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(RESEARCH ARTICLE)

The chemistry of the interaction of brucine with mercurous nitrate

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Abstract

The interaction of brucine with mercurous nitrate gives a carmine colour (Flückiger test for brucine). In this communication the chemistry and mechanism of this assay are provided for the first time. Since strychnine is inert with the reagent, it can be deduced that the methoxy groups in 2,3-dimethoxy-strychnine (brucine) are the reaction site. A methoxy group can be demethylated in special conditions. This is in accordance with the experimental fact that is needed to heat at the water bath in order to obtain a positive result. The positive charge in mercurous nitrate, vicinal to another positive charge, is the driving force and captures an electron from a methoxyl, leaving a radical ion. Separation of a methyl radical originates electron coupling at the oxygen atom. The residual positive charge at this atom produces a synchronous mechanism, forming an ortho-benzoquinone and displacement of a methyl-carbonium ion.

In the inorganic intermediate, the captured electron produces metal-metal breaking and elemental mercury is formed, with two electrons in the 6s subshell.

Keywords: Brucine; Driving force; Electron coupling; Flückiger test; Mercurous nitrate; Strychnine

1. Introduction

Brucine is an alkaloid found in the *Strychnos nux vomica* tree and in St. Ignatius bean (*Strychnos ignatii*). It is 2,3-dimethoxy-strychnine and possesses wide pharmacological activities, such as antitumor, anti-inflammatory, and analgesic. Brucine has also effects on cardiovascular and nervous systems, [1].

Brucine is a weak alkaline indole alkaloid that crystallises as white needles from acetone-water. Figure 1.

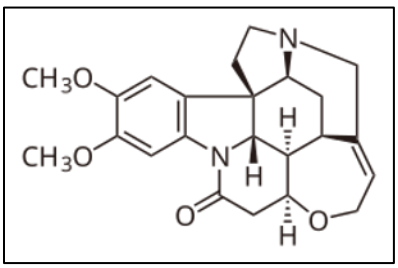

Figure 1 Brucine structure

In China *Nux vomica* is used for treatment of dyspepsia, nervous system diseases and chronic rheumatism, [2].

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Brucine produces nausea, vomiting, restlessness. Convulsions can be controlled with diazepam or with phenobarbital. The content of brucine is 1% in both seeds, but the bark of *S. nux-vomica* contains 2.4 % of brucine, [3].

In this communication the chemistry and mechanism of the Flückiger test for brucine are given for the first time. It is a follow up of our studies on reaction mechanism, [4-8].

2. Antecedents

F. A. Flückiger employed an aqueous solution of mercurous nitrate in order to detect brucine. No colouration was obtained when the reagent was added to a solution of a brucine salt, but when heated gently on the water bath, a fine carmine colour was produced, which is very durable. Strychnine does not give this reaction.

The test was published in Germany [9, 10], in the United States [11], and in England [12], as well as in books of analytical tests, [13-15].

If a solution of mercury(I) nitrate is boiled, it disproportionate into elemental mercury and mercury (II) nitrate, [16].

