SINOMENINE AND DISINOMENINE. PART XIII.(1)
ON THE REDUCTION OF BROMSINOMENINE.

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In 1923, one of the authors reported(2) that the bromination of sinomenine in acetic acid leads to two different monobromsinomenines, viz. monobromsinomenine and isobromsinomenine. The properties of these two substances may, for the sake of convenience, be given here in the following table.

		Bromsinomenine	Isobromsinomenine
Yield		8 %	20%
Solubility in alcohol		soluble in cold	insoluble in hot
M. p. of free base		153°	214°
Sp. rotation	free base	$[\alpha]_D^{25} = -2.62°$	$[\alpha]_D^{25} = +14.65°$
	hydrochloride	$[\alpha]_D^{25-5} = -30.19°$	$[\alpha]_D^{25} = +51.79°$
M. p. of HBr salt		110° (with 3 Aq.) 231° (anhydrous)	229 (anhydrous)
M. p. of ICH_3		80°	210~211°
Methoxyls		(not determined)	14.22% (calc. 15.19%)
M. p. of semicarbazone		270° (dec.)	amorphous.
$FeCl_3$		1,250(3)	400
Diazo-reaction		5,000	800
$K_3Fe(CN)_6$		100,000	no
Formaline—H_2SO_4		same as sinomenine.	reddish violet.

As regards the position occupied by the bromine atom, it may be reasonably assumed to be the position (1), opposed to the free phenol hydroxyl, since the diazo-reaction is remarkably diminished in the both brom-sinomenines. In isobromsinomenine, moreover, the third nucleus of the phenanthrene may have been undergone some change, as it does not give the potassium ferricyanide reaction.

This assumption, in regard to the position of bromine atom, is enforced by the following two facts.

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(1) Parts XI and XII will be published later.

(2) *J. Chem. Soc. Japan*, **44** (1923), 815; *J. Agr. Chem. Soc. Japan*, **1** (1924), 3.

(3) The figures show the dilution, at which the reactions are still visible.

1. In contrary to sinomenine bromsinomenine is not linked together by means of oxidising agents such as $AgNO_3$, $K_3Fe(CN)_6$ and $AuCl_3$.

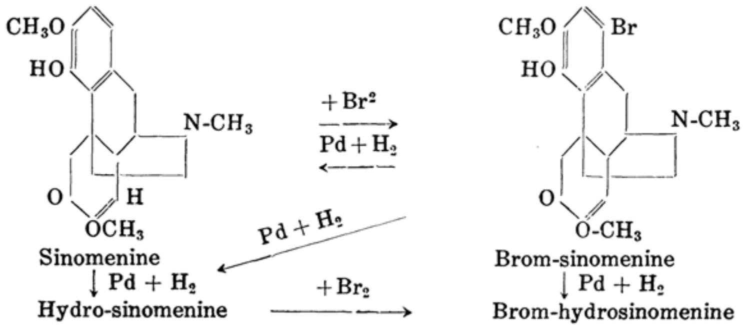
2. Disinomenine,⁽¹⁾ in which the position (1) is also regarded to be occupied by the linking of two sinomenine molecules, behaves quite differently from sinomenine on bromination. It does not given an easily manipulable substance, except a small quantity of yellow needles, which become quickly amorphous on exposure to air.

By the reduction of bromsinomenine with palladinised charcoal and and hydrogen, the authors could isolate the following substances.

Br-sinomenine (5 gr.)	With 1 mol H_2	With ca. 2 mol H_2
(1) Unchanged subst. (HBr)	2 gr.	2 gr.
(2) Br-dihydrosinomenine	0.4 gr.	0.5 gr.
(3) Hydro-sinomenine	—	0.5 gr.
(4) Sinomenine HBr	0.1 gr.	—

From these results, it may be concluded that the reduction of bromine atom and that of the double linking go on simultaneously.

Hydrosinomenine can be brominated in the same way as with sinomenine. The brom-dihydro-sinomenine thus obtained is quite the same with that produced by the reduction of bromsinomenine. By the reduction of brom-dihydrosinomenine, hydrosinomenine was obtained in 65% yield.



Experimental.

Attempts to Link together Bromsinomenine by Oxidation. The condition of the oxidation was the same as was given in p. 109, this Vol. this

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(1) This Bulletin, **4** (1929), 107.

journal. Gold chloride was also employed in this experiment. The greater part of the substance became amorphous. The only crystalline substance isolated was unchanged brom-sinomenine hydrochloride (m. p. 232° dec.)

Reduction of Monobrom-sinomenine. The condition of the reduction was almost the same as was given in p. 131, this Vol. this journal, only palladinised charcoal being used instead of colloidal palladium in this case. As to the yield, see the theoretical part.

Bromination of Hydrosinomenine. Hydrosinomenine (2gr.) in glacial acetic acid solution (55 c.c.) was added with Bromine (1 gr.) dissolved in glacial acetic acid (40 c.c.). No precipitate was formed. After being made alkaline with potassium carbonate, the base was extracted with chloroform. On evaporating chloroform, brom-dihydrosinomenine crystallised out in long prisms, which are boild with a large quantity of alcohol to remove impurities. M.p. 237° (dec.). Yield 80%. This bromdihydro-sinomenine gave hydrosinomenine on catalytic reduction in 63% yield.

Properties of Brom-hydro-sinomenine. Almost insoluble in boiling alcohol. M. p. 237° (dec.).

Specific rotation $[\alpha]_D^{24} = +102.4°$ (1.0841 gr. subst. in 50 c.c. chloroform solution, $l=1$ dm. $\alpha=2.22°$)

Ferric chloride reaction	+ in 1,000th dilution
Diazo reaction	+ in 10,000th dilution
$K_3Fe(CN)_6$ reaction	+ in 50,000th dilution
$CH_2O-H_2SO_4$	yellowish brown (no fluorescence).

Anal. Found: C=55.37; H=6.50; N=3.54; Br=18.96, 18.77%. Calc. for $C_{19}H_{24}BrNO_4$: C=55.59; H=5.85; N=3.41; Br=19.48%.

Hydrobromide. M. p. 229~232° (dec.). It is remarkable that this hydrobromide crystallised very easily, whereas no salt of hydrosinomenine was obtained in a crystalline form up to present.

Methiodide. Prepared in the ordinary way. Prisms of m.p. 225° (dec.). (Found: J=21.03%. Calc.: J=22.99%).

Semicarbazone. Beautiful flat prisms from dilute methyl alcohol. Dec. p. 250° (Found: N=11.31%. Calc.: N=11.99%).

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