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Toshikazu Yazima[a] & Katsura Munakata[a]
[a] Laboratory of Pesticide Chemistry, Faculty of Agriculture, Nagoya University, Nagoya, Japan
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Synthesis of Furoquinolines

Toshikazu YAZIMA and Katsura MUNAKATA

Laboratory of Pesticide Chemistry, Faculty of Agriculture, Nagoya University, Nagoya, Japan

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Furoquinolines, *viz.*, kokusagine (**I**), maculine (**II**), dictamnine (**III**) and 6-methoxydictamine (**IV**) were synthesized via ethyl 2-anilino-4,5-dihydro-4-oxofuran-3-carboxylate derivatives. 6-Methoxy-2-methyldictaminne (**V**) and its dihydro-derivative (**XXI**) were synthesized *via* analogous ethyl 4,5-dihydro-2-(4-methoxyanilino)-5-methyl-4-oxofuran-3-carboxylate. Stereochemical assignments of 2,3-*cis* and *trans* 2,3-dihydro-3-hydroxy-4,6-dimethoxy-2-methylfuro[2,3-b]quinoline having insect antifeeding activity were made on the basis of their spectrometric data (PMR and MS).

A variety of furoquinolines (4-methoxy [2,3-b]quinoline derivatives) are distributed widely in *Rutaceous* plants.[1] Kokusagine belonging to the furoquinoline alkaloids was clarified by us to be a minor insect antifeedant in *Orixa japonica*.[2] Maculine, dictamnine and 6-methoxydictamnine were isolated from the respective plants of *Flindersia* spp., *Dictamnus* spp. and *Platydesma* spp.[3~5]

Kokusagine was synthesized *via* 2,4-dichloro-3-(2-chloroethyl)-7, 8-methylenedioxyquinoline by Pai *et al.*[6] Maculine was synthesized via 3-(2-benzyloxyethyl)-4-hydroxy-6,7-methylendioxy-carbostyril by Ohta *et al.* and *via* substituted α-benzylidene-γ-butyrolactone by Zimmer *et al.*[7,8] Dictamnine synthesis has been reported by several authors.[9] We report here the synthesis of kokusagine, maculine and dictamnine based on the method for 6-methoxydictamnine of Pai *et al.*[10] In addition, the synthetic method was successfully applied to the synthesis of 4,6-dimethoxy-2-methyl-furo[2,3-b]quinoline. The synthetic compounds were examined for their insect antifeeding activities.*

SYNTHETIC METHODS

(I) *Synthesis of kokusagine, maculine, dictamnine and 6-methoxydictamnine.* The above furoquinolines were synthesized via ethyl 2-anilino-4,5-dihydro-4-oxofuran-3-carboxylate derivatives (**VIIIa–d**) as key intermediates. For example, kokusagine was synthesized as follows.

Condensation of 2,3-methylenedioxyaniline (**VIa**) with ethyl 2-ethoxy-4,5-dihydro-4-oxofuran-3-carboxylate (**VII**) (prepared *in situ* from chloroacetyl chloride and sodiomalonic ester) afforded ethyl 4,5-dihydro-2-(7, 8-methylenedioxyanilino)-4-oxofuran-3-carboxylate (**VIIIa**). The structure of (**VIIIa**) was indicated by IR absorption at 1700 cm^{-1}, 1630 cm^{-1} (C=0) and 3180 cm^{-1} (>NH), see Table I.

The PMR spectrum also showed its secondary amino proton signal at δ 10.36 (1 H) which disappeared on addition of D_2O. Furthermore, a singlet, resonating at δ 4.74, had a chemical shift of methylene protons adjacent to the carbonyl group and oxygen (Table II).

Thermal ring closure of the ester (**VIIIa**) was conducted at 250°C in paraffin oil for 10 min under an inert gas atmosphere, and 2,3,4,9-tetrahydro-7,8-methylenedioxy-3,4-dioxofuro[2,3-b]quinoline (**IXa**) was formed. The IR spectrum of (**IXa**) showed carbonyl absorption at 1697 cm^{-1} and 1640 cm^{-1}. Methylation of (**IXa**) with diazomethane in dioxane containing 1% of methanol yielded an *O*-methyl compound (**Xa**). The PMR spectrum of (**Xa**) indicated the presence of *O*-methyl protons resonating at δ 4.63 (s,3 H) (Table II). Sodium borohydride reduction of (**Xa**) afforded 2, 3-dihydro-3-hydroxy-4-methoxy-7, 8-methylenedioxy-furo[2,3-b]quinoline (**XIa**). IR absorption at 3230 cm^{-1} indicated the presence of the intermolecular bonded hydroxy group of (**XIa**). (Table I) Dehydration of (**XIa**) with potassium bisulfate gave kokusagine (**I**) identical with the natural product in every respect (MS, PMR, IR, UV and mp).[2]

2,3-Methylenedioxyaniline was synthesized in the following manner. Acid hydrolysis of commercially available *o*-vanillin (**XIIa**) yielded 1, 2-dihydroxybenzaldehyde (**XIIb**). Methylenation of (**XIIb**) with

* To be published elsewhere in detail.

TABLE I. IR SPECTRAL DATA OF THE COMPOUNDS, (VIIIa–d), (IXa–d), (XIa–d), (XIV), (XV) AND (XVII).

(VIIIa)	(VIIIb)	(VIIIc)	(VIIId)	(XIV)	Groups indicated
1700	1693sh.	1686	1698	1686 sh	C=O
1630	1648	1643	1635	1641	
3180	3200	3290	3280	3260	>NH
(IXa)	**(IXb)**	**(IXc)**	**(IXd)**	**(XV)**	
1697	1662	1688	1705	1704	C=O
1640	1648	1634	1645	1645	
1625	1615	1619	1578	1580	C=C and
1556	1586	1562	1550	1550	C=N of
		1527			the ring
(XIa)	**(XIb)**	**(XIc)**	**(XId)**	**(XVII)**	
3230	3240	3630*	3125	3120(a)	OH
				3270(b)	

ν_{max}^{KBr} cm^{-1}, * in chloroform solution.

