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A Novel Synthesis of Revenine and Related Alkaloids by Means of a Photo-rearrangement Reaction of 4-Alkoxy-2-methylquinoline 1-Oxides[1,2]

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Two alkaloids, 1-methyl-4-(3-methylbut-2-enyloxy)-2-quinolone (revenine: IIc) and 4-methoxy-1-methyl-2-quinolone (IIa), were synthesized by means of a photochemical rearrangement reaction of the corresponding 4-alkoxy-2-methylquinoline 1-oxide (Ic and Ia), which were conveniently prepared from 4-chloro-2-methylquinoline 1-oxide (XVII), which in turn is readily obtainable from 2-methylquinoline 1-oxide *via* the 4-nitrated compound (XVIII).

The mechanism of the photo-rearrangement reaction of 4-alkoxy-2-methylquinoline 1-oxides (Ia—d) in methanol is discussed.

Keywords——4-alkoxy-1-methyl-2-quinolones; 4-alkoxy-3-methyl-2-quinolones; 4,4-dialkoxy-3,4-dihydro-3-methyl-2-quinolones; NMR spectra; UV spectra; mechanism of photorearrangement reactions; synthesis of alkaloids

As reported previously,[4] irradiation of 2-methylquinoline 1-oxide in methanol affords 2-quinolones (carbostyrils) as the major rearrangement products. The 3-methyl derivative was predominant over the 1-methyl derivative, and the oxazepine was formed as a minor product (*ca.* 10%). In continuing studies on the photo-reactions of aromatic amine N-oxides, we have found that the migration of the 2-methyl group of quinoline 1-oxides to the 1- or 3-position in the resulting carbostyrils is dependent on the nature of 4-substituent of the starting N-oxide; 1-methylcarbostyril is the major product with an electron-donating substituent and 3-methylcarbostyril with an electron-withdrawing one.

4-Alkoxy-2-methylquinoline 1-oxides (Ia—d) were irradiated in methanol in the expectation of obtaining 4-alkoxy-1-methyl-2-quinolones (II), and as a result, we found a new and general synthetic route to the desired products (II), including two alkaloids, revenine (IIc) and its 4-methoxy derivative (IIa), which occur in some Rutaceous plants.[5,6] The present paper also reports the mechanistic features of these photo-rearrangement reactions, and a convenient preparation procedure for 4-alkoxy-2-methylquinoline 1-oxides (Ia—d) from 2-methyl-4-nitroquinoline 1-oxide (XVIII) *via* the 4-chloro derivative (XVII).

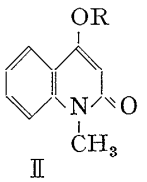
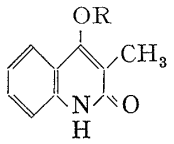
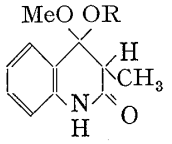
Irradiation of 4-Alkoxy-2-methylquinoline 1-Oxides (Ia—d) in Methanol: A Convenient Synthesis of 4-Alkoxy-1-methyl-2-quinolones (IIa—d)

Irradiation of 4-alkoxy-2-methylquinoline 1-oxides (Ia—d) in methanol at $\geq$300 nm afforded three rearrangement products, II, III, and IV (with II as the major product), but

1) This paper forms Part XXXIII of "Studies on the N-Oxides of π-Deficient N-Heteroaromatics." Part XXXII: C. Kaneko, A. Yamamoto, and M. Hashiba, *Chem. Pharm. Bull.* (Tokyo), **27**, 946 (1979).
2) Presented at the 47th Meeting of the Hokuriku Branch, Pharmaceutical Society of Japan, Toyama, November 1978, Abstracts, p. 9.
3) Location: *13-1, Takara-machi, Kanazawa 920, Japan.*
4) M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **14**, 1102 (1966).
5) M.N.S. Nayar, C.V. Sutar, and M.K. Bhan, *Phytochem.*, **10**, 2843 (1971).
6) B.P. Paul and P.K. Bose, *J. Indian Chem. Soc.*, **45**, 552 (1968); *idem*, *ibid.*, **46**, 678 (1969).

the oxazepines and further solvolyzed products were not obtained. The results of these irradiation experiments are summarized in Table I.