3. Discussion

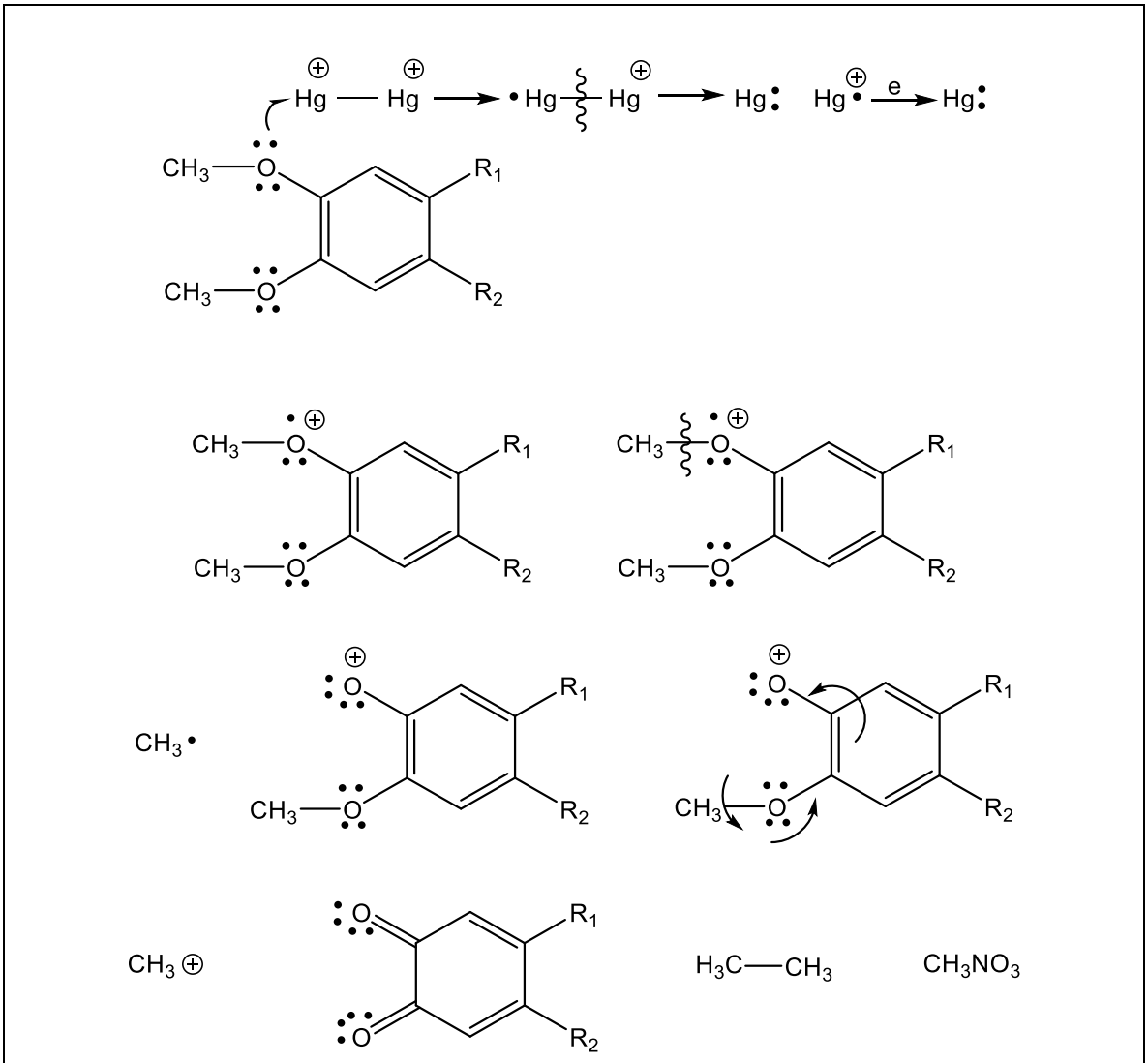

Figure 2 Oxidation route of brucine with mercurous nitrate

Brucine is 2,3-dimethoxy strychnine. The remark that strychnine does not give the Flückiger test for brucine is very important because it indicates that the reaction occurs at the methoxy groups of brucine, groups that are missing in the strychnine molecule.

A methoxyl group can be demethylated in special conditions. This is in accord with the experimental fact that brucine doesn't react at room temperature, but it must be heated in the water bath in order to obtain a positive result, see above.

The positive charge in mercurous nitrate constitutes the driving force for reaction with an electron from a methoxyl, leaving a radical ion at the organic molecule, Figure 2. The free radical produces separation of a methyl radical for radical-coupling at the oxygen atom. The free radical at the mercury atom produces rupture of the metal-metal bond, and elemental mercury is formed, with two electrons at the 6s subshell. Cf. [17].

After separation of the methyl-radical, a positively charged oxygen remains at C-2 position, whose neutralization originates a synchronous mechanism. An ortho-benzoquinone is formed with elimination of a methyl-carbonium ion.

The methyl radicals give ethane, and methyl nitrate comes from the respective ions.

Ortho-benzoquinones are red [18] and this explains the carmine colour observed in the test.

4. Conclusion

The chemistry and the mechanism of the Flückiger test for brucine has been cleared. It is a redox process in which mercurous nitrate is reduced to elemental mercury, and brucine is oxidised to an ortho-benzoquinone via demethylation involving free radical transfer and radical-ion intermediate. The other methyl group is lost as methyl-carbonium ion in a concerted reaction mechanism. The inorganic reagent is a free radical acceptor.

Compliance with ethical standards

Disclosure of conflict of interest

There is no conflict of interest to declare

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