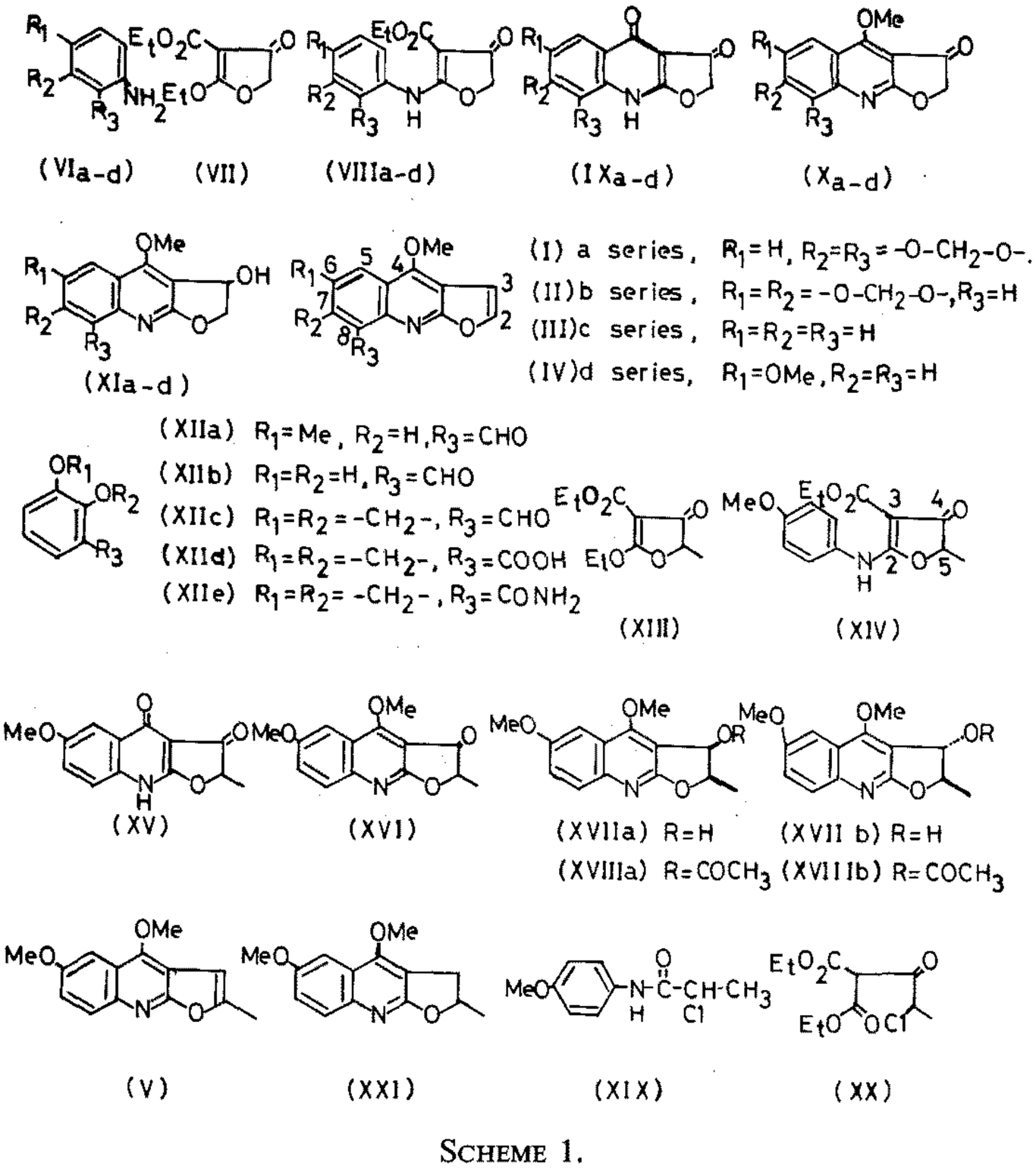
TABLE II. PMR SPECTRAL DATA OF THE COMPOUNDS, (VIIIa–d), (XIV), (Xa–d) AND (XVI)*

(VIIIa)	(VIIIb)	(VIIIc)	(VIIId)	(XIV)	Protons assigend
10.36 b.s.	10.11 b.s.	10.23 b.s.	10.03 b.s.	10.03 b.s.	>NH
4.74 s	4.64 s	4.68 s	4.61 s	[1.54 d, J=7]** [4.73 q, J=7]	–C(=O)–CH_2–O–
1.40 t, J=7	1.40 t, J=7	1.41 t, J=7	1.38 t, J=7	1.38 t, J=7	–CH_2–CH_3
4.44 q, J=7	4.33 q, J=7	4.37 q, J=7	4.34 q, J=7	4.35 q, J=7	
6.10 s	6.02 s				–O–CH_2–O–
			3.80 s	3.92 s	–OCH_3
6.75~	6.80 s, 1H	7.35 s, 5H	6.88 d, J=9,	6.90 d, J=9,	Arom. H
7.25 m, 3H			2H	2H	
	6.94 s, 1H		7.25 d, J=9,	7.30 d, J=9,	
			2H	2H	
(Xa)	**(Xb)**	**(Xc)**	**(Xd)**	**(XVI)**	
4.63 s	4.56 s	4.64 s	4.63 s	4.62 s	–OMe
			3.88 s	3.90 s	
4.69 s	4.65 s	4.65 s	4.67 s	[1.58 d, J=7]** [4.72 q, J=7]	–C(=O)–CH_2–O–
6.21 s	6.06 s				–O–CH_2–O–
7.00 d,	7.08 s,1H	7.24~7.48 m,	7.2–7.6 m,	7.3–7.5 m,	Arom. H
J=9, 1H		1H	2H	2H	
7.86 d,	7.40 s,1H	7.68~7.88 m,	7.68 d,	7.68 d,	
J=9, 1H		2H	J=9, 1H	J=9, 1H	
		8.18 d, d,			
		J=9, J=1, 1H			

* $\delta_{TMS}^{CDCl_3}$, J values in Hz.

** [–C(=O)–CH(–CH_3)–O–]

methylene bromide, followed by oxidation with potassium permanganate, yielded 2,3-methylenedioxybenzoic acid (**XIId**). Ammonolysis of the acid (**XIId**) with ammonium acetate *via* the acid chloride gave an amide (**XIIe**). Hofmann rearrangement of (**XIIe**) with sodium hypochlorite afforded 2,3-methylenedioxyaniline (**VIa**). The overall yield of (**VIa**) was 9% based on *o*-vanillin (**XIIa**).



SCHEME 1.

The other furoquinolines, *viz.*, maculine, dictamnine and 6-methoxydictamnine were synthesized in the same manner as for kokusagine. The spectral deta of the intermediates in the synthesis are given in Tables I and II. The only difficulty which arose in the above synthesis of furoquinolines was the poor yields (10~45%) of the intermediates (**VIIIa–d**).