Table I. Products obtained by Irradiation of 4-Alkoxy-2-methylquinoline 1-Oxides in Methanol

		Products; mp (yield in %)		
I $\xrightarrow[\text{MeOH}]{\geq 300\text{ nm}}$	R	 II	 III	 IV
a	$-CH_3$	101.5—103° (55)	198.5—199.5° (9)	147 —149° (12)
b	$-CH_2-CH=CH_2$	86 — 86.5° (45)	131 —132.5° (8)	147.5—148.5° (13)
c	$-CH_2-CH=C(CH_3)_2$	121.5—122.5° (47)	147 —149° (6)	107 —109° (13)
d	$-CH_2-C\equiv CH$	175 —176° (48)	173.5—174.5° (6)	Oil[a] (14)

a) The product (IVd) did not crystallize.

The compounds II and III were determined to be 1-methyl- and 3-methylcarbostyrils, respectively, mainly from spectral evidences. Both products (II and III) showed typical carbostyril absorptions in the ultraviolet (UV) spectra. The positions of methyl groups in these compounds were deduced from their nuclear magnetic resonance (NMR) spectra, which showed chemical shifts of 1-methyl protons at around δ 3.6 in II and those of 3-methyl protons at around δ 2.2 in III. The third rearrangement product (IV) showed typical acetoanilide absorption in the UV spectra, and hence, was considered to contain a 3,4-dihydrocarbostyril chromophore. The NMR spectrum of IVa showed the presence of two methoxy groups, together with C_3-methyl protons as a doublet. Other products (IVb—d) of this type also showed the expected NMR spectra, though the stereochemistry of the 3,4-positions could not be determined. The finding that acid hydrolyses of IVa—d afforded 2,4-dihydroxy-3-methylquinoline (V) as a common product further supported the assigned structures (IV). The spectral properties of two 1-methylcarbostyril derivatives (IIa and IIc) are summarized in Table II. The spectrum of the former (IIa) was identical with that of the alkaloid isolated

Table II. UV and NMR Spectra of the Photo-rearrangement Products obtained from Ia and Ic

		II		III		IV	
		a	c	a	c	a	c
λ_{max}^{MeOH} nm (log ε)		229(4.71)	229.5	228(4.61)	223	250(4.10)	250
		269(3.85)	270	269(3.88)	271	281(3.47)	281
		279(3.85)	279.5	278(3.83)	280	291(3.37)	291
		319(3.76)	319	322(3.88)	322		
NMR: δ ($CDCl_3$)	O–CH_3	3.94, s	—	3.94, s	—	3.30, s 2.90, s	2.86, s
	1–CH_3	3.66, s	3.59, s	—	—	—	—
	3–CH_3	—	—	2.25, s	2.22, s	1.02, d[c]	1.05, d[d]
	3–H	6.00, s	5.90, s	—	—	3.09, q[c]	3.15, q[d]
	$-O-CH_2-$	—	4.56, d[a]	—	4.53, d[b]	—	4.03, d[e]
	–CH=	—	5.47, t[a]	—	5.50, t[b]	—	5.35, t[e]
	$=C(Me)_2$	—	1.76, s 1.81, s	—	1.69, s 1.79, s	—	1.70, s 1.77, s

a, *b*) J (coupling const.)=6.5 Hz. *c*, *e*) J=7.0 Hz. *d*) J=7.5 Hz.

from *Hesperethusa crenulata* M. ROME[5] and that of the latter (IIc) with the spectrum of ravenine isolated from *Ravenia spectrabilis* ENGL.[6] Though ravenine (IIc) was synthesized previously by Chamberlain *et al.*[7] from 4-hydroxy-1-methyl-2-quinolone by O-alkylation with 3,3-dimethylallyl bromide in the presence of an appropriate base, the yield was quite low ($\leq$20%) due to the formation of C-alkylation products. Taking this into consideration, and in view of the ready availability of the starting N-oxides (*vide infra*), this photochemical rearrangement of 4-alkoxy-2-methylquinoline 1-oxides provides a very convenient synthetic route to these alkaloids. Furthermore, since the ratios of the three products (II, III, and IV) were not affected by the 4-alkoxy groups in the N-oxides (I), the synthesis of 4-alkoxy-1-methyl-2-quinolones (*e.g.*, IIa—d) by this route should prove to have wide applicability.

