UDC 547.94 : 582.751.9

91. **Masanobu Terasaka**: Alkaloids of the Root-bark of *Orixa japonica* THUNB. IX.[1] The Structure of Orixine.

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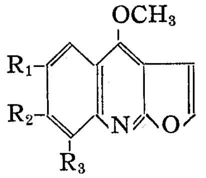
From the root-bark of *Orixa japonica* THUNB., the stems and leaves of which are used in some regions as an insecticide, an alkaloid was isolated in 1931 and was named orixine.[2] Its molecular formula was given as $C_{18}H_{21(23)}O_6N$, but was altered to $C_{17}H_{21}O_6N$ by later examinations.[1] Orixine is characterized by its melting point (152.5°), chloroaurate (m.p. 155°, decomp.), and $[\alpha]_D$ +83.29°, as well as by its sublimation, solubility, and color reactions. It can also be detected by paper electrophoresis[1] in which the alkaloidal spot appears as a faint violet fluorescence (the best result being obtained by using Michaelis' buffer I (pH 10.6; *N* NH_4Cl-*N* NH_4OH=1:8, diluted to 20 vol. with water), Rf at 62 in case of 19.9 v/cm., 0.93 mA/cm., 3.5 hr., using Toyo Roshi No. 50). Orixine is a very weak, tertiary base, contains, besides one methylenedioxy group and two methoxyl groups, 1,2-glycol and one terminal methyl group. In contrast to kokusagine,[3] kokusaginine,[4] and skimmianine,[5] which occur in this plant, orixine undergoes neither catalytic reduction nor isomerisation by methyl iodide under pressure, from which furoquinoline structure for orixine is excluded.



Kokusagine : R_1=H, R_2+R_3=-O-CH_2-O-
Kokusaginine : R_1=R_2=CH_3O, R_3=H
Skimmianine : R_1=H, R_2=R_3=CH_3O

When orixine is warmed with 20% hydrochloric acid, demethylation and dehydration occur and orixine is converted into orixidine, m.p. 195°, $C_{15}H_{13}O_4N$, and a phenolic base, orixidinine, m.p. 213°, $C_{15}H_{15}O_5N$.

By the study of ultraviolet and infrared spectra of the above-mentioned compounds, a ring closure between C-3 and C-4 in the quinoline ring seems to have occurred and α-quinolone has been formed.[*2] It is of interest to note that demethylation of orixine also occurs by the action of hydrochloric acid in ether. Dried hydrochloric acid was passed into the ether solution of orixine, an amorphous substance that precipitated was collected, washed with ether, and dried in vacuum. After being left overnight, dehyd. ethanol was added and colorless prisms, m.p. 199~200°, were obtained. Formerly, this was assumed to be isoörixine, $C_{18}H_{21}O_6N$, but in reality it is nor-orixine, $C_{16}H_{19}O_6N$, a substance with one methoxyl group less than orixine. Nor-orixine is soluble in potassium hydroxide solution and contains, like orixine, one methylenedioxy group, 1,2-glycol, and one terminal methyl group. It forms a dibenzoate with *p*-nitrobenzoyl chloride, m.p. 221~222°. It reacts with diazomethane, but does not return to orixine and is converted to an N-methylated substance, i.e. isoörixine, prisms, m.p. 127°, $C_{17}H_{21}O_6N$. It has

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[*2] Further information will be published later.

1) Part Ⅷ: Tokyo Yakka Daigaku Nempo, **9**, 249(1959).

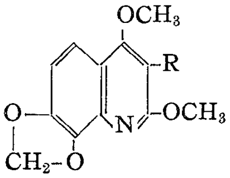
2) M. Terasaka: Yakugaku Zasshi, **51**, 707(1931).

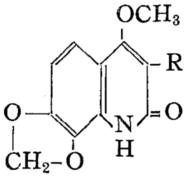
3) M. Terasaka, T. Ohta, K. Narahashi: This Bulletin, **2**, 159(1954).

4) *Idem*: *Ibid.*, **75**, 1040(1955); F.A.L. Anet, P.T. Gilham, P. Gow, G.K. Hughes, E. Ritchie: Australian J. Sci. Research, A, **2**, 429(1949).

5) Y. Asahina, M. Inubuse: Yakugaku Zasshi, **50**, 1133(1930); M. Terasaka: *Ibid.*, **62**, 304(1942).

been revealed by examination of ultraviolet spectra of nor- and iso-orixines that they belong to α-quinolone and, it is noteworthy to learn that their absorption spectra are very similar to that of 3-ethyl-4-methoxy-7,8-methylenedioxycarbostyril[3] (VII), which is derived from kokusagine by catalytic reduction in the presence of platinum dioxide. A comparison of ultraviolet spectra of kokusagine and skimmianine, which contain methylenedioxy or methoxyl groups in the 7- and 8-positions of the quinoline ring, and that of kokusaginine, which has its methoxyl groups in the 6- and 7-positions and exhibits a bathochromic shift on acidification, suggests that the position of methylenedioxy and methoxyl groups in nor-orixine is the same as those in (VII).