(II) *Synthesis of 6-methoxy-2-methyldictamnine* (**V**) *and its dihydro derivative* (**XXI**). This furoquinoline was successfully synthesized via ethyl 4,5-dihydro-2-(4-methoxyanilino)-5-methyl-4-oxofuran-3-carboxylate (**XIV**) as a key intermediate. Condensation of *p*-anisidine (**VId**) with ethyl 2-ethoxy-4,5-dihydro-5-methyl-4-oxofuran-3-carboxylate (**XIII**) (prepared *in situ* from α-chloropropionyl chloride (**XXII**) and sodiomalonic ester) afforded an ester of (**XIV**). In the synthesis of ethyl 4,5-dihydro-2-(4-methoxyanilino)-4-oxofuran-3-carboxylate (**VIIId**), the reported method by Pai *et al.* used two mole equivalents of sodiomalonic ester. Accordingly, one mole equivalent of sodiomalonic ester functioned as a base. Exact application of the method, however, was unsuccessful for the synthesis of 4,5-dihydro-2-(4-methoxyanilino)-5-methyl-4-oxofuran-3-carboxylate. (**XIV**) When triethylamine was used as a base, successful formation of (**XIV**) was observed with a 33% yield. The structure of (**XIV**) was indicated by IR absorption at 1686 cm^{-1} sh. and 1641 cm^{-1} (C=O) and 3260 cm^{-1} (>NH), see Table I. The PMR spectrum also showed its secondary amino proton signal at δ 10.12 (1H) which disappeared on addition of D_2O. One of the by-products in the ester synthesis was identified as an amide (**XIX**). This by-product might be formed by a decomposition reaction of a possible intermediate (**XX**) with *p*-anisidine. Thermal ring closure of the ester (**XIV**) gave a γ-quinolone (**XV**). The IR spectrum of (**XV**) showed carbonyl absorption at 1704 cm^{-1} and 1645 cm^{-1} similar in magnitude to those of (**IXd**). Methylation of (**XV**) with diazomethane yielded an *O*-methyl compound (**XVI**). The PMR spectrum (**XVI**) showed two *O*-methyl proton signals at δ 4.62 (s, 3H) and δ 3.90 (s, 3H). Sodium borohydride reduction of (**XVI**) afforded 2,3-*cis* and *trans* isomers of 2,3-dihydro-3-hydroxy-4-methoxy-2-methylfuro[2,3-b]quinoline (**XVIIa** and **XVIIb**). The IR spectra of both isomers showed a hydroxy group absorption at 3120 cm^{-1} for the 2,3-*cis* isomer (**XVIIa**) and at 3270 cm^{-1} for the 2,3-*trans* isomer (**XVIIb**), respectively. Dehydration of the 2,3-*cis* isomer with potassium bisulfate gave 4,6-dimethoxy-2-methylfuro [2,3-b]quinoline (**V**). It was derived also from the *trans* isomer in the same manner. Hydrogenolysis of an acetate (**XVIIIa**) derived from 2,3-*cis* alcohol afforded 2,3-

TABLE III. PMR DATA OF *Cis* ISOMER (**XVIIa**) AND *Trans* ISOMER (**XVIIb**) IN d_5-PYRIDINE AND *d*-CHLOROFORM* (*J* values in Hz)

Cis isomer			*Trans* insomer			Protons
d_5-Pyridine	*d*-Chloroform	Δ**	d_5-Pyridine	*d*-Chloroform	Δ**	assigned
1.72 d, J=6.4	1.68 d, J=6.6	+0.04	1.36 d, J=6.6	1.39 d, J=6.6	−0.03	CH_3–CH(O–)–CH(OH)–
4.74 d,q, J=5.4, J=6.4	4.74 d,q, J=5.5, J=6.6	0	5.00 d,q, J=1.7, J=6.6	4.89 d,q, J=1.7, J=6.6	+0.11	CH_3–CH(O–)–CH(OH)–
5.63 d,d, J=5.4, J=8.8	5.41 d, J=5.5	+0.22	5.50 d,d, J=1.7, J=8.3	5.16 d, J=1.7	+0.34	–CH(O–)–CH(OH)–
3.76 s	3.84 s	−0.08	3.75 s	3.80 s	−0.05	$-OCH_3$
4.55 s	4.52 s	+0.03	4.53 s	4.46 s	+0.07	
***	5.14 s		7.99 d, J=8.3	*ca.* 2.5	+5.5	–OH
7.37 d,d J=2.9, J=9.0 7.65 d, J=2.9	7.0~7.3 m, 2H		7.36 d,d J=2.9, J=9.0 7.62 d, J=2.9	7.0–7.3 m, 2H		Arom. H
7.89 d, J=9.0	7.55 d, J=10, 1H	+0.34	7.90 d, J=9.0	7.50 d, J=9.5, 1H	+0.40	

* Tetramethyl silane used as an internal standard.

** $\Delta = \delta$ d_5-Py—δ *d*-Chloroform

*** Masked by solvent.

dihydro-4, 6-dimethoxy-2-methylfuro[2, 3-b]quinoline (**XXI**). Structures of (**V**) and (**XXI**) were determined on the basis of their spectrometric data (MS, PMR, IR and UV).

DISCUSSION

Stereochemical assignments of 2,3-*cis* and *trans* 2,3-dihydro-3-hydroxy-4-methoxy-2-methylfuro[2,3-b]quinoline (**XVIIa** and **XVIIb**) and their acetates (**XVIIIa** and **XVIIIb**) were based on the spectrometric data (PMR and MS). The assignments, assuming the validity of the Karplus equation for these compounds, should give the 2,3-*cis* isomers for $J_{2,3}$=5.5 Hz (**XVIIa**) and $J_{2,3}$=5.4 Hz (**XVIIIa**); the 2,3-*trans* isomers for $J_{2,3}$=1.7 Hz (**XVIIb**) and $J_{2,3}$=1.0 Hz (**XVIIIb**).[11]

In the PMR spectrum of the 2,3-*trans* isomer (**XVIIb**) in *d*-chloroform, a doublet of a quartet at δ 4.89 (1 H, J=1.7 Hz, J=6.6 Hz) was attributed to the C-2 proton which was associated with a doublet at δ 1.39 (3 H, J=6.6 Hz) and a doublet at δ 5.16 (1 H, J=1.7 Hz) (Table III). By changing the solvent from *d*-chloroform to d_5-pyridine, a clear shift of the C-2 proton signal to a lower field was observed (δ 4.89→δ 5.00, Δ+0.11 ppm), whereas only a silght shift of the C-2 methyl signal to an upper field was detected (δ 1.39→δ 1.36, Δ−0.03 ppm).[12] In contrast to the above results, no solvent effect was found on the chemical shift of the C-2 proton of the 2,3-*cis* isomer (**XVIIa**). A downfield shift of the C-2 methyl signal of the *cis* isomer, however, was observed to some extent (δ 1.68→δ 1.72, Δ+0.04 ppm). The C-3 proton is attached to a carbon bearing the hydroxy group, and accordingly a large downfield shift of the proton was observed in both the 2,3-*cis* and *trans* isomers. (Δ+0.02 ppm for the 2,3-*cis* isomer (**XVIIa**) and Δ+0.34 ppm for the *trans* isomer (**XVIIb**)). This can be explained by assuming that the C-2 proton of the 2,3-*trans* isomer (**XVIIb**) and the C-2 methyl group of the 2,3-*cis* isomer (**XVIIa**) are located on the same side of the ring as the hydroxy group in each molecule, and hence clear downfield shifts of these protons in pyridine were observed. These data supported the initial assignments of 2,3-*cis*

TABLE IV. THE RELATIVE PROBABILITY OF THE LOSS OF A CH_3COOH AND CH_3COO FRAGMENT IN THE $J_{2,3}=1.0$ Hz AND $J_{2,3}=5.4$ Hz ISOMERS OF (**XVIIIb**) AND (**XVIIIa**).