Discussion of the Photo-rearrangement Reactions of the N-Oxides (I) in Methanol

The mechanism of formation of the three rearrangement products (II, III, and IV) will now be discussed. First, we will consider why the oxazepines (XIV) are not formed from 4-alkoxy-2-methylquinoline 1-oxides (Ia—d) in these photolyses. Since 2-methylquinoline 1-oxide afforded the corresponding oxazepine in only *ca.* 10% yield on irradiation in methanol,[4] 4-methoxycarbonyl-2-methylquinoline 1-oxide (VI) was irradiated in the same solvent in order to determine the effect of the 4-substituent in the starting N-oxides. As a result, a series of indole derivatives (X, XI, and XII), presumably formed *via* the oxazepine (VII),[9] were obtained as the major products (in 53% total yield), together with 3- and 1-methylcarbostyrils (VIII and IX in a ratio of 1:4) as minor products (Chart 1).

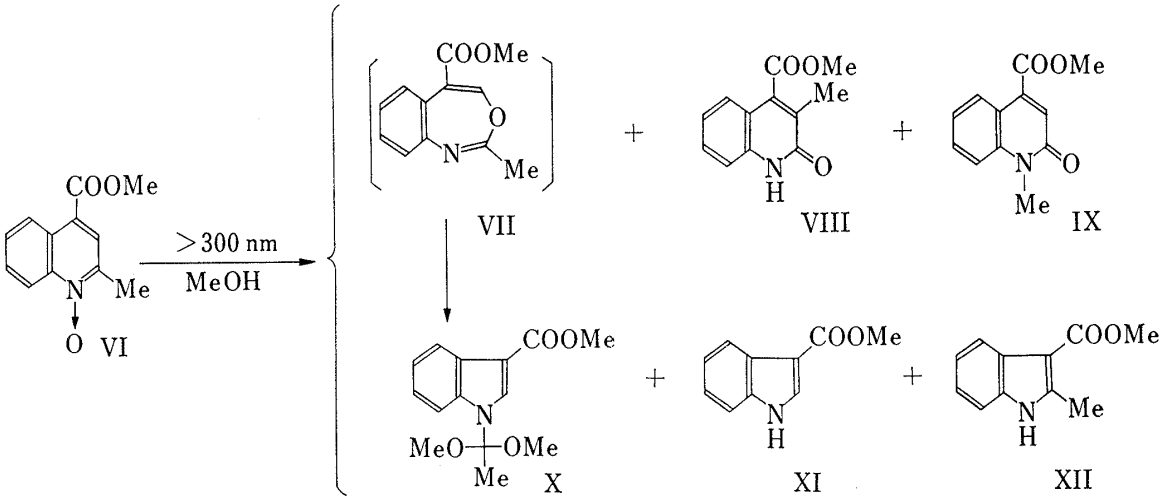


Chart 1

The results of photolyses of I, 2-methylquinoline 1-oxide, and VI in methanol are in good accord with our previous proposal[9a] shown in Chart 2. Here, the formation of carbostyrils is assumed to occur through a thermal carbonium ion rearrangement of the 2-methyl group from the oxaziridine species (*e.g.*, XIII), whose transition state is a π-complex represented by

7) T.R. Chamberlain and M.F. Grundon, *J. Chem. Soc.* (*C*), **1971**, 910. Ravenine was not only demonstrated to be the biogenetic precursor of 3-prenylated 2,4-dihydroxy-1-methylquinoline alkaloids contained in Rutaceous plants (*e.g.*, ifflaiamine, ravenoline, spectrabiline) by ^{14}C-feeding experiments,[8] but also converted to these alkaloids by chemical means.

8) T.R. Chamberlain, J.F. Collins, and M.F. Grundon, *J.C.S. Chem. Commun.*, **1969**, 1269.

