Notes

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Hidehiko Kaneko : A New Color Test for Yohimbine-type Compounds; with Special Reference to Rauwolfia Alkaloids.

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As the coloring reagents for yohimbine-type alkaloids, oxidation agents dissolved in sulfuric acid, e.g. Adamkiewitz reagent, are often used. Hofmann[1] carried out discrimination of various Rauwolfia alkaloids by the so-called Keller reaction by dissolving a sample in acetic acid containing trivalent iron ion (such as ferric chloride), superimposing concentrated sulfuric acid over this solution, and observing the color developed at the zone of contact of these two layers. However, this color reaction is positive only in compounds of the tetrahydro-β-carboline type and not in β-carboline type compounds (e. g. anhydronium base).

The present writer attempted a color reaction to be described below and found that not only the tetrahydro-β-carboline type but β-carboline type compounds also undergo coloration by this procedure. In this reaction, a sample is dissolved in a small amount of acetic acid and approximately equal volume of concentrated sulfuric acid containing about 0.5% of sodium or potassium nitrite is superimposed over the acid solution, by which a color appears at the zone of contact; green to blue or bluish violet in tetrahydro-β-carboline type compounds and deep pink to reddish purple in β-carboline type compounds. In compounds with anhydronium structure, the color that appears is deep

Table I. Compounds tested and Their Color Reactions with the Nitrite Reagent and the Keller Reagent

Compound	Color developed			
	Upper layer	Contact zone	Lower layer	Keller test
Reserpine	yellow	sky blue → brown	colorless	sky blue → green → yellow
Methyl reserpate	yellow	sky blue → brown	colorless	sky blue → green → yellow
Rescinnamine	brown	sky blue → brown	colorless	sky blue → green → yellow
Deserpidine	yellow	green → brown	brown	yellowish green
Isoreserpine	yellowish brown	green → brown	colorless	blue → green
Yohimbine	yellow	blue-violet	colorless	blue-violet
Sarpagine	dark violet	purple	colorless	rose red
Ajmalicine	yellow	green → brown	colorless	yellowish green
Reserpinine	yellow	blue → dark brown	blue	blue → green
Ajmaline	light red	carmine red	orange yellow	slightly brown
Serpentine	yellow	rose red	colorless	colorless
Serpentinine	yellow	blue → rose red	colorless	blue
Tetradehydro-yohimbine	colorless (fluorescence)	rose red	colorless	colorless
Tetradehydro-yohimbic acid	colorless (fluorescence)	rose red	colorless	colorless
Tetradehydro-reserpic acid	colorless (fluorescence)	purple	colorless	colorless
Tetradehydro-reserpic acid lactone	colorless (fluorescence)	purple	colorless	colorless
Flavoserpentine	colorless (fluorescence)	rose red	colorless	colorless
7-Methoxy-yobyrine	colorless (fluorescence)	purple	colorless	colorless

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1) A. Hofmann : Helv. Chim. Acta, **37**, 314, 849(1954).

pink in serpentine, tetradehydroyohimbine, sempervirine, and flavoserpentine,[2] and reddish purple in tetradehydroreserpic acid or its lactone.[3] Serpentinine, which is considered to be a complex molecule with tetrahydro-β-carboline and anhydronium structures, first shows blue coloration which gradually changes to deep pink, suggesting the presence of an anhydronium structure. Specific color reaction is observed in indoline alkaloids, ajmaline giving a bright red color and sarpagine, dark violet.

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Summary

The color developed by superimposing concentrated sulfuric acid, containing 0.5% of nitrite, over acetic acid solution of a sample of yohimbine-type alkaloids was found to be specific not only for tetrahydro-β-carboline type but also to anhydronium bases.

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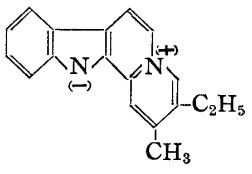
2) Unpublished work. The dehydrogenation product, m.p. 200~202°, of serpentine has been named flavoserpentine whose empirical formula is assumed as follows :



3) S. Uyeo, H. Kaneko : J. Am. Chem. Soc., in press.