(Ionizing potential, 75 eV: Probe inlet temp. 85°C)

	$J_{2,3}=1.0$ Hz (**XVIIIb**)	$J_{2,3}=5.4$ Hz (**XVIIIa**)
$R_1=\frac{m/e\ 243}{m/e\ 244}$	0.838	0.485
$R_2=\frac{m/e\ 228}{m/e\ 229}$	1.88	1.09
$\frac{R_1(\mathbf{XVIIIb})}{R_1(\mathbf{XVIIIa})}=\frac{0.838}{0.485}=1.73$		
$\frac{R_2(\mathbf{XVIIIb})}{R_2(\mathbf{XVIIIa})}=\frac{1.88}{1.09}=1.72$		

and *trans* isomers.

The only difference between the mass spectra of the 2,3-*cis* acetate (**XVIIIa**) and that of the 2,3-*trans* acetate (**XVIIIb**) is in the relative abundance of the peaks at *m/e* 243 and 244 (loss of CH_3COOH and CH_3COO, respectively) as well as the peaks at *m/e* 228 and 229 (loss of the CH_3 and CH_3COOH or CH_3COO). The relative easiness to lose a AcOH fragment compared with the loss of a AcO fragment in the mass spectra of both isomers is represented as R_i ($i=1$ and 2) values (Table IV). The relative values of R_1^{trans}/R_1^{cis} and R_2^{trans}/R_2^{cis} were 1.73 and 1.72, respectively. It appears that the 2,3-*trans* isomer has a greater tendency to lose a AcOH fragment relative to the loss of a AcO fragment than the 2,3-*cis* isomer does. This can be explained by assuming that the 2, 3-*trans* isomer would be in a favorable configuration to undergo a McLafferty rearrangement with the abstraction of the C-2 proton.[13] This agrees well with results observed in the mass spectra of 2,3-*cis* and *trans* 2,3-dihydro-3-hydroxy-2-methylbenzofuran derivatives and supported the initial assignments of both isomers.[11]

Insect antifeeding activity of the synthetic compounds was examined with 3rd instar larvae of *Spodoptera litura* (tobacco cutworm) by using a leaf-disc method.[14] It was notable that 2, 3-dihydro-4, 6-dimethoxyfuro-[2,3-b]quinoline (**XXI**) and its 3-hydroxy-derivatives (**XVIIa** and **XVIIb**) showed clear antifeeding activity at 300 ppm. Among furoquinolines, kokusagine was first found to be an antifeedant. But there is no chiral center in the kokusagine molecule. Among the synthesized compounds related to kokusagine, some racemic dihydrofuroquinoline derivatives showed insect antifeeding activity and are suitable for furthur study.

EXPERIMENTAL PROCEDURES

MS spectra were measured with a JEOL D-100 mass spectrometer: high resolution mass spectra with a JEOL 01SG mass spectrometer. PMR spectra were recorded with a JEOL MH-100 (100 MHz) and a JEOL FX-100 (99.6 MHz) Fourier transform spectrometer: CMR spectra with a JEOL FX-100 (25.05 MHz) Fourier transform spectometer. IR spectra were recorded with a JASCO IR-G and a JASCO A-3 spectrophotometer. UV spectra were measured with a Hitachi EPS-3T and a JASCO UVIDEC-505 spectrophotometer. Melting points were uncorrected.

Ethyl 4, 5-dihydro-2-(2, 3-methylenedioxyanilino)-4-oxofuran-3-carboxylate (**VIIIa**). The ester was synthesized from aniline (**VIa**, 2.7 g), diethyl sodiomalonate (7.0 g) and chloroacetyl chloride (2.4 g) with a 14% yield. Pale yellow needles recrystallized from aq. EtOH; mp 159~60°C. MS *m/e*: 291 (M^+), 246, 245 (M^+ −EtOH, base peak), 187, 163. UV λ_{max}^{EtOH} nm (ε): 300 sh., 284 (18,300), 241 (15,700), 202 (16,100).

2,3-Dihydro-4-hydroxy-7,8-methylenedioxy-3-oxofuro-[2,3-b]-quinoline (**IXa**). The crude product (79% yield) was recrystallized from DMF to afford colorless needles, decomposing above 310°C. MS *m/e*: 245 (M^+, base peak), 244 (M^+ −1), 217, 216, 214, 189, 186. PMR δ_{TMS}^{*}: 3.52 (s, 2H), 4.98 (s, 2H), 5.72 (d, $J=8$Hz, 1H), 6.49 (d, $J=8$Hz, 1H), 13.8 (s, 1H): The amino proton disappeared on addition of D_2O. UV λ_{max}^{EtOH} nm (ε): 362 sh., 316 (5,400), 260 (25,500), 219 (13,500).

2,3-Dihydro-4-methoxy-7,8-methylenedioxy-3-oxofuro-[2,3-b]-quinoline (**Xa**). The crude product was purified by preparative TLC [silica gel, developed with a mixture of EtOAc and Benz. (1:2)] to afford the

* d_6-DMSO-CD_3OD

O-methyl compound (**Xa**) with a 27% yield. On crystallization from EtOH, it gave yellow needles decomposing above 280°C. MS *m/e*: 259 (M^+, base peak), 258, 230, 202, 201, 171. IR ν_{max}^{KBr} cm^{-1}: 1712, 1609, 1525, 1455, 1382, 1344, 1278, 1212, 1104, 1060, 1040, 967, 913, 824, 789, 743, 713. UV λ_{max}^{EtOH} nm (ε): 380 sh,. 347 (9,700), 238 (26,200), 277 (40,000).