Orixine


Nor-orixine

The side-chain (R) of nor-orixine is composed of five carbon atoms and has α-glycol and C-CH_3.

Oxidation of orixine with periodic acid gave acetone (2,4-dinitrophenylhydrazone, m.p. 128°) and an aldehyde (IV), $C_{14}H_{13}O_5N$, fine needles of m.p. 122° (*p*-nitrophenylhydrazone, m.p. 226.5°). Nor-orixine produces, likewise, in a good yield, acetone and an aldehyde (VIII), $C_{13}H_{11}O_5N$, needles, m.p. 230°. Since the ultraviolet spectra of these aldehydes are very similar to those of orixine and nor-orixine, it is very probable that the oxidation was effected in the side-chain with no change in their rings. The structure of orixine is, therefore assumed to be (I) and those of nor- and iso-orixine as (II) and (III), respectively.

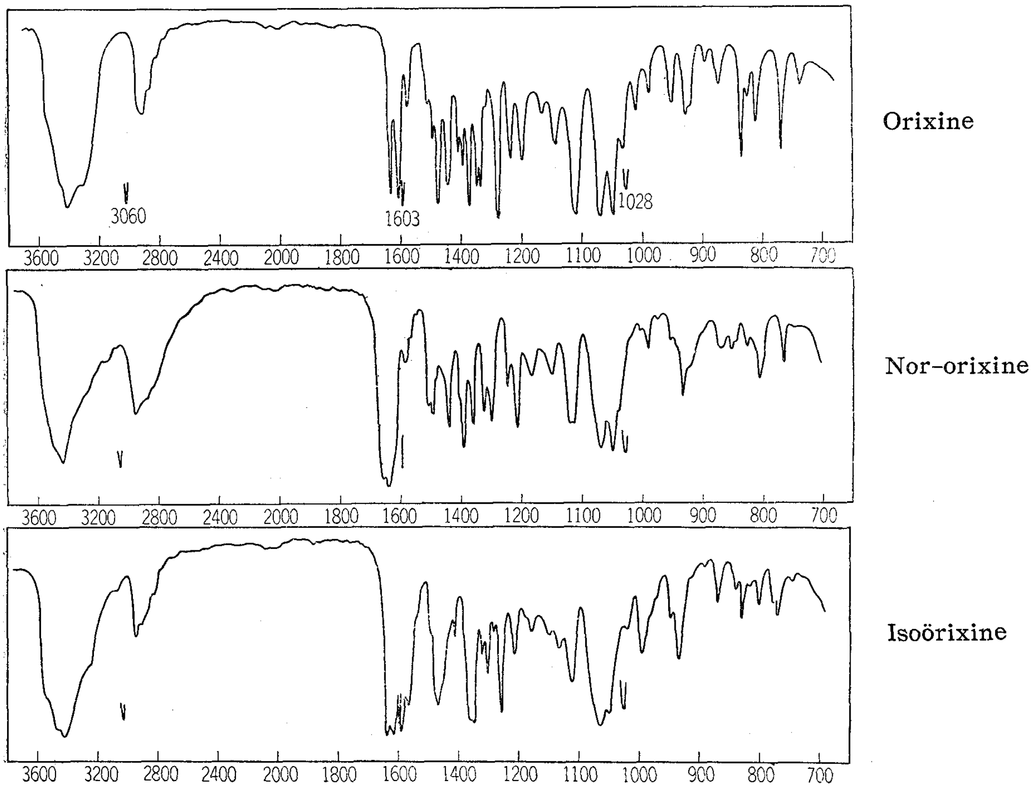
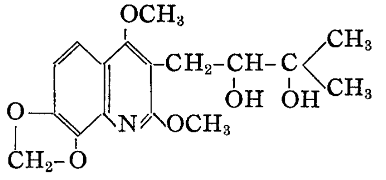
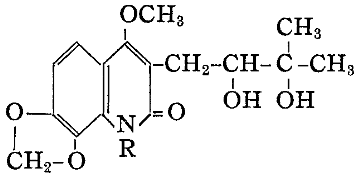


Fig. 1. Infrared Spectra of Orixine, Nor-orixine, and Isoörixine



(I)



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

Further evidence was obtained by the following sequence of reactions:

