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On the chemistry of Jorissen test for morphine

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Abstract

The Jorissen's test for morphine employs warm sulphuric acid both as solvent and reagent. Care must be taken in order to prevent morphine-apomorphine rearrangement. The species for sulphonation derives from sulphuric acidium ion whose dehydration produces the reactive cation HSO₃+. Reaction with the phenolic group in morphine gives an organic sulphate. Interaction with a hydrion and water elimination produces a key intermediate. There is separation of sulphur dioxide, ketone formation, and formation of a new sulphate at the activated C-2 position. Isomerization of dienone to phenol restores aromaticity. Finally, dehydration by acidolysis gives rise to a concerted push-pull mechanism: water, SO₂, and an ortho-benzoquinone are formed. Added ferrous sulphate and ammonia water originate halochromism: red to violet colour and the ammonia turns blue.

Keywords: Acidolysis; Halochromism; Hydrion; ortho-Benzoquinone; Push-pull mechanism; Sulphur dioxide

1 Introduction

Papaver somniferum is the species of plant from which both opium and poppy seeds are derived and is also a valuable ornamental plant grown in gardens.

Poppy seeds are prized for their nutty flavor and nutritional content. The flowers are cultivated for their striking appearance.

The latex of the plant is known as opium and contains various alkaloids with medicinal properties.

While the resin, or latex, contains potent alkaloids, the seeds and ornamental flowers do not contain these alkaloids and are harmless. All plants of the Papaver genus produce opium alkaloids, but Papaver somniferum is the most potent and important.

The mixture of alkaloids from the whole resin (opium) may produce a more balanced pharmacological effect, reducing the immediate intensity of euphoria and the subsequent risk compared to isolated opiates such as morphine.

The term "opiate" refers specifically to the natural derivatives of the opium poppy. "Opioids" is a broader term that includes both opiates and the synthesized products.

Morphine is the most potent analgesic extracted from the plant and constitutes 10-15% of opium. The dose is 5-30 mg depending on the level of pain. Figure 1.

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Figure 1 Morphine chemical structure

Codeine constitutes 1-3% of opium. The dose is 15-60 mg to relieve pain and suppress cough.

Papaverine is used for its antispasmodic effects. The dose ranges from 100 to 300 mg per day.

Noscapine is an antitussive. The dose is 50-100 mg up to four times a day, [1].

Jorissen proposed a test for morphine based on warm sulphuric acid, with additives for colour development.

In the present communication the chemistry of this test is described. It is a follow up of our studies on reaction mechanism, [2-6].

2 Antecedents

Professor Jorissen heated morphine on a water bath with a few drops of sulphuric acid and a crystal of ferrous sulphate and poured the resulting liquid into a few ml of ammonia water. At point of contact a red colour develops, soon changing to violet, while the ammonia solution turns blue, [7].

The reactive group in morphine is the phenol at C-3. It is responsible of many oxidation reactions of morphine. So, we looked for the chemical deportment of sulphuric acid as oxidizer.

Sulphuric acid is a strong oxidizer that can oxidize many organic compounds and metals, [8]. Hot concentrated sulphuric acid transforms copper, silver and mercury into oxides plus water and SO₂. The oxides give the sulphates, [9].

Many of the applications of sulphuric acid depend upon the oxidizing power of the concentrated acid, for example, removing organic sulphides from petroleum, [10]. There is still an old theory stating that sulphuric acid in concentrated form gives nascent oxygen and forms sulphurous acid, which is not stable compound and will dissociates into SO₂ plus H₂O, [11].

The theory of nascent elements, such as hydrogen or oxygen, has been discarded. A modern point of view is described in the next section.

3 Discussion

In the Jorissen test morphine is heated on the water bath with few drops of sulphuric acid. However, it must be taken into account that the heating must be brief in order to prevent the morphine-apomorphine rearrangement, [12, 13].

Let's see the formation of the reactive species. Figure 2.





Figure 2 Mechanism of the Jorissen test for morphine

Interaction of a hydrion [14, 15] with sulfuric acid produces sulphuric acidium ion, H_3SO_4+ , whose dehydration gives the active species. [16, 17]. Reaction of HSO_3+ with the phenolic group in morphine forms an organic sulphate. Protonation of the hydroxyl in this sulphate and water elimination gives rise a concerted mechanism with detachment of SO₂, ketone formation, and activation of C-2 position. The electrophilic character of this site permits reaction with sulphuric acid, and a new sulphate is obtained. There is isomerization of dienone to phenol, recovering aromaticity.

The last step is water elimination from the sulphate via acidolysis, generating a synchronized mechanism in combination with the electrodotic effect [18, 19] of the phenol group, that is, a push-pull mechanism. This way SO₂ is separated, and two vicinal carbonyl groups are formed. In other words, an ortho-benzoquinone results. Compounds of this type are red, [20-22]. However, the colours observed in the test are due to halochromism, [23, 24].

In this redox process the organic compound is oxidized, and sulphuric acid is reduced to SO₂ (sulphurous anhydride). This in combination with the water also formed is equivalent to unstable sulphurous acid.

4 Conclusion

The chemistry of Jorissen test for morphine has been cleared. The chemical deportment of the reagent was revised. The cationic reactive-species is in accordance with the mechanisms proposed in related reactions. The proposed reaction mechanism generates Umpolung at C-2, facilitating formation of a sulphate. Acidolysis leads to the final oxidation product, an ortho-benzoquinone.

Compliance with ethical standards

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Disclosure of conflict of interest

There is no conflict of interest to declare

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