2, 3 - Dihydro- 3 -hydroxy- 4 -methoxy- 7, 8 - methylenedioxy-furo[2,3-b]-quinoline (**XIa**). Colorless needles crystallized from EtOH; mp 213–5°C. Yield, 59%. MS *m/e*: 262 ($M^+ + 1$), 261 (M^+, base peak), 244 (M^+ –OH), 243 ($M^+ - H_2O$), 228, 214, 186. UV λ_{max}^{EtOH} nm (ε): 310 (41,00), 254 (48,000), 221 (31,600).

Kokusagine (**I**). The dehydration reaction was conducted in dry tetrahydrofuran using 160-fold amounts of fused potassium bisulfate. The yield was 25%. On crystallization from MeOH, kokusagine was obtained as colorless needles, mp 200~202°C. The alkaloid was found to be identical in every respect to the authentic material (MS, IR, UV, PMR and mixed mp).[2)]

Ethyl 4, 5-dihydro-2- (4-methoxyanilino) -5-methyl-4-oxofuran-3-carboxylate (**XIV**). Sodium (2.9 g) was dissolved in a dry tetrahydrofuran solution (60 ml) of diethyl malonate (20 g). To the solution, cooled in an ice bath, was added, with stirring, freshly prepared α-chloropropionic acid chloride (15.5 g). The mixture was stirred at 0°C for 40 min. To the reaction mixture was added, at room temperature, a solution of triethylamine (12.6 g) and *p*-anisidine (14.9 g) in dry tetrahydrofuran (40 ml). This was kept for 40 min with stirring and then refluxed for 20 min. The cooled mixture was poured into ice water (1.0 liter), the solidified materials were filtered off, washed with cooled water and crystallized form alcohol to afford the ester (**XIV**, 12.0 g) as pale yellow needles; mp 146~147°C. Yield, 33%. MS *m/e*: 291 (M^+), 245 (M^+ –EtOH), 207, 186. UV λ_{max}^{EtOH} nm (ε): 275 (19,000), 203 (11,600).

2, 3- Dihydro-4-hydroxy- 6 -methoxy- 2 -methyl- 3 -oxofuro[2,3-b]quinoline (**XV**). Finely powdered ester (**XIV**, 13.6 g) suspended in paraffin oil (200 g) was heated with vigorous stirring at 250°C for 20 min under a continuous stream of argon. The solid which separated out on cooling was filtered off, washed with *n*-hexane and then with ethyl acetate–ethanol. After drying under reduced pressure, a pale yellow powder (10.4 g) was obtained. Yield, 91%. On crystallization from DMF, colorless needles decomposing slowly above 300°C were obtained. MS *m/e*: 245 (M^+, base peak), 230, 216, 202, 176. High resolution mass *m/e*: 245.0710 (245.0708 calcd. for $C_{13}H_{11}O_4N$). PMR δ_{TMS}^{*}: 1.48 (d, J=7Hz, 3H), 3.85 (s, 3H), 4.93 (q, J=7Hz, 1H), 7.3–7.6(m, 3H). The amino proton was masked by solvent. UV λ_{max}^{EtOH} nm (ε): 344 (2,700), 332 (2,700), 301 (2,400), 268 (16,600), 241 (21,600), 223 (18,000).

2,3-Dihydro-4,6-dimethoxy-2-methyl-3-oxofuro[2,3-b]-quinoline (**XVI**). The quinolone was methylated in dioxane solution with diazomethane and afforded an *O*-methyl compound (**XVI**) with a 58% yield. When the reaction was conducted in methanol, the yield of the product was 40% and 29%, respectively, in two runs. Pale yellow needles recrystallized from EtOH; mp 132~133°C (decomp.). MS *m/e*: 259 (M^+, base peak), 244 ($M^+ - 15$), 230, 216, 202, 157. IR ν_{max}^{KBr} cm^{-1}: 2990, 2940, 1716, 1601, 1572, 1510, 1470, 1439. UV λ_{max}^{EtOH} nm (ε): 387 (3,800), 302 (17,700), 292 (14,300), 246 (41,500), 213 (22,300).

2,3-Cis and trans 2,3-dihydro-3-hydroxy-4,6-dimethoxy-2-methylfuro[2,3-b]quinoline (**XVIIa** *and* **XVIIb**) *and their acetates* (**XVIIIa** *and* **XVIIIb**). The ketone (**XVI**, 720 mg) was dissolved in a mixture of dry methanol (100 ml) and dry tetrahydrofuran (70 ml). To the solution, sodium borohydride (312 mg) was added as several portions with stirring at 0°C. After the reduction was complete (2 hr), the reaction mixture was concentrated to a small volume (5 ml) under reduced pressure, and then poured into ice water. The resulting precipitates (661 mg) were collected, washed with water and dried in a vacuum dessicator. The yield was 93%. The white powder was separated into two fractions by dissolving in a small volume of EtOH. The insoluble fraction (423 mg) was almost pure 2,3-*cis* alcohol (**XVIIa**). The 2,3-*cis* alcohol was acetylated with acetic anhydride and pyridine at room trmperature, affording quantitatively the 2,3-*cis* acetate (**XVIIIa**). On crystallization from EtOH, the acetate was obtained as rods, mp 181~182°C. The crystals of the acetate were hydrolyzed with 6 N potassium hydroxide in MeOH to afford pure 2,3-*cis* alcohol, mp 255~256°C. (**XVIIa**) MS *m/e*: 261 (M^+, base peak), 246 ($M^+ - CH_3$), 243 ($M^+ - H_2O$), 232, 228, 216, 200, 188, 186, 171, 135. UV λ_{max}^{EtOH} nm (ε): 343 (4,600), 329 (4,600), 276 sh., 265 (54,00), 258 (5,700), 234 (47,000). (**XVIIIa**) MS *m/e*: 303 (M^+, 100%), 244 (87.5%), 243 (70.5%), 229 (39.8%), 228 (75.0%), 218 (22%), 186 (35%). PMR $\delta_{TMS}^{CDCl_3}$: 1.47 (d, J=6Hz, 3H), 2.13 (s, 3H), 3.86 (s, 3H), 4.19 (s, 3H), 4.78 (d, q, J=5.4Hz, J=6Hz, 1H), 6.75 (d J=5.4Hz 1H), 7.08~7.40 (m, 2H), 7.69 (d, J=10Hz, 1H). IR ν_{max}^{KBr} cm^{-1}: 2990, 2960, 2920, 1725, 1625, 1604, 1590, 1518, 1420, 1370, 1310, 1230, 1150, 1115, 1045, 985, 830, 756, 605. UV λ_{max}^{EtOH} nm (ε): 346 (5,000), 333 (5,000), 277 sh., 267 (7,200), 260 (7,400), 235 (54,600).