9) 3,1-Benzoxazepines having no substituent or an alkyl group at the 2-position are quite susceptible to solvolytic reactions.[a] The formation of indole derivatives from oxazepines under solvolytic[a] or photochemical conditions[b] is well documented; *a*) C. Kaneko, *Yuki Gosei Kagaku Kyokai Shi* (*J. Syn. Org. Chem. Japan*), **26**, 758 (1968); *b*) R. Kitamura, H. Fujii, K. Hashiba, M. Somei, and C. Kaneko, *Tetrahedron Lett.*, **1977**, 2911, and references cited therein.

the formula XV. Such a complex would clearly be stabilized by an electron-donating group attached to the pyridine nucleus, but destabilized by an electron-withdrawing group. However, since the kinds of substituent on the pyridine nucleus would not significantly affect the activation energy of the intramolecular 1,5-oxygen shift (a thermally allowed pericyclic reaction) from the oxaziridine to the oxazepine, the proportion of the carbostyril to the oxazepine would be governed only by the relative ease of the carbonium ion rearrangement process, and hence, the results obtained in the above experiments (increased formation of carbostyrils in the order VI<2-methylquinoline 1-oxide<I) are in good accord with this view.

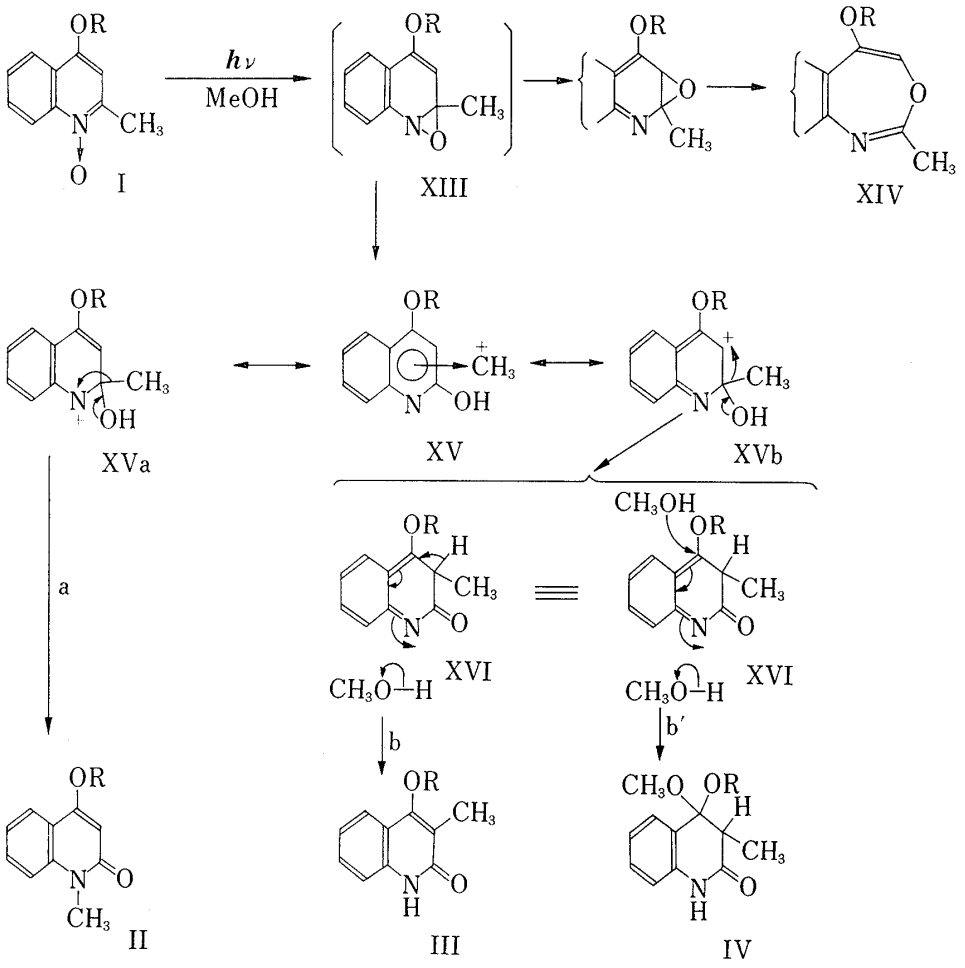


Chart 2

The same mechanism can also account for the formation of II, III, and IV from I. For convenience, we will represent the π-complex (XV) by a set of Kekulé structures (XVa and XVb). Then, as seen in path a, the migration of the methyl group (depicted by formula XVa) would give 1-methylcarbostyrils (II), which are the main products in the photolysis of I. The migration of the methyl group as depicted by formula XVb would give the intermediate (XVI), which affords either III by prototropy (path b) or IV by the addition of methanol (path b′). It should be noted that if the proposed mechanism for path b′ is correct, the products (IVb—d) are expected to possess a *trans* relationship between the entering MeO group and the C-3 methyl group; the actual stereochemistry remains to be clarified.[10] An alternative route for