The aldehyde (IV) from orixine was dissolved in ethanethiol, reacted with boron trifluoride-diethyl ether, maintaining the temperature at about 0°, and the mixture was stood overnight,6) by which a dithioacetal (V), $C_{18}H_{23}O_4NS_2$ was obtained as plates, m.p. 83.5~84°. The aldehyde was refluxed in dehyd. ethanol with Raney nickel and yielded an alcohol, $C_{14}H_{15}O_5N$, of prisms, m.p. 81°, which underwent demethylation through the action of dry hydrochloric acid gas, as in the case of orixine, and formed needles, m.p. 169°, $C_{13}H_{13}O_4N$. This substance showed no depression of the melting point when mixed with an authentic sample of α-quinolone (VII) from kokusagine and their infrared spectra were identical.[*3] The aldehyde (VIII) from nor-orixine likewise forms at first dithioacetal (IX), $C_{17}H_{21}O_4NS_2$, m.p. 123~124°, then undergoes desulfurization with Raney nickel to a substance of m.p. 169°, which shows no depression of the melting point on admixture with (VII). Therefore, the structures (I), (II), and (III) are unequivocally established.

Recently, Goodwin, *et al.*7) isolated hydroxylunacridine, an alkaloid, from the leaves of *Lunasia amara* BLANCO and established its structure. They obtained an alcoholic substance by the ring cleavage of dihydro-γ-fagarine produced by the catalytic reduction of γ-fagarine. In analogy, the aldehyde (VIII) from nor-orixine was reduced with sodium borohydride in ethanol and an alcoholic substance (X), m.p. 200~201°, $C_{13}H_{13}O_5N$, was produced. It yields with diazomethane an N-methylated substance (XI) as prisms, m.p. 145.5°. (XI) is the same as the substance produced by methylation of dihydrokokusagine (XII), $C_{13}H_{11}O_4N$, plates, m.p. 165~166°, a hydrogenation product of kokusagine in the presence of palladium-carbon with methyl iodide and subsequent warming of the N-methylated sub-

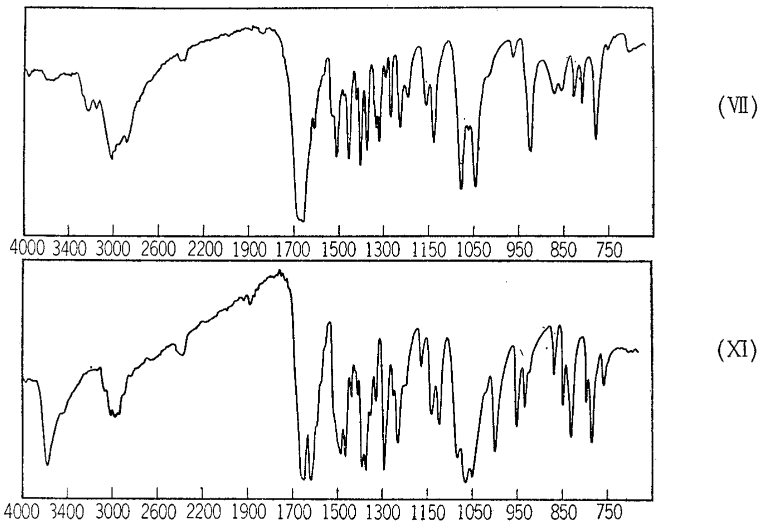


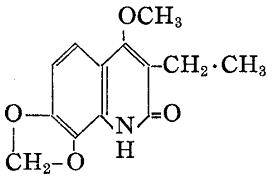
Fig. 2. Infrared Spectra of (VII) and (XI)

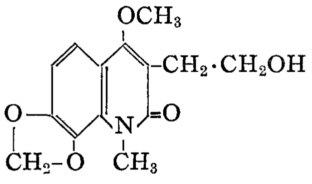
[*3] It has been reported that the reduction of $R-CH_2\cdot CHO$ to $R-CH_2\cdot CH_3$ was not successful in the case of balfourodendron (H. Rapoport, *et al.*: J. Am. Chem. Soc., **81**, 3738(1959)).