* d_6-DMSO-CD_3OD

The 2, 3-*trans* alcohol was purified from the ethanol soluble fraction by repeated recrystallization from aq. MeOH. The 2,3-*trans* acetate was derived from the alcohol in the usual manner. **(XVIIb)** Needles; mp 210~212°C. MS *m/e*: 261 (M^+, base peak), 246, 243, 232, 228, 216, 200, 188, 186, 171, 135, 119. UV λ_{max}^{EtOH} nm (ε): 343 (5,200), 330 (5,200), 258 (7,100), 253 sh., 233 (57,000).

(XVIIIb) Rods recrystallized from petroleum ether; mp 143~145°C. MS *m/e*: 303 (M^+, 100%), 244 (67.8%), 243 (56.8%), 229 (27.1%), 228 (50.8%), 218 (28%), 186 (33%). PMR $\delta_{TMS}^{CDCl_3}$: 1.47 (d, J=7.0Hz, 3H), 2.08 (s, 3H), 3.81 (s, 3H), 4.16 (s, 3H), 4.69 (d, q, J=1.0Hz, J=7.0 Hz, 1H), 6.15 (d, J=1.0Hz, 1H), 7.08~7.40 (m, 2H), 7.56 (d, J=9.0Hz, 1H). IR ν_{max}^{KBr} cm^{-1}: 3030, 2960, 2840, 1727, 1620, 1581, 1512, 1441, 1310, 1220, 1018, 980. 838. UV λ_{max}^{EtOH} nm (ε): 346 (4,900), 332 (4,900), 277 sh., 266 sh., 234 (55,500).

6-Methoxy-2-methyldictamnine **(V)**. The 2,3-*cis* alcohol **(XVIIa**, 9.0 mg) was dissolved in dry dioxane (1.0 ml). To the solution was added fused potassium bisulfate (62 mg). The turbid solution was refluxed for 45 min. After evaporation of the solvent, the residue was purified by preparative TLC [silica gel, developed with a mixture of Benz., CH_2Cl_2 and EtOAc (4: 1: 1)]. On crystallization of the dehydrated product **(V)** from aq. MeOH, colorless cubes (6.0 mg), mp 176–8°C, were obtaned with a 67% yield. Dehydration of the 2,3-*trans* alcohol **(XVIIb**, 9.0 mg) was carried out in the same conditions as for the 2,3-*cis* alcohol and afforded the same product (5 mg). MS *m/e*: 243 (M^+), 228 (M^+-15), 186 (M^+-57), 175, 174, 159, 145, 134, 133 (base peak), 105, 101, 79, 78, 77. PMR $\delta_{TMS}^{CDCl_3}$: 2.49 (s, 3 H), 3.93 (s, 3 H), 4.42 (s, 3 H), 6.68 (br.s, 1 H), 7.3~7.5 (m, 2 H), 7.97 (d, J=9 Hz, 1 H). UV λ_{max}^{EtOH} nm (ε): 344 (4,700), 326 (5,800), 309 (11,300), 296 (7,700), 252 (32,700), 235 (34,600).

N-(p-Methoxyphenyl)-2-chloropropionamide **(XIX)**. Leaflets crystallized from petroleum ether; mp 105~107°C. MS *m/e*: 215 (M^++2), 213 (M^+), 178, 150, 137, 123, 122 (base peak), 108. PMR $\delta_{TMS}^{CDCl_3}$: 1.78 (d, J=7 Hz, 3 H), 3.74 (s, 3 H), 4.50 (q, J=7 Hz, 1 H), 6.87 (d, J=10 Hz, AB type, 2 H), 7.46 (d, J=10 Hz, AB type, 2 H), 8.26 (br.s, 1 H). On addition of D_2O, the last broad singlet due to the amide proton disappeared. CMR $\delta_{TMS}^{CDCl_3}$ 22.36 (q), 55.47 (d), 55.81 (q), 114.26 (d), 122.36 (d), 130.22 (a), 157.08 (s). 167.91 (s). IR ν_{max}^{KBr} cm^{-1}: 3500, 1655, 1538, 1514, 1305, 1250, 1118, 1073, 1033, 993, 825, 786. Beilstein test; positive.

2, 3 - Dihydro - 4, 6 - dimethoxy -2- methylfuro [2, 3-b]-quinoline **(XXI)**. A suspension of 30% palladium on charcoal (28 mg) in acetic acid (1.0 ml) was placed in the reaction bottle of a catalytic reduction apparatus. The apparatus was evacuated and then filled with hydrogen. A solution of 2,3-*cis* acetate **(XVIIIa**, 25.4 mg) in acetic acid (1.0 ml) was added to the reaction bottle and the mixture was shaken with hydrogen at 70°C for 7 hr and at 80°C for 1/2 hr. After the usual workup procedure, the product was purified by preparative TLC [silica gel, developed with a mixture of EtOAc, CH_2Cl_2 and *n*-Hex. (1: 1: 2)], to afford a hydrogenolysis product **(XXI**, 9.0 mg). Plates crystallized from aq. MeOH; mp 133~134°C. MS *m/e*: 245 (M^+, base peak), 230 (M^+-15), 202, 187, 186. PMR $\delta_{TMS}^{CDCl_3}$ 1.53 (d, J=6.0 Hz, 3 H), 3.17* (d, d, J=15.3 Hz, J=6.8 Hz, 1 H), 3.75* (d, d, J=15.3 Hz. J=8.2 Hz, 1 H), 3.87 (s, 3 H), 4.18 (s, 3 H), 4.95* (d, d, d, J=6.8 Hz, J=8.2 Hz, J=6.0 Hz, 1 H), 7.04~7.80 (m, 2 H), 7.67 (d, J=9.0 Hz, 1 H). IR ν_{max}^{KBr} cm^{-1}: 3000, 2960, 2930, 1618, 1582, 1510, 1455, 1310, 1227, 1096, 830, 740. UV λ_{max}^{EtOH} nm (ε): 340 (6,800), 326 (6,800), 276 sh., 269 (8,700), 261 (9,000), 233 (50,400).

Ethyl 4, 5-dihydro-2-(3, 4-methylenedioxyanilino)-4-oxofuran-3-carboxylate **(VIIIb)**. Prepared from **(VIb)** and **(VII)** with a 10% yield. Colorless needles recrystallized from EtOH; mp 171~172°C. MS *m/e*: 291 (M^+), 246, 245 (M^+-46, M^+ –EtOH, base peak), 201, 187, 163. UV λ_{max}^{EtOH} nm (ε): 300 sh., 282 (17,900), 241 (15,700), 202 (17,000).