10) Attempted elimination of an alcohol from the adducts (IVb—d) with trifluoroacetic acid only gave 2,4-dihydroxy-3-methylquinoline (V: a simple hydrolysis product) and no 4-alkoxy-3-methyl-2-quinolones were obtained.

the formation of IV including the photo-Michael addition of methanol to III[11] is rigorously excluded, because III was found to be stable under the appropriate irradiation conditions.[12]

Though the reason for the predominant formation of 1-methylcarbostyrils over the 3-methyl derivatives in the irradiation products of I is not clear, the results obtained in the present study (Table I) suggest that methyl migration to the 1-position occurs more readily than that to the 3-position in these N-oxides (Ia—d).

A General Synthetic Method for 4-Alkoxy-2-methylquinoline 1-Oxides (I) from 2-Methylquinoline 1-Oxide

As both 4-nitroquinoline 1-oxide and 4-chloroquinoline 1-oxide were reported to give 4-alkoxyquinoline 1-oxides on reaction with alkoxide ion,[13] 2-methyl-4-nitroquinoline 1-oxide (XVIII: readily obtainable by the nitration of 2-methylquinoline 1-oxide[14]) and 4-chloro-2-methylquinoline 1-oxide (XVII: obtained from XVIII in *ca.* 80% yield by treatment with conc. hydrochloric acid at 80°) were treated with methoxide ion under conditions similar to those used for the preparation of 4-alkoxyquinoline 1-oxides to yield the desired product (Ia) in *ca.* 50% yield from XVIII and 80% yield from XVII. Thus, a general preparative route to 4-alkoxy-2-methylquinoline 1-oxides (I) from XVII was established as follows. 4-Chloro-2-methylquinoline 1-oxide (XVII) was dissolved in an excess of an alcohol containing 2 mol equivalents of powdered potassium hydroxide and the whole was warmed on a boiling water bath for 3—5 hr. Though *t*-butyl alcohol did not react under these conditions, primary alcohols reacted smoothly with XVII to give the desired 4-alkoxylated products (Ia—d) in satisfactory yields (*ca.* 80%). 3,3-Dimethylallyl alcohol, not commercially available, was prepared from 1,1-dimethylallyl alcohol by the procedure reported by Babler *et al.*[15]

The structures of these 4-alkoxy N-oxides (Ia—d) were determined from the spectral data shown in Table III.

Table III. The Properties of 4-Alkoxy-2-methylquinoline 1-Oxides (Ia—d)

	R	mp	λ_{max}^{MeOH} nm (log ε)			NMR, δ ($CDCl_3$)	
						3-H	2-Me
Ia	$-CH_3$	135 —136°	222.5 (4.52)	244.5 (4.28)	332 (3.86)	6.52	2.67
Ib	$-CH_2-CH=CH_2$	140.5—142.5°	223 (4.56)	245 (4.34)	333 (3.94)	6.53	2.68
Ic	$-CH_2-CH=C(Me)_2$	98 — 98.5°	222.5	245.5	333	6.56	2.70
Id	$-CH_2-C\equiv CH$	198 —199°	223 (4.57)	243.5 (4.37)	332 (3.93)	6.69	2.71

Experimental

All melting points were determined in a capillary tube and are uncorrected. IR spectra were determined with a JASCO-IRA-2 spectrometer, UV spectra with a Hitachi 323 spectrometer, NMR spectra with a JEOL JNM-C-60H spectrometer (chemical shifts are in δ-units with coupling constants in Hz). Mass spectra (MS) were recorded on a JEOL JNM-01SG spectrometer using the direct insertion technique. For spectroscopic data, the following abbreviations are used: d=doublet, d-d, doublet of doublets, m=multiplet, s=singlet, sh=shoulder, and t=triplet.

