## Notes

### Shoshichiro Kimoto and Masao Okamoto: Studies on the Alkaloids of *Amsonia elliptica* Roem et Schult. III.[1] Identity of Amsonine with β-Yohimbine.

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About ten years ago, it was reported[1] that a new base had been isolated from *Amsonia elliptica* Roem et Schult (Apocynaceae) and was named amsonine.

This substance has m.p. 235~237°(decomp.), $[\alpha]_D$: −8.9°, and it was assumed by chemical means and ultraviolet absorption that this base belonged to an alkaloid of yohimbine series.

The authors reinvestigated the data reported in an earlier paper and tried to establish whether amsonine is identical with or different from the known alkaloids of yohimbine series.

From the results of the present investigation on the physical properties (Table I), it seems most reasonable to conclude that amsonine is identical with β-yohimbine.

Table I.

| | β-Yohimbine[2] | | Amsonine | | |
|---|---|---|---|---|---|
| | m.p.(°C) | $[\alpha]_D$ | m.p.(°C) | $[\alpha]_D$ | temp. |
| Free base | 236~237 | −46.6°(Py) | 236~237 | −38.6°(Py) | (25°) |
| | | −18.5°(E) | | −17.6°(E) | (9°) |
| Hydrochloride | 297 | +29.3°(W) | 303~305 | +37.4°(W) | (27°) |
| Amino-acid | 265 | +15.5°(Py) | 257~259 | +16.8°(Py) | (13°)[1] |
| Yohimbone | 307 | −104° (Py) | 307~309 | −96.0°(Py) | (10°) |

Py: pyridine E: ethanol W: water

The melting point of amsonine was not depressed on admixture with β-yohimbine[3] and the infrared spectra of these two samples are entirely identical. Furthermore, amsonine produced yohimbone, m.p. 307~309°(decomp.), by the Oppenauer oxidation using aluminum phenoxide and cyclohexanone in xylene according to the direction of Witkop,[4] and as a result, it was found that amsonine was identical with β-yohimbine.

We wish to express our appreciation to Dr. Schlittler for his kindness in giving advices, and we thank Mr. Z. Nakajima who kindly collected the plant material and Mr. M. Yamaguchi for the determination of infrared absorption spectra.

### Experimental

**Oppenauer Oxidation of Amsonine**—To a mixture of amsonic acid[1] (0.95 g.), dried at 110° *in vacuo*, and Al phenoxide (5.0 g.), prepared from Al powder (3.0 g.) and phenol (15 g.), were added 25 cc. of abs. xylene and 25 cc. of purified cyclohexanone (b.p. 156°), and the mixture was heated at 155~165° in an oil bath for 49 hrs., until in reddish brown solution. After cooling, upper layer was decanted and the residue was extracted repeatedly with a mixture of ether and xylene. Combined organic solution was treated successively with 2*N* NaOH and water. Organic layer was shaken with successive portions of 2*N* HCl until the aqueous layer no longer produced precipitate with Meyer reagent. Then the aq. acidic layer, after treated once with ether, was neutralized with satd. aq. $Na_2CO_3$, and the neutral solution was extracted repeatedly with ether. The

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1) S. Kimoto, S. Honjo: J. Pharm. Soc. Japan, **63**, 159(1943).
2) A. Le Hir, R. Goutarel: Bull. soc. chim. France, **1953**, 1023.
3) The authors are indebted to Prof. M. M. Janot for the gift of the authentic sample of β-yohimbine.
4) Ann., **554**, 83(1943).

ether extract was washed with water, dried over $Na_2SO_4$, and the ether distilled off, leaving a crude crystalline base from which 0.5 g. of yohimbone was obtained as colorless needles, m.p. 307~309°(decomp.)(corr.), upon recrystallization from MeOH. The melting point of this base was not depressed by admixture with an authentic sample of yohimbone prepared by us from yohimbine. $[\alpha]_D^{10}$: −96.0°(50 mg. in 15 cc. pyridine, $l$=1 dm.).

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**Shigehiko Sugasawa and Kitaro Mizukami**: Application of Ball Reaction to Aromatic Alcohols. II.

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In the first paper[1] we reported that several aromatic primary alcohols could be oxidized to the corresponding aldehydes by means of active manganese dioxide in a suitable solvent and expressed our views that this method may generally be applied on various aromatic alcohols.

Since that time there appeared two papers dealing with the same subject, which reported contradictory results. According to Turner[2] benzhydrol and xanthydrol were converted into the corresponding ketones, but benzyl alcohol and furfuryl alcohol failed to give the aldehydes. On the contrary, Harfenist, *et al.*[3] reported that benzyl alcohol, veratryl alcohol, and furfuryl alcohol could be successfully oxidized to the corresponding aldehydes, and so his results are on the whole the same as ours.[1] The results of our further experiments are shown in the accompanying table and there has been no unsuccessful experience so far as our experiments are concerned.

TABLE[4]

| R-$CH_2$OH→R-CHO R | Solvent | Time | Temp. | Yield of Semicarbazone |
|---|---|---|---|---|
| 1-Pyridyl | Ether | 2.5 hrs. | 32~34° | 45%(m.p. 194~196°) |
| 4-Antipyryl | $CHCl_3$ | 3 〃 | 35° | 83%(m.p. 221~223°(decomp.)) |
| 2-Thienyl | Ether | 3 〃 | 34° | 70%(m.p. 222~224°(decomp.)) |
| 2-Quinolyl | 〃 | 1.5 〃 | 33° | 70%(m.p. 233°) |

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1) This Bulletin, **2**, 341(1954).
2) D. L. Turner: J. Am. Chem. Soc., **76**, 5175(1954).
3) M. Harfenist, A. Bavley, W. A. Lazier: J. Org. Chem., **19**, 1608(1954).
4) For procedure see Footnote 1).