dioxy-dimethoxy-phenanthrene, gives a beautiful blue colour, when treated with ammoniacal silver in an acetone solution. The author regarded that this

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(1) The former papers of this series were published in *Journal of the Agricultural Chemical Society of Japan*, **1** (1924), 3; **1** (1925), 50 and 89; others in Japanese.

(2) *Proc. Imp. Acad.*, **2** (1926), 7.

blue colour, might have come from the formation of an ortho-chinone from sinomenol by the oxidising agent.

The provisional formula could explain the formation of sinomenol from sinomenine by potash fusion, etc. very easily, but it was not without its difficulties. The principal one was that it could not explain the formation of dihydro-sinomenine, which is a phenol as well as a ketone, as the original sinomenine itself. The author, admitting these deficiencies, expected to reform it in future.

Meantime, Kondo and Ochiai⁽¹⁾ converted sinomenine into dihydrothebakodin by a series of reduction and moreover synthetised the dimethylsinomenol by Pschorr's method, proving that it is 3, 4, 6, 7-tetramethoxyphenanthrene.⁽²⁾ From these two facts, they withdrew their former views and assigned to sinomenine the formula (II), retaining the linking position of ethanamine chain in 5 or 13.

It seemed, therefore, very desirable to compare the ferri-cyanide reaction of sinomenine with that of thebainon and the reaction of sinomenol with that of 3-methoxy-4, 6-dioxy phenanthrene. The results in this respect are given in the following (The figure shows the dilution of the alkaloids, at which the colour is still visible).

	Ferri-cyanide reaction (chloroform)	Diazo-reaction
Sinomenine	1 : 500,000	1 : 2,000,000
Thebainon	1 : 1,000,000	1 : 1,500,000
Morphothebain	weak	1 : 2,000,000

Ammoniacal silver reaction in acetone (blue colour).

	Cold	Warmed
Sinomenol	1 : 10,000	1 : 50,000
3-Methoxy-5, 6-dioxyphenanthrene .	1 : 10,000	1 : 50,000
Morphol	—	—

From these results, it may be assumed that the relative position of the hydroxyl, and the ketone group in sinomenine is quite analogous to that of thebainone. The author, in cooperation with H. Sudzuki, synthetised dimethyl-sinomenol (this will be published later) and found also that it is 3, 4, 6, 7-dimethoxy-phenanthrene. The Kondo and Ochiai's sinomenine formula must, therefore, be admitted to be superior to my provisional one, even from the side of my investigation.

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(1) *J. Pharm. Soc. Japan*, No. 538, p 1015.
(2) Ibid., No. 539, p. 20.

As regards the linking point of methyl-aminoethyl group and the position of the double bond, Kondo and Ochiai assumes that they must be same with those in thebainon, in supposing that sinomenine is an optical antipode of a hypothetical 7-methoxythebainone. But the present author wishes to reserve this question for future, since there is some discrepancy in the reactions of sinomenine and thebainone, as for instance, sinomenine is easily decomposed by acetic anhydride into diacetyl-sinomenol and methylethyl-amine, whereas thebainone is very resistant to this treatment. The linking point of the side chain in morphine alkaloids is now rather the centre of the discussions› than to be regarded as determined. And the author hopes that sinomenine might give some clew in this problem in future.

Department of Chemotherapy,
Kitasato Institute, Tokyo.