11) The photo-Michael addition of an alcohol to α,β-unsaturated carbonyl systems is well known. M. Somei, R. Kitamura, H. Fujii, K. Hashiba, S. Kawai, and C. Kaneko, *J.C.S. Chem. Commun.*, **1977**, 899, and references cited therein.

12) An interesting photo-cyclobutane formation between the double bonds in the allyl and enone systems was observed when 4-allyloxycarbostyrils were irradiated at 254 nm. This and related intramolecular photo-cycloaddition reactions will be reported separately.

13) T. Okamoto, *Yakugaku Zasshi*, **71**, 297 (1951).

14) E. Ochiai and K. Satake, *Yakugaku Zasshi*, **71**, 1078 (1951).

15) H.J. Babler and D.O. Olsen, *Tetrahedron Lett.*, **1974**, 351.

Photolyses were carried out in an immersion apparatus equipped with a 400W Toshiba high-pressure mercury lamp with a Pyrex filter and cooled internally with running water. Irradiation was carried out under argon or nitrogen with stirring.

Synthesis of 4-Methoxy-2-methylquinoline 1-Oxide (Ia) by the Reaction of 2-Methyl-4-nitroquinoline 1-Oxide (XVIII) with Sodium Methoxide in Methanol——Compound XVIII (4.14 g) was added to a solution of 1 g of sodium dissolved in 100 ml of absolute methanol.[14] This mixture was stirred at room temperature for 1 hr. The residue obtained after removal of the solvent *in vacuo* was diluted with water, extracted with dichloromethane, and dried over Na_2SO_4. The residue left after removal of the solvent was chromatographed on 60 g of active alumina. Elution with CH_2Cl_2–benzene (1: 1 v/v) gave Ia (1.88 g, 49%), mp 135—136° (recrystallized from acetone). MS *m/e* 189 (M^+). Spectral data for Ia are listed in Table III. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.68; H, 5.73; N, 7.26.

4-Chloro-2-methylquinoline 1-Oxide (XVII) from 2-Methyl-4-nitroquinoline 1-Oxide (XVIII)——A mixture of 5.24 g of 2-methyl-4-nitroquinoline 1-oxide (XVIII) and 80 ml of conc. hydrochloric acid was warmed on a water bath (80°) for 7 hr. The reaction mixture was evaporated to dryness *in vacuo*, then the residue was made basic with aqueous potassium carbonate, extracted with dichloromethane, and dried over Na_2SO_4. The residue left after removal of the solvent was recrystallized from benzene to afford 4.03 g (81%) of 4-chloro-2-methylquinoline 1-oxide (XVII), mp 142—143°. MS *m/e* 193, 195 (M^+). UV λ_{max}^{MeOH} nm: 232, 237 sh, 330, 341 sh. NMR δ^{CDCl_3}: 2.66 (3H, s, CH_3), 7.30 (1H, s, H-3), 7.5—7.9 (2H, m, H-6 and -7), 8.04 (1H, m, H-5), 8.66 (1H, m, H-8). *Anal.* Calcd. for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 62.16; H, 4.28; N, 7.05.

General Procedure for the Synthesis of 4-Alkoxy-2-methylquinoline 1-Oxides (1a—d) from 4-Chloro-2-methylquinoline 1-Oxide (XVII)——4-Chloro-2-methylquinoline 1-oxide (XVII) (1 g) was added to a solution of 560 mg of powdered potassium hydroxide (*ca.* 2 mol equivalents relative to the N-oxide) in an excess of a primary alcohol (5—50 mol equivalents relative to the N-oxide). The mixture was heated on a boiling water bath for 3—5 hr. The reaction mixture was evaporated to dryness *in vacuo*, then the residue was diluted with water, extracted with dichloromethane, and dried over Na_2SO_4. The residue left after removal of the solvent was chromatographed on 30 g of alumina. Elution with CH_2Cl_2–benzene (1: 1 v/v) gave the corresponding 4-alkoxy-2-methylquinoline 1-oxides (Ia—d) in 80—85% yields (these yields were obtained if 20—50 mol equivalents of the alcohol were used; in cases where 5 mol equivalents of the alcohol were used, the yields decreased to *ca.* 50%). These products were characterized by means of spectral data (Table III). MS *m/e*: Ib ($C_{13}H_{13}NO_2$); 215 (M^+), Ic ($C_{15}H_{17}NO_2$); 243 (M^+), and Id ($C_{13}H_{11}NO_2$); 213 (M^+). *t*-Butanol did not react with XVII under the above conditions, and the starting material was recovered.