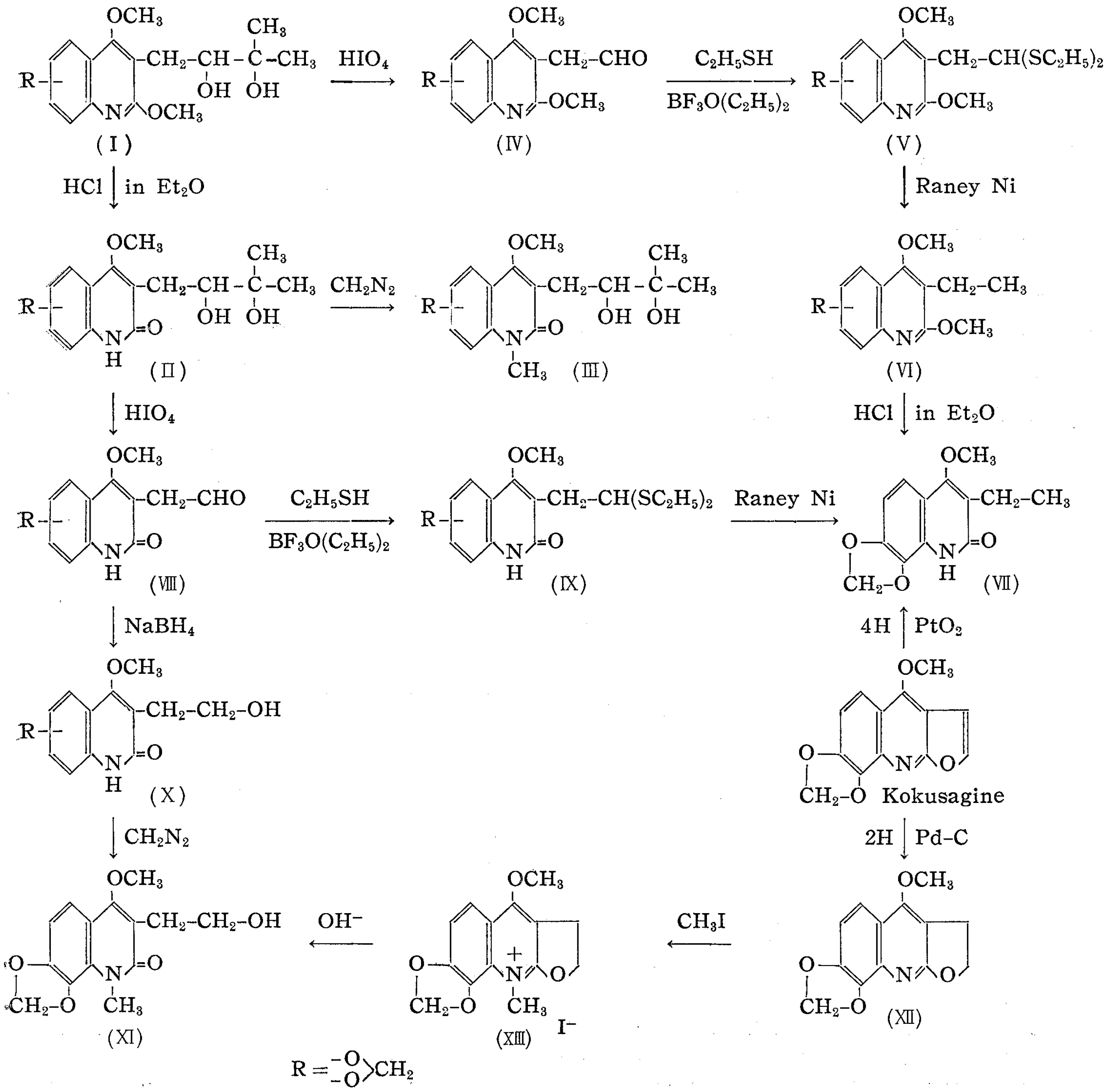
6) M. L. Wolfrom, J. V. Karabinos: J. Am. Chem. Soc., **66**, 909(1944); H. Rapoport, A. Batcho, J. E. Gordon: *Ibid.*, **80**, 5756(1958).

7) S. Goodwin, J. N. Shooley, E. C. Horning: *Ibid.*, **81**, 3736(1959).

stance (XIII) with dilute alkali to open the labile ring. The identity of (XI) was established by admixture and comparison of infrared spectra. It is noteworthy that ultraviolet spectrum of dihydro-kokusagine is similar to that of orixine and the spectrum of the alcohol (XI) to that of isoörixine. Thus, all evidences confirm the reliability of the structure of orixine.


