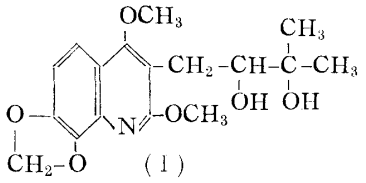
Note

UDC 547.544.8.05

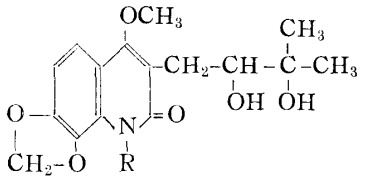
Masanobu Terasaka, Kazuko Narahashi, and Yoko Tomikawa : Alkaloids of the Root-bark of *Orixa japonica* THUNB. X.[1] Isolation of Nor-orixine.

(*Womens' Department, Tokyo College of Pharmacy*[*1])

Previously, one of the authors (Terasaka[2]) established the structure of orixine (I) as well as those of nor-orixine (II), and iso-orixine (III), and has shown that nor-orixine can be derived from orixine by the action of hydrochloric acid in ether and iso-orixine from nor-orixine by the action of diazomethane on nor-orixine.



(I)



(II) R=H
(III) R=CH_3

A substance of m.p. 199~200° is obtained after orixine, kokusagine, skimmianine, and evolitrine, all of which are insoluble in potassium hydroxide and can be extracted with ether, have been removed from methanol extract of Orixa, water-soluble portion made acid with hydrochloric acid, and extracted with chloroform. This substance, $C_{16}H_{19}O_6N$, was identified as nor-orixine by mixed m.p., infrared and ultraviolet spectra, and paper electrophoresis. Nor-orixine colors yellow-green with conc. sulfuric acid or fuming nitric acid. It is to be noted that although orixine is characteristic in ease with which it loses one methyl group by the action of hydrochloric acid in ether, it is never converted into nor-orixine on warming with 2% sulfuric acid.

Recently, Goodwin, *et al.*[3] isolated from *Lunasia amara* BLANCO, iso-orixine and named it hydroxylunidine, hence it is possible that iso-orixine is also present in Orixa, but it has not been isolated to date.

Experimental

Nor-orixine—A mixture of 550 g. of MeOH extract from the root and stem bark of *Orixa japonica* THUNB. and 2% H_2SO_4 was warmed on a steam bath, the solution was filtered through Celite, made alkaline with NH_4OH, and extracted several times with Et_2O. On evaporating the Et_2O solution and adding small quantities of $CHCl_3$ to the residue, 5.896 g. of crude alkaloid was obtained, which by crystallization from EtOH afforded 1.881 g. of orixine (m.p. 152.5°).

From the mother liquor of orixine, the solvent was evaporated and the residue was extracted with 2% HCl. The clear yellowish brown acid solution so obtained was made alkaline, extracted with Et_2O, and the extract gave 1.539 g. of white prisms, which were proved to be a mixture of evolitrine (m.p. 193°), kokusagine (m.p. 196°), and skimmianine (m.p. 176°). They were each isolated by chromatography on Al_2O_3[4] and identified by mixed m.p. and Rf value in paper electrophoresis.[5] The Et_2O-insoluble alkaline solution was made acid with HCl and extracted with $CHCl_3$. After removal of the solvent the residue was crystallized from andyd. EtOH to colorless needles or prisms, m.p.

*1 Ueno-Sakuragi-cho, Taito-ku, Tokyo (寺阪正信, 奈良橋和子, 富川陽子).

1) Part IX : This Bulletin, 8, 523(1960).
2) M. Terasaka : *Ibid.*, **7**, 946(1959).
3) S. Goodwin, A.F. Smith, A.A. Velasquez, E.C. Horning : J. Am. Chem. Soc., **81**, 6209(1959).
4) M. Terasaka, S. Hara, K. Narahashi, Y. Tomikawa, Y. Tokushige : Tokyo Yakka Daigaku Nempo, **9**, 249(1959).
5) M. Terasaka, K. Narahashi, Y. Tomikawa : Syoyakugaku Zasshi, **13**, 68(1959).

199—200°. Yield, 0.356 g. The identity of this substance with nor-orixine was confirmed by mixed m.p., and by infrared and ultraviolet spectra. Nor-orixine is soluble in KOH, insoluble in Na_2CO_3, soluble in EtOH, benzene, and $CHCl_3$, and less soluble in Et_2O. Yellow-green color was observed with conc. H_2SO_4 or fuming HNO_3. *Anal.* Calcd. for $C_{16}H_{19}O_6N$: C, 59.80; H, 5.96; N, 4.36. Found: C, 60.23; H, 6.08; N, 4.30. IR ν_{max}^{KBr} cm^{-1}: 3459 (OH), 3155, 3080 (NH), 1660, 1640 (NH-CO). UV λ_{max}^{EtOH} mμ (log ε): 245 (4.53), 258 (4.47), 265 (4.49), 320 (4.12); UV λ_{min}^{EtOH} mμ (log ε): 245.5 (4.53), 273 (3.69).

Paper Electrophoresis of Nor-orixine—Applying the previously reported procedure,[5] Michaelis buffer (*N* NH_4Cl/*N* NH_4OH 1/8 was diluted to 20 volumes and adjusted to pH 10.6) was used as the electrolyte and electrophoresis was performed at 700 V for 3 hr. Rf of nor-orixine: 70 mm., 19.9 V/cm., 1.07 mA/cm.

The authors are indebted to Misses K. Ishida and Y. Kanno for their technical assistance in this work.

Summary

Nor-orixine, previously derived from orixine, was found in free state in the methanol extract of the Orixa root. This is the seventh alkaloid isolated from it.

(Received April 2, 1960)