4 - Hydroxy - 7, 8 - methylenedioxy -3- oxofuro [2, 3-b]-quinoline **(IXb)**. Prepared from **(VIIIb)** with a 91% yield. Colorless needles recrystallized from DMF; decomposed slowly above 300°C. MS *m/e*: 246 (M^+ +1), 245 (M^+, base peak), 187, 163, 105. PMR δ_{TMS}^{**}: 4.78 (s, 2 H), 6.16 (s, 2 H), 6.94 (s, 1 H), 7.44 (s, 1 H). The amino proton was masked by solvent. UV λ_{max}^{EtOH} nm (ε): 333 sh., 307 (2,700), 271 (9,100), 249 (11,800).

4 - Methoxy - 6, 7 - methylenedioxy -3- oxofuro [2, 3-b]-quinoline **(Xb)**. Prepared from **(IXb)** with a 40% yield. Yellow needles recrystallized from EtOH; decomposed slowly above 150°C. MS *m/e*: 260 (M^+ +1), 259 (M^+, base peak), 241, 230, 216, 214, 203, 202, 201, 172, 171, 170, 158, 100. IR ν_{max}^{KBr} cm^{-1}: 3120, 2930, 1697, 1609, 1573, 1445, 1353, 1245, 1181, 1015, 923, 827, 714, 536. UV λ_{max}^{EtOH} nm (ε): 377 (1,600), 367 sh., 313 (2,400), 302 (3,300), 283 sh., 266 (4,100), 245 (10,600), 221 (11,400).

2,3-Dihydro-3-hydroxy-6,7-methylenedioxyfuro[2,3-b]-quinoline **(XIb)**. Prepared from **(Xb)** with a 31% yield. Colorless rods recrystallized from EtOH;

* The three protons formed an ABX system.

** d_6-DMSO-CD_3OD

mp 230–5°C. MS *m/e*: 262 (M^++1), 261 (M^+, base peak), 245, 244, 243 (M^+ –H_2O), 229, 228, 105, 77. UV λ_{max}^{EtOH} nm (ε): 336 (7,800), 322 (6,800), 310 sh., 283 (4,000), 272 (4,300), 263 (4,200), 229 (37,100).

Maculine (**II**). Prepared from (**XIb**) with a 40% yield. Colorless needles recrystallized from EtOH; mp 193~195°C (lit., 197°C).[8] MS *m/e*: 243 (M^+, base peak), 228, 200, 185, 151, 150, 85, 57. PMR $\delta_{TMS}^{CDCl_3}$: 4.41 (s, 3 H), 6.09 (s, 2 H), 7.07 (d, *J*=2.8 Hz, 1 H), 7.25 (s, 1 H), 7.50 (s, 1 H), 7.59 (d, *J*=2.8 Hz, 1 H). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3030, 2970, 1628, 1595, 1464.

Ethyl 4,5-dihydro-2-anilino-4-oxofuran-3-carboxylate (**VIIIc**). Prepared from (**VIc**) and (**VII**)in the presence of triethylamine with a 13% yield. Plates crystallized from aq. EtOH; mp 114~115°C (lit., 116~117°C).[9] MS *m/e*: 247 (M^+), 202, 201 (base peak), 143, 105, 77. UV λ_{max}^{EtOH} nm (ε): 273 (22,200), 243 sh., 210 (10,800).

2, 3-Dihydro-4-hydroxy-3-oxofuro[*2, 3-b*]*quinoline* (**IXc**). Prepared from (**VIIIc**) with a 72% yield. Needles crystallized from DMF; decomposed slowly above 290°C. (lit., decomposed above 320°C).[9] MS *m/e*: 202 (M^++1), 201 (M^+, base peak), 143, 105, 77. PMR δ_{TMS}^{*}: 4.81 (s, 2 H), 7.3–7.8 (m, 3 H), 8.11 (d, d, *J*=1 Hz, *J*=7.9 Hz, 1 H). The amino proton was masked by solvent. UV λ_{max}^{EtOH} nm (ε): 319 (5,000), 308 (5,500), 298 (4,300), 267 sh., 259 (20,200), 240 (32,900), 213 (25,900).

2, 3-Dihydro-4-methoxy-3-oxofuro[*2, 3-b*]*quinoline* (**Xc**). Prepared from (**IXc**) with a 32% yield. Pale yellow needles recrystallized from EtOH; mp 155~163°C (decompositon), (lit., 152~159°C).[9] MS *m/e*: 216 (M^++1), 215 (M^+, base peak), 186, 169, 159, 158, 130, 129, 128, 127, 114. IR ν_{max}^{KBr} cm^{-1}: 2970, 2940, 2860, 1701, 1591, 1547, 1447, 1355, 1290, 1187, 1016, 77. UV λ_{max}^{EtOH} nm (ε): 362 (2,900), 352 (3,300), 302 (16,600), 292 sh., 244 (33,500), 237 (32,700), 215 (19,500).

2, 3-Dihydro-3-hydroxy-4-methoxyfuro[*2, 3-b*]*quinoline* (**XIc**). Prepared from (**Xc**) with a 95% yield. Rods recrystallized from aq. MeOH; mp 210~213°C. MS *m/e*: 217 (M^+, base peak), 200 (M^+ –OH), 199 (M^+ –H_2O), 186, 185, 184, 170, 156, 130, 128, 127. PMR δ_{TMS}^{**}: 4.45 (s, 3 H), 4.3~4.7 (m, 2 H), 5.67 (br. s, 1 H), 5.93 (very broad m, 1 H), 7.3 (m, 1H), 7.6 (m, 1 H), 8.05 (d, t, *J*=7.7 Hz, *J*=1.1 Hz, 1 H).

Dictamnine (**III**). Prepared from (**XIc**) with an 83% yield. Colorless cubes crystallized from EtOH; mp 133~135°C (lit., 134~135°C).[9] MS *m/e*: 199 (M^+), 184, 151, 150, 85 (base peak). PMR $\delta_{TMS}^{CDCl_3}$: 4.37 (s, 3 H), 6.96 (d, *J*=2.7 Hz, 1 H), 7.52 (d, *J*=2.7 Hz, 1 H), 7.2~7.7 (m, 2 H), 7.92 (d, *J*=9 Hz, 1 H), 8.17 (d, *J*=8 Hz, 1 H). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3120, 2970, 1621, 1576, 1504, 1368, 1262, 801, 756, 722. UV λ_{max}^{EtOH} nm (ε): 330 (4,500), 314 (5,100), 308 (5,400), 241 (29,800), 236 (31,600), 206 sh.

Ethyl 4, 5-dihydro-2-(4-methoxyanilino)-4-oxofuran-3-carboxylate (**VIIId**). Prepared from (**VId**) and and (**VII**) in the presence of triethylamine with a 45% yield. Pale yellow cubes crystallized from aq. MeOH; mp 135°C (lit., 130~132°C).[10] MS *m/e*: 277 (M^+), 231 (M^+ –EtOH, base peak), 216, 173. UV λ_{max}^{EtOH} nm (ε): 273 (16,500), 206 (12,000).