(VII)


(XI)



Experimental

Orixine (I)2)—Root-bark (also stem-bark) of *Orixa japonica* Thunb., cut into small pieces, was extracted with MeOH. The extract was evaporated to syrupy consistency, which was extracted with 2% H_2SO_4, the acid solution was made alkaline with NH_4OH, and repeatedly extracted with Et_2O. On evaporating the Et_2O solution and by adding $CHCl_3$ in the cold, orixine was obtained as a pasty solid, m.p. 152.5°, as recrystallized three times from EtOH. Besides color reactions, paper electrophoresis[*1] was used for its identification. *Anal.* Calcd. for $C_{17}H_{21}O_6N$: C, 60.88; H, 6.31; O, 28.63; N, 4.18; OCH_3, 18.51; mol. wt., 335.35. Found : C, 60.80; H, 6.15; O, 28.57; N, 4.14; OCH_3, 18.81; mol. wt. (Rast), 315.91. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 3450, 3350 (OH); $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3440, 3350 (OH), 1477, 1275, 1047, 927$\left(\begin{smallmatrix}-O\\-O\end{smallmatrix}\!>CH_2\right)$. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε) : 254 (4.66), 318 (3.51); $\lambda_{\min}^{\text{EtOH}}$ mμ (log ε) : 237 (4.22), 270 (3.28).

Nor-orixine (II)—Into a solution of 1.1 g. of orixine dissolved in 360 cc. of dehyd. Et_2O, dried HCl gas was passed until saturation. Faint yellow amorphous material produced was kept over night. When exposed to the air, the filtered substance became oily, but on addition of dehyd. EtOH it soon crystallized. Colorless needles (from EtOH), m.p. 199~200°. Yield, 0.649 g. *Anal.* Calcd. for $C_{16}H_{19}O_6N$: C, 59.80; H, 5.96; O, 29.88; N, 4.36; OCH_3, 9.66. Found : C, 59.96; H, 6.10; O, 29.40; N, 4.67; OCH_3, 9.32. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3459 (OH), 3155, 3080 (NH), 1660, 1640 (NH-CO). UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε) : 224 (4.53), 258 (4.47), 265(4.49), 320(4.12); $\lambda_{\min}^{\text{EtOH}}$ mμ (log ε) : 245.5 (4.20), 278.5(3.69).

p-Nitrobenzoate of nor-orixine : 32 mg. of nor-orixine was mixed with 65 mg. of *p*-nitrobenzoyl chloride and 0.5 cc. of pyridine, and the mixture was kept for 2 days at room temperature. After adding small quantities of water to the solution, the benzoate was taken up in $CHCl_3$, the $CHCl_3$ layer was washed with 5% HCl, 5% $NaHCO_3$, and water, and dried. Distillation residue from $CHCl_3$ was submitted to chromatography over alumina and eluted consecutively with benzene, $CHCl_3$, and 1% MeOH containing $CHCl_3$. Recrystallization of 50 mg. of yellow oily substance so obtained from MeOH gave yellow prisms, m.p. 221~222°. *Anal.* Calcd. for $C_{30}H_{25}O_{12}N_3$: C, 58.16; H, 4.08; N, 6.78. Found : C, 58.27; H, 4.34; N, 6.53.

Isoörixine (III)—To a solution of 300 mg. of nor-orixine (II) dissolved in 90 cc. of dehyd. EtOH, 6 cc. of Et_2O solution of CH_2N_2 was added to it in three parts and the mixture was allowed to stand over night. After evaporation of the solvent and excess CH_2N_2, the residue was crystallized from $CHCl_3+Et_2O$ (1:5) to colorless prisms, m.p. 127°. Yield, 200 mg. Isoörixine is readily soluble in EtOH and MeOH, soluble in Me_2CO and $CHCl_3$. It exhibits green color with conc. H_2SO_4. *Anal.* Calcd. for $C_{17}H_{21}O_6N$: C, 60.88; H, 6.31; N, 4.18; OCH_3, 4.48; NCH_3, 4.48. Found : C, 61.11, H, 5.98; N, 4.14; OCH_3, 3.81; NCH_3, 6.91. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3440 (OH), 1640, 1620 (R_2N-CO). UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε) : 228(4.47), 260(4.36), 267(4.40), 320 (4.00); $\lambda_{\min}^{\text{EtOH}}$ mμ (log ε) : 249 (4.18), 281 (3.63).

HIO_4 Oxidation of Orixine and Nor-orixine—i) To the solution of 5 mg. of accurately weighed orixine dissolved in 1 cc. of dioxane, 5 cc. of $NaIO_4$ solution (65.142 mg. in 50 cc. of water) was reacted for several hours to liberate I_2, which was precipitated by adding 5 cc. of 2*N* H_2SO_4 and 3 cc. of 10% KI, and titrated with 0.01*N* $Na_2S_2O_3$. The amount of $NaIO_4$ consumed was calculated from the volume of 0.01*N* $Na_2S_2O_3$ required. Control test was also performed.

