World Journal of Organic Chemistry, 2020, Vol. 8, No. 1, 5-6
Available online at http://pubs.sciepub.com/wjoc/8/1/2
Published by Science and Education Publishing
DOI:10.12691/wjoc-8-1-2

On the Sabanin-Laskowski Test for Citric Acid

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Received December 10, 2019; Revised January 11, 2020; Accepted January 29, 2020

Abstract The Sabanin-Laskowski test for citric acid, the reaction of citric acid with ammonia under pressure, produces a yellow compound which on standing turns blue. This uncommon chemical deportment deserves a study of this almost forgotten chemical test in order to update it, since it has been found that this yellow compound has unique luminescent properties that now are used in nanotechnology and is studied in Organic Chemistry, Physical Chemistry as well as in Biological Chemistry.

Keywords: *citrazinic acid, colorimetry, fluorescence, O-nanodots, pyridones, reactive intermediates*

Cite This Article: Francisco Sánchez-Viesca, and Reina Gómez, "On the Sabanin-Laskowski Test for Citric Acid." *World Journal of Organic Chemistry*, vol. 8, no. 1 (2020): 5-6. doi: 10.12691/wjoc-8-1-2.

1. Introduction

In the records of Chemical Tests [1,2], there is the Sabanin-Laskowski test for citric acid. It is performed by heating the acid with excess of ammonia in a sealed tube at 120°C for six hours. A yellow color develops which on standing for several hours changes to blue.

This change cannot be attributed to aerial oxidation in alkaline medium since this reaction produces ortho- or para-quinones which are yellow, orange or even red.

In a recent book on Citric Acid [3], there is a brief comment on a cognate reaction. Citrazinic acid amide can be prepared by treating citric acid with a large excess of ammonia under pressure in the 165-200°C temperature range.

As it can be seen, the temperature is higher than the employed in the Sabanin-Laskowski test. These Russian chemists are not mentioned, nor chemical structures given.

When urea is heated to 150-160° biuret, NH_2CO-NH-$CONH_2$, and ammonia are formed [4], thus explaining the presence of ammonia for further reactions.

2. Discussion

Citrazinic acid is 2,6-dihydroxypyridine-4-carboxylic acid, that is, 2,6-dihydroxyisonicotinic acid. However, the tautomeric 2-pyridone structure is preferred, Figure 1.

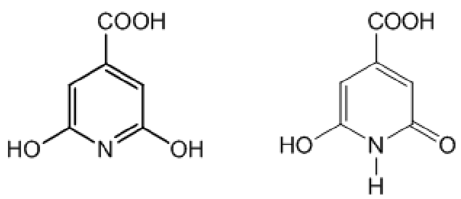

Figure 1. Citrazinic acid tautomeric atructures

This compound is a yellow solid and its alkaline solutions turn blue on standing [5].

Citric acid, 2-hydroxypropane-1,2,3-tricarboxylic acid, is represented in Figure 2

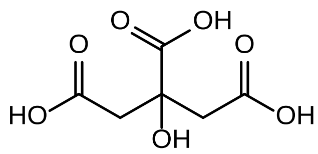

Figure 2. Citric acid structure

Since citrazinic acid has only one nitrogen atom, a terminal citric acid mono-amide must be the precursor molecule in order to react with the more distant carboxyl group and form a six member ring. However, the modern representation of the acid does not fit the reactivity of the amide for cyclization. The older curved structure is satisfactory for imide formation and cyclization, Figure 3. The central mono-amide would yield a five member ring.

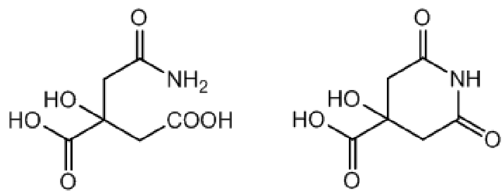

Figure 3. Adequate citric acid mono-amide and resulting imide

The question at which stage the hydroxy group is lost by dehydration is treated now. Direct dehydration of citric acid would yield aconitic acid with trans-configuration. This would permit subsequent cyclization. However, citric acid dehydrates to trans-aconitic acid at 175°C, [5], and the reaction temperature of our test is 120°C, preventing direct dehydration.

In the metabolism of animal cells citric acid is dehydrated to cis-aconitic acid [6,7] but this compound turns to the trans-form by heating [8], Figure 4.

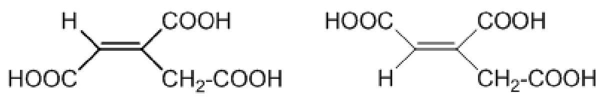

Figure 4. Trans- and cis-aconitic acid

If dehydration occurs after citric acid imide formation it would yield trans-aconitic acid imide, Figure 5.

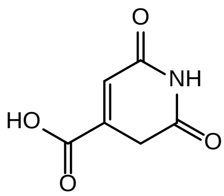

Figure 5. Trans-aconitic acid imide

But why dehydration can be achieved at 120°C since dehydration of citric acid occurs at 175°C? This can be explained by previous enolization of one amido group. This can enhance dehydration, extending conjugation to an α,β,γ,δ-unsaturated system, and affording citrazinic acid, Figure 6.

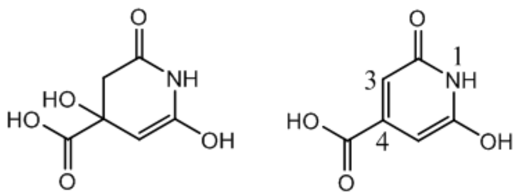

Figure 6. Key intermediate for dehydration and citrazinic acid

This 2-pyridone absorbs at 600 nm (formerly mμ), [9]. The absorbance or optical density occurs in the red range of the visible spectrum, 6000 Å, [10]. However, other authors [11,12] set this absorption in the orange range, 590-625 nm whose complementary color is green-blue. When only six principal colors are considered there is no boundary problem: the complementary color of red is green, and of orange is blue [13], the color presented by citrazinic acid solutions after day-light absorption.

The aqueous solutions of citrazinic acid glows blue under UV light (fluorescence). Thus, this compound is fluorophore. It exhibits a 365 nm absorption peak and a 440 nm fluorescent peak, [9].

3. Conclusion

Actually there is a great interest in citrazinic acid since it is used in nanotechnology as carbon dots, luminescent nanoparticles that can be used to track biological processes inside cells.

Thus, the Sabanin-Laskowsky reaction has been used again, with some variations. For instance, hydrothermal treatment of a solution of sodium citrate and ammonium bicarbonate at 180°C for 4 hours leads to the formation of O-dots (organic dots), [14].

Other preparation of citrazinic acid is by thermolysis of citric acid and urea melt. The luminescent organic dots are used for cell staining, [15].

Nitrogen doped carbon dots were synthesized from citric acid and urea via a microwave assisted route. The NCDs show emission maximum at 500 nm, on excitation at 400 nm, [16].

The structure of the yellow compound formed in the Sabanin-Laskowski test for citric acid has been cleared up, as well as its formation mode and its optical properties (colorimetry). Citrazinic acid is very important in actual nanotechnology and thus it is in frontier science.

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