2, 3-Dihydro-4-hydroxy-6-methoxy-3-oxofuro[*2, 3-b*]-*quinoline* (**IXd**). Prepared from (**VIIId**) with a 94% yield. Colorless needles crystallized from DMF; decomposed above 300°C. (lit., decomposed above 285°C).[10] MS *m/e*: 231 (M^+, base peak), 216 (M^+ −15), 188, 71, 69. PMR δ_{TMS}^{*}: 3.83 (s, 3 H), 4.76 (s, 2 H), 7.23 (d, d, *J*=2.7 Hz, *J*=9 Hz, 1 H), 7.38 (d, *J*=9 Hz, 1 H), 7.59 (d, *J*=2.7 Hz, 1 H). The amino proton signal was masked by solvent.

2, 3-Dihydro-4, 6-dimethoxy-3-oxofuro[*2, 3-b*]*quinoline* (**Xd**). Prepared from (**IXd**) with a 94% yield. Yellow needles crsytallized from EtOH; mp 193°C (decomp.) (lit., 176~178°C).[10] MS *m/e*: 245 (M^+, base peak), 230 (M^+ −15), 216, 202, 188. IR ν_{max}^{KBr} cm^{-1}: 2950, 1720 sh., 1707, 1623, 1602, 1570, 1507, 1447.

2, 3-Dihydro-3-hydroxy-4, 6-dimethoxyfuro[*2, 3-b*]-*quinoline* (**XId**). Prepared from (**Xd**) with a 90% yield. Cubes crystallized from aq. MeOH; mp 190~192°C (lit., 180~182°C).[10] MS *m/e*: 247 (M^+, base peak), 232, 230 (M^+ –OH), 229 (M^+ –H_2O), 214, 186. PMR $\delta_{TMS}^{CDCl_3}$: 3.83 (s, 3 H), 4.40 (s, 3 H), 4.3~4.6 (m, 2 H), 5.63 (br.s, 1 H), 5.7 (very broad m, 1 H), 7.06 (d, d, *J*=9.0 Hz, *J*=2.7 Hz, 1 H), 7.34 (d, *J*=2.7 Hz, 1 H), 7.49 (d, *J*=8.7 Hz, 1 H). UV λ_{max}^{EtOH} nm (ε): 342 (4,300), 329 (5,900), 277 sh., 266 (5,900), 259 (5,900), 237 (12,200).

6-Methoxydictamnine (**IV**). Prepared from (**XId**) with an 80% yield. Colorless needles crystallized from aq. MeOH; mp 133~135°C (lit., 134~135°C).[10] MS *m/e*: 229 (M^+), 214 (M^+ −15), 199, 151, 150, 85, 43 (base peak). PMR $\delta_{TMS}^{CDCl_3}$: 3.92 (s, 3 H), 4.40 (s, 3 H), 6.99 (d, *J*=2.8 Hz, 1 H), 7.3~7.5 (m, 2 H), 7.56 (d, *J*=2.8 Hz, 1 H), 7.87 (d, *J*=9 Hz, 1 H). IR ν_{max}^{KBr} cm^{-1}: 3130, 3110, 3000, 2950, 1628, 1585, 1511, 1368,

* d_6-DMSO-CD_3OD

** $CDCl_3$-d_6-DMSO

1305, 1240, 1224, 1090, 982, 824.

2,3-Methylenedioxyaniline (**VIa**). Prepared from the amide (**XIIe**) with a 46% yield. The *N*-benzoyl derivative of (**VIa**) was prepared in the usual manner and crystallized from MeOH to afford colorless needles; mp 137~138°C. MS *m/e*: 242 (M^++1), 241 (M^+), 105 ($C_6H_5CO^+$), 77, 51. PMR $\delta_{TMS}^{CDCl_3}$ 5.96 (s, 2 H), 7.5~8.0 (m, 9 H). IR ν_{max}^{KBr} cm^{-1}: 1676, 1453, 1442, 1254, 1058. UV λ_{max}^{EtOH} nm (ε): 255 sh., 228 (17,500), 208 (23,500).

2,3-Dihydroxybenzaldehyde (**XIIb**). Prepared from *o*-vanillin wth a 49% yield. Pale yellow rods crystallized from benzene; mp 104~106°C. MS *m/e*: 138 (M^+), 137, 120, 110, 92, 81. PMR $\delta_{TMS}^{CDCl_3}$: 6.7~7.2 (m, 3 H), 9.75 (s, 1 H), 5.69 (s, 1 H), 10.94 (s, 1 H). The last two singlets due to the hydroxy groups were lost on addition of D_2O. IR ν_{max}^{KBr} cm^{-1}: 1655, 1640, 1610, 1585, 1480.

2, 3-Methylenedioxybenzaldehyde (**XIIc**). Prepared from (**XIIb**) in the presence of cupric oxide as a catalyst with a 67% yield.[15] Reddish oil.[16] MS *m/e*: 150 (M^+, base peak), 136, 71, 69. PMR $\delta_{TMS}^{CDCl_3}$: 6.13 (s, 2 H), 6.8~7.1 (m, 2 H), 7.25 (d, d, J=2 Hz, J=7 Hz, 1 H), 10.08 (s, 1 H). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1695, 1638.

2,3-Methylenedioxybenzoic acid (**XIId**). Prepared from (**XIIc**) with an 81% yield. Pale yellow powder; mp 227~233°C. (lit., 227°C).[16] MS *m/e*: 166 (M^+), 165, 136 (base peak), 108, 71. IR ν_{max}^{KBr} cm^{-1}: 3050, 3000, 2900, 2800, 2650, 2550, 2330, 1702, 1690, 1670, 1630, 1595.

2, 3-Methylenedioxybenzamide (**XIIe**). Prepared from (**XIId**) with an 87% yield. White powder; mp 175~176°C (lit., 176°C).[16] MS *m/e*: 165 (M^+, base peak), 136, 57. PMR $\delta_{TMS}^{CDCl_3}$: 6.03 (s, 2 H), 6.5~7.0 (m, 2 H), 7.49 (d, d, J=3 Hz, J=6 Hz, 1 H), *ca.* 5.8 (very broad s, 2 H). The last two proton signals disappeared on addition of D_2O. IR ν_{max}^{KBr} cm^{-1}: 3480, 3340, 3290, 3240, 3180, 2900, 1675, 1653, 1590. UV λ_{max}^{EtOH} nm (ε): 307 (3,700), 221 (11,000).

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