Amt. of orixine (mg.)	Period (hr.)	0.01*N* $Na_2S_2O_3$ (F=0.9564) (cc.)	Control (cc.)	$NaIO_4$ consumed (mole)
6.132	0.5	22.93	24.97	0.533
4.547	1	22.72	24.97	0.793
5.266	2	21.61	24.97	1.022
5.509	4	21.12	24.97	1.118
6.584	10	20.14	24.97	1.175

ii) To the solution of 5 mg. of accurately weighed nor-orixine dissolved in 2 cc. of dioxane and 5 cc. of water, 5 cc. of $NaIO_4$ solution (58.162 mg. dissolved in 50 cc. of water) was added and the mixture was maintained for several hours. Estimation was made as in the case of orixine.

Amt. of nor-orixine (mg.)	Period (hr.)	0.01*N* $Na_2S_2O_3$ (cc.)	Control (cc.)	$NaIO_4$ (mole)
5.0465	3	21.70 (F=0.9564)	23.65	0.59
3.795	5	21.10 (F=1.007)	23.32	0.95

The Aldehyde of Orixine (IV)—2,4-Dimethoxy-7,8-methylenedioxy-3-quinolineacetaldehyde : To the solution of 500 mg. of orixine dissolved in 10 cc. of dioxane, 500 mg. of $NaIO_4$ in 80 cc. of water

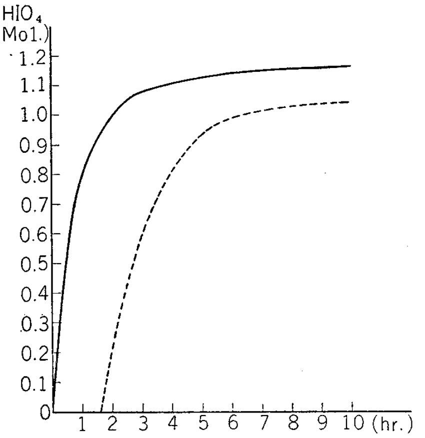


Fig. 3. Periodic Acid Oxidation of Orixine (I) and Nor-orixine (II)

was added gradually. Colorless needles began to separate out after 20 min. The mixture was kept for another 2 hr. The filtered and vacuum-dried crystals melted at 122°. Yield, 340 mg. IR ν_{max}^{KBr} 1722 (CO) cm^{-1}. UV λ_{max}^{EtOH} mμ (log ε) : 254 (4.70), 318 (3.54); λ_{min}^{EtOH} mμ (log ε) : 237 (4.25), 270 (3.30).

***p*-Nitrophenylhydrazone of the Aldehyde (IV)**—To the solution of 50 mg. of the aldehyde (IV) dissolved in 3 cc. of dehyd. EtOH, 35 mg. of *p*-nitrophenylhydrazine in 4 cc. of dehyd. EtOH and 2 drops of glacial AcOH was added and the mixture was refluxed for 10 min. on a steam bath. Yellow silky crystals, m.p. 220~221°, were obtained. Yield, 64 mg. Recrystallization from EtOH gave yellow prisms, m.p. 225~226.5°. *Anal.* Calcd. for $C_{20}H_{18}O_6N_4$: C, 58.53; H, 4.42; N, 13.65. Found : C, 58.42; H, 4.61; N, 13.68.

The Aldehyde of Nor-orixine (VIII)—4-Methoxy-7,8-methylenedioxy-1,2-dihydro-2-oxo-3-quinolineacetaldehyde : To the solution of 100 mg. of nor-orixine dissolved in 6 cc. of dioxane, 100 mg. of $NaIO_4$ in 10 cc. of water was added slowly and the mixture was kept for 16 hr. Separated colorless needles were dried in vacuum for 3 hr. at 100°. m.p. 230°. Yield, 68 mg. IR ν_{max}^{KBr} cm^{-1} : 3200, 3130 (NH), 1722 (CO), 1650 (NH-CO). UV λ_{max}^{EtOH} mμ (log ε) : 224 (4.38), 258 (4.31), 265 (4.34), 320 (3.96); λ_{min}^{EtOH} mμ (log ε): 245 (4.05), 278 (3.54).

***p*-Nitrophenylhydrazone of the Aldehyde (VIII)**—To the solution of 10 mg. of the aldehyde (VIII) dissolved in 5 cc. of EtOH, a solution of 7 mg. of *p*-nitrophenylhydrazine in 1 cc. of EtOH and one drop of glacial AcOH was added and refluxed for 15 min. on a steam bath. Separated yellow crystals were recrystallized from EtOH. m.p. 224° (decomp.).

Acetone 2,4-Dinitrophenylhydrazone : Mother liquor of the aldehyde (IV) was distilled with steam and HCl solution of 2,4-dinitrophenylhydrazine was added to the distillate. Orange-red needles were obtained and recrystallized from EtOH to tablets, m.p. 127~128°, undepressed on admixture with authentic acetone 2,4-dinitrophenylhydrazone, m.p. 128°. *Anal.* Calcd. for $C_9H_{10}O_4N_4$: N, 23.52. Found : N, 23.31.