Irradiation of 4-Methoxycarbonyl-2-methylquinoline 1-Oxide (VI) in Methanol——A solution of VI (699 mg) in 500 ml of methanol was irradiated at room temperature for 40 min (the reaction was monitored by TLC and continued until all of the N-oxide was consumed). The reaction products obtained after removal of the solvent were then mixed with 6 g of celite and the whole was chromatographed on 50 g of silica gel. Elution with hexane–ether (2: 1 v/v) afforded methyl 1-(α,α-dimethoxyethyl)indole 3-carboxylate (X), methyl 2-methyl quinoline 4-carboxylate (XIX), and methyl 2-methylindole 3-carboxylate[16] (XII) in yields of 12.3, 5.9, and 11.5%, respectively. Elution with hexane–ether (1: 2 v/v) then afforded 142 mg (25.2%) of methyl indole 3-carboxylate (XI) and 30 mg (4.3%) of methyl 1-methyl-2-quinolone 4-carboxylate (IX). Elution with ether afforded 110 mg (15.7%) of methyl 3-methyl-2-quinolone 4-carboxylate (VIII). Finally, 73 mg of a crystalline product [mp 148—150° (methanol). UV λ_{max}^{MeOH} nm: 233, 260 sh, 294. MS *m/e* 217 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3400, 1723, 1680—1665, 1246] whose structure is now under investigation was obtained by elution with dichloromethane.

The structures of these products were determined by elemental analyses, mass, and other spectral data as shown below. X, mp 70—71°, (recrystallized from hexane). MS *m/e* 263 (M^+). UV λ_{max}^{MeOH} nm: 213, 225 sh, 272 sh, 282, 287 sh. IR ν_{max}^{KBr} cm^{-1}: 1720. NMR δ^{CDCl_3}: 1.78 (3H, s, CH_3), 3.27 (6H, s, $OCH_3\times 2$), 3.83 (3H, s, $COOCH_3$), 7.1—7.4 (2H, m), 7.68 (1H, m), 8.15 (1H, s, H-2), 8.1—8.2 (1H, m, H-4). *Anal.* Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.64; H, 6.38; N, 5.12. XIX, mp 54—56°. λ_{max}^{MeOH} nm: 242, 322. MS *m/e* 201 (M^+). XII,[16] mp 162—163° (hexane–ether), MS *m/e* 189 (M^+). λ_{max}^{MeOH} nm: 214, 228 sh, 252, 282, 288 sh. XI, mp 140—141° (hexane–ether). MS *m/e* 175 (M^+). λ_{max}^{MeOH} nm: 213, 225 sh, 248, 281, 287 sh. IX, mp 117—119° (hexane–ether). MS *m/e* 217 (M^+). λ_{max}^{MeOH} nm: 233, 258, 287, 346. δ^{CDCl_3}: 3.74 (3H, s, N-CH_3), 3.97 (3H, s, OCH_3), 7.18 (1H, s, H-3), 7.2—7.7 (3H, m), 8.34 (1H, m, H-5). This compound was hydrolyzed to 1-methyl-2-quinolone 4-carboxylic acid, mp 240—241° (recrystallized from methanol).[17] VIII, mp 164—167° (recrystallized from acetone). MS *m/e* 217 (M^+). λ_{max}^{MeOH} nm: 214, 221 sh, 230 sh, 273, 319 sh, 330, 345 sh. δ^{CDCl_3}: 2.08 (3H, s, CH_3), 4.00 (3H, s, OCH_3), 7.0—7.6 (4H, m), 8.0 (1H, broad s, NH). *Anal.* Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.38; H, 5.07; N, 6.24. 3-Methyl-2-quinolone 4-carboxylic acid (mp>300°) obtained by the hydrolysis of VIII was identical with an authentic sample obtained in our previous work.[17]

16) R. Kitamura, H. Fujii, K. Hashiba, M. Somei, and C. Kaneko, *Tetrahedron Lett.*, **1977**, 2911.
17) C. Kaneko and R. Kitamura, *Heterocycles*, **6**, 117 (1977).