The mother liquor of the aldehyde (VIII) was treated as in the case of the aldehyde (IV) and the same acetone 2,4-dinitrophenylhydrazone, m.p. 128°, was obtained and identified.

Dithioacetal (V) from Orixine-aldehyde (IV)—2,4-Dimethoxy-7,8-methylenedioxy-3-(2,2-bisethylthioethyl)quinoline (V) : To 400 mg. of the aldehyde (IV), 3 cc. of EtSH was added, followed by 2 cc. of $BF_3O(Et)_2$, cooling with ice and occasionally stirring. In 5 min., prismatic crystals separated out from the clear solution. The mixture was allowed to stand in an ice box over night and then at room temperature for 4 hr. After adding 5 cc. of water to the mixture, the reaction product was extracted with CH_2Cl_2, which was washed, dried, and evaporated to a syrup. From MeOH, prisms or tablets, m.p. 83.5~84°, were obtained. Yield, 450 mg. *Anal.* Calcd. for $C_{18}H_{23}O_4NS_2$: C, 56.67; H, 6.08; N, 3.67. Found : C, 56.86; H, 6.26; N, 3.64.

2,4-Dimethoxy-3-ethyl-7,8-methylenedioxyquinoline (VI)—A solution of 200 mg. of dithioacetal (V) dissolved in 70 cc. of dehyd. EtOH was refluxed on a steam bath for 12 hr. with 20~30 times in wt. of Raney Ni W-5. Desulfurization product was isolated by filtration of Ni and evaporation of the solvent. Prismatic crystals, m.p. 81°, were obtained from MeOH. Yield, 100 mg. *Anal.* Calcd. for $C_{14}H_{15}O_4N$: C, 64.36; H, 5.79; N, 5.36. Found : C, 64.33; H, 5.98; N, 5.25.

Reaction of HCl with (VI)—3-Ethyl-4-methoxy-7,8-methylenedioxycarbostyril (VII) : Dry HCl gas was passed into the solution of 20 mg. of (VI) dissolved in dehyd. Et_2O until saturation. The mixture was allowed to stand over night. Separated crystals were recrystallized from MeOH to needles, m.p. 169°. The substance was identified with the authentic (VII), obtained from kokusagine by its catalytic reduction over PtO_2,[3] in regard to its m.p. and IR spectrum. *Anal.* Calcd. for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67. Found : C, 63.33; H, 5.70; N, 5.37. IR ν_{max}^{KBr} cm^{-1} : 3210, 3145

(NH), 1660, 1650 (NH-CO). UV λ_{max}^{EtOH} $m\mu$ ($\log\varepsilon$): 224 (4.43), 258 (4.30), 265 (4.33), 320 (3.96); λ_{min}^{EtOH} $m\mu$ ($\log\varepsilon$): 245 (4.07), 278 (3.60).

Dithioacetal (IX) from Nor-orixine Aldehyde (VIII)—4-Methoxy-7,8-methylenedioxy-3-(2,2-bisethylthioethyl)carbostyril (IX): To 400 mg. of nor-orixine aldehyde (VIII), 5 cc. of EtSH was added with cooling and to the mixture 4 cc. of $BF_3O(Et)_2$ was added, agitating frequently. After keeping the mixture over night, it was allowed to stand at room temperature for 4 hr., 10 cc. of water was added, and extracted with CH_2Cl_2. After washing and drying, CH_2Cl_2 was evaporated in vacuum and stirred with MeOH, when crystals separated. Yield, 400 mg. Recrystallized from MeOH to tablets, m.p. 123~124°. *Anal.* Calcd. for $C_{17}H_{21}O_4NS_2$: C, 55.56; H, 5.76; N, 3.81. Found: C, 55.60; H, 5.89; N, 3.81.

3-Ethyl-4-methoxy-7,8-methylenedioxycarbostyril (VII)—A solution of 250 mg. of dithioacetal (IX) dissolved in 70 cc. of EtOH with warming was refluxed for 12 hr. on a steam bath with 20~30 times in wt. of Raney Ni W-5. The product was isolated in the usual manner and crystallized from EtOH to colorless prisms, m.p. 169°. Yield, 130 mg. The substance was identified with an authentic sample[3] from kokusagine in regard to its m.p. and IR spectrum. *Anal.* Calcd. for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.42; H, 5.64; N, 5.65. IR ν_{max}^{KBr} cm^{-1}: 3210, 3145 (NH), 1660, 1650 (NH-CO).