Preparation of 3,3-Dimethylallyl Alcohol from 1,1-Dimethylallyl Alcohol[15]——A solution of 8.71 g of 1,1-dimethylallyl alcohol in 250 ml of acetic acid was added rapidly to a mixture of 250 ml of acetic acid and 100 ml of acetic anhydride containing 5.97 g of *p*-toluenesulfonic acid. After stirring at room temperature for 10 min, the reaction mixture was poured into 6 l of ice-water and kept standing overnight to decompose the anhydride. The resulting solution was saturated with sodium chloride and extracted with benzene (*ca.* 1 l). The residue obtained by removal of the solvent was distilled under reduced pressure to give 7.42 g (57%) of 3,3-dimethylallyl acetate, bp 35 mmHg 65.5°. NMR δ ^{CDCl_3}: 1.72 (6H, broad s, $(CH_3)_2C=$), 1.94 (3H, s, CH_3CO), 4.41 (2H, d, $J=7.5$ Hz, $-CH_2-$), 5.23 (1H, t, $J=7.5$ Hz, $=CH-$).

A solution of the acetate (3.21 g) in 45 ml of 5% KOH–MeOH was refluxed for 15 min. After removal of methanol using a Widmer column, the residue was extracted with ether, and dried over Na_2SO_4. The residue after evaporating off the ether was distilled to give 1.33 g (62%) of 3,3-dimethylallyl alcohol, bp 140°. NMR δ ^{CDCl_3}: 1.63, 1.73 (each 3H, s, $CH_3\times2$), 4.49 (2H, d, $J=7.2$ Hz, $-CH_2-$), 5.24 (1H, t, $J=7.2$ Hz, $-CH=$).

General Procedure for the Irradiation of 4-Alkoxy-2-methylquinoline 1-Oxides (Ia—d) in Methanol——A solution of I (3 mmol) in 300 ml of methanol was irradiated until I disappeared completely (*ca.* 12—16 min). After irradiation, the whole was evaporated under reduced pressure. The residue thus obtained was mixed with 3.0 g of celite and chromatographed on 20 g of active alumina. Elution with benzene afforded the deoxygenation products (<5%). Elution with benzene–CH_2Cl_2 (2: 1 v/v) afforded 1-methyl-2-quinolones (IIa—d), which were recrystallized from ether–hexane. Elution with benzene–CH_2Cl_2 (1: 1 v/v) gave the corresponding solvent addition products (IVa—d) which were recrystallized from ether, except for IVd. Finally, elution with dichloromethane afforded 3-methyl-2-quinolones (IIIa—d), which were recrystallized from acetone. All of the rearrangement products (II—IV) showed the expected molecular ions in their mass spectra, and their yields are summarized in Table I. UV and NMR data for IIa, c, IIIa, c, and IVa, c are summarized in Table II; the melting points and spectra of IIa and IIc are identical with those of natural alkaloids.[5,6] The other 2-quinolones (IIb, d and IIIb, d) also showed typical carbostyril absorptions in their UV spectra and were characterized by NMR. The addition products (IVb and IVd) showed UV spectra quite similar to those of IVa and IVc, and their structures were also supported by mass and NMR spectra.

Formation of 2,4-Dihydroxy-3-methylquinoline (V) from 4,4-Dialkoxy-3-methyl-2-quinolones (IVa and c)——a) Using Trifluoroacetic Acid: The adduct (IVc: 49.5 mg) was dissolved in 1.2 ml of trifluoroacetic acid, and the mixture was left to stand at room temperature overnight. The residual solid obtained after removal of the solvent was recrystallized from acetone to give V[18] in quantitative yield, mp>300°. MS *m/e* 175 (M^+). UV λ_{max}^{MeOH} nm: 229, 273, 282, 315, 327 sh. NMR δ ^{CDCl_3}: 2.07 (3H, s, CH_3).

b) Using HCl–Methanol: The adduct (IVa: 20 mg) was dissolved in 5 ml of methanol containing 1 ml of 10% HCl and the mixture was warmed at 50° for 1 hr. Removal of the solvent under reduced pressure followed by recrystallization from acetone afforded the dihydroxyquinoline (V), which was identical with the sample obtained in a), in quantitative yield.

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