Dihydrokokusagine (XII)—A solution of 150 mg. of kokusagine in 30 cc. of MeOH was added to a mixture of Pd-C previously prepared from 1% of $PdCl_2$ and 70 mg. of charcoal and the mixture was stirred at room temperature in H_2 atmosphere, ca. 16 cc. of H_2 being absorbed in 20 min. The product was isolated in the usual manner and crystallized from Me_2CO and MeOH to colorless prisms, m.p. 165~166°. Melting point was depressed (135~143°) by admixture with authentic (VII) (m.p. 169°) derived from kokusagine by catalytic reduction in the presence of PtO_2.[3] *Anal.* Calcd. for $C_{13}H_{11}O_4N$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.79; H, 4.86; N, 5.88. UV λ_{max}^{EtOH} $m\mu$ ($\log\varepsilon$): 254 (4.67); 316 (3.62); λ_{min}^{EtOH} $m\mu$ ($\log\varepsilon$): 233 (4.00), 270 (3.30).

4-Methoxy-7,8-methylenedioxy-1-methyl-3-(2-hydroxyethyl)carbostyril (XI)—i) Dihydrokokusagine methiodide (XIII): 85 mg. of dihydrokokusagine was dissolved in 0.5 cc. of CH_3I and 1 cc. of MeOH. Ten min. later prismatic needles began to separate, but the mixture was allowed to stand for 2 days. Isolated crystals colored brown when exposed to air. The labile substance was submitted to the following reaction without further purification.

ii) Alkali decomposition of the methiodide of dihydrokokusagine: The colorless solution of the methiodide of dihydrokokusagine produced by the addition of 2.5 cc. of 10% NaOH and 10 cc. of MeOH was warmed on a steam bath for 15 min. By distilling off MeOH oily residue remained which crystallized on standing. Isolated crystals were washed with water, dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with water, dried, and evaporated. Yield, 90 mg. Recrystallization from MeOH containing water, and from MeOH gave colorless prisms, m.p. 144.5~145°. *Anal.* Calcd. for $C_{14}H_{15}O_5N$: C, 60.64; H, 5.45; N, 5.05. Found: C, 61.09; H, 5.49; N, 4.87. IR ν_{max}^{KBr} cm^{-1}: 3560 (OH), 1630 (R_2N-CO). Its UV spectrum is very similar to that of isoörixine. UV λ_{max}^{EtOH} $m\mu$ ($\log\varepsilon$): 228 (4.41), 260 (4.30), 267 (4.34), 320 (3.93); λ_{min}^{EtOH} $m\mu$ ($\log\varepsilon$): 249 (4.12), 281 (3.63).

The Alcohol (X) from Nor-orixine—4-Methoxy-7,8-methylenedioxy-3-(2-hydroxyethyl)carbostyril (X): To a solution of 50 mg. of the aldehyde (VIII) in 4 cc. of dehyd. EtOH 30 mg. of $NaBH_4$ in 4 cc. of dehyd. EtOH was added, the mixture was kept for 20 hr. in an ice box, and 1*N* HCl was added to destroy an excess of $NaBH_4$. After adding 10 cc. of water, EtOH was distilled off, the colorless needles obtained were washed with water, and dried in vacuum. M.p. 200~202° (from MeOH). Yield, 44 mg. *Anal.* Calcd. for $C_{13}H_{13}O_5N$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.49; H, 5.54; N, 5.55. IR ν_{max}^{KBr} cm^{-1}: 3478 (OH or NH), 3200 (NH), 1660, 1640 (NH-CO). UV λ_{max}^{EtOH} $m\mu$ ($\log\varepsilon$): 224 (4.43), 258 (4.37), 265 (4.39), 320 (4.02); λ_{min}^{EtOH} $m\mu$ ($\log\varepsilon$): 245 (4.10), 278 (3.60).

Methylation of (X)—4-Methoxy-7,8-methylenedioxy-1-methyl-3-(2-hydroxyethyl)carbostyril (XI): To a solution of 20 mg. of the alcohol (X) dissolved in MeOH, Et_2O solution of CH_2N_2 was added and the mixture was kept overnight. An excess of CH_2N_2 was destroyed with AcOH and evaporation of the solvent afforded colorless prisms, m.p. 144~145°, as recrystallized from water containing MeOH. The substance was identified with (XI), m.p. 144.5~145°, by admixture and comparison of IR spectra. IR ν_{max}^{KBr} cm^{-1}: 3560 (OH), 1630 (R_2N-CO).

Summary

The structure of orixine (I) was established by the comparison of its decomposition products with the catalytic reduction products (VIII) of kokusagine as well as with (XI) derived from dihydrokokusagine.

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