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Selective Substitution Reactions of Quinoline Derivatives by Redox Systems[1] Nucleophilic Character of Hydroxyalkyl Radicals

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Homolytic hydroxyalkylation of quinoline derivatives by redox systems is described. The direct introduction of hydroxyalkyl groups into heteroaromatic ring of quinoline derivatives has been achieved by means of hydrogen peroxide. The good yields and the complete selectivity obtained are due to the nucleophilic character at heteroaromatic ring of the hydroxyalkyl radicals. It is useful to apply this reaction to other synthetic reactions.

F. Minisci, *et al.* had reported about introductions of alkyl groups into quinolines and other aromatic amines by redox systems, which is formed by reductive ions (Fe^{2+} or Cu^{+} *etc.*) and organic peroxides.[3]

They used *t*-butylhydroperoxide and methylethyl ketone peroxide as alkylating reagents and made to react them with N-protonated quinolines. Substitutions with alkyl radicals occurred at the parts of lower electron density, that is C-2 or C-4 position of quinolines. More-

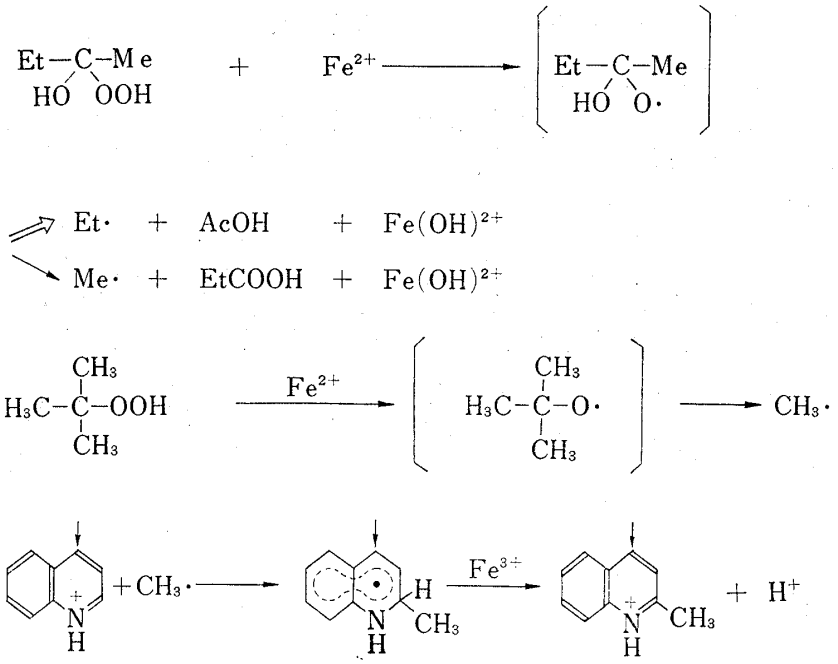

Chart 1

1) Presented at the 93rd Annual Meeting of Pharmaceutical Society of Japan, Tokyo, April 1973 and the 94th Annual Meeting, Sendai, April 1974.
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3) F. Minisci, R. Galli, M. Cecere, V. Malatesta, and T. Caronna, *Tetrahedron Letters*, **1968**, 5609; F. Minisci, M. Cecere, R. Galli, and R. Bernardi, *Tetrahedron*, **25**, 2667 (1969); F. Minisci, R. Galli, V. Malatesta, and T. Caronna, *Tetrahedron*, **26**, 4083 (1970).

over, in the case of methylethylketone peroxide, ethyl radical ($C_2H_5\cdot$) was preferentially introduced than methyl radical ($CH_3\cdot$) (Chart 1).

Then, the authors tried to introduce longer alkyl group to quinoline ring, using methyl-*n*-hexylketone to give *n*-hexyl derivatives. The reactions were carried out mainly according to Minisci's method. In such case, *n*-hexyl quinoline expected was not obtained, but other three products were detected by thin-layer chromatography (TLC) (Chart 2). They were chromatographed on silica gel column, and then colorless needles (I), mp 61.5—62°; colorless needles (II), mp 92—92.5°; pale yellow needles (III), mp 136—137° were obtained. All of them showed by nuclear magnetic resonance (NMR) spectroscopy, singlet peaks at about 5.0 ppm (δ), broad peaks at 3.0—4.0 ppm (δ) which disappeared by D_2O.

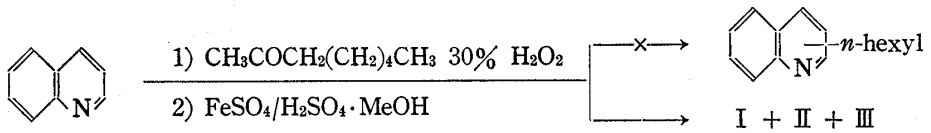

Chart 2

By NMR, mass spectroscopy and elemental analysis, I was assigned as 2-hydroxymethylquinoline (*m/e* 159 (M^+), $C_{10}H_9ON$), II was 4-hydroxymethylquinoline (*m/e* 159 (M^+), $C_{10}H_9ON$) and III was 2,4-dihydroxymethylquinoline (*m/e* 189 (M^+), $C_{11}H_{11}O_2N$) respectively.[4] Moreover, I and II were identified by comparing with authentic samples synthesized through other methods.

Consequently, it was supposed that substituents were originated from the solvent, and it was very interesting new fact to be able to introduce active groups as hydroxymethyl to quinoline ring.

Therefore, the following procedures were carried out.

1. The Reaction in Methanol Solution

The authors tried to react *t*-butyl hydroperoxide and $FeSO_4\cdot 7H_2O$ in methanol solution with quinoline. Also in this case, methylation was not occurred, but the same compounds (I), (II) and (III) were obtained.

The redox reaction in methanol solution was differentiated from that in aqueous solution. So, the reaction was made by the combination of 30% H_2O_2 and $FeSO_4\cdot 7H_2O$, to know if substituted hydroxymethyl groups were introduced from organic peroxide or methanol solvent. Then similarly, compounds (I), (II) and (III) were obtained as above. Each production ratio was as follows, I 30%, II 20%, III 1—2% (Chart 3). Moreover, the same reactions were made by using quinaldine (2-methylquinoline) and lepidine (4-methylquinoline). Quinaldine was reacted with 30% H_2O_2 under the condition of the presence of $FeSO_4\cdot 7H_2O$ in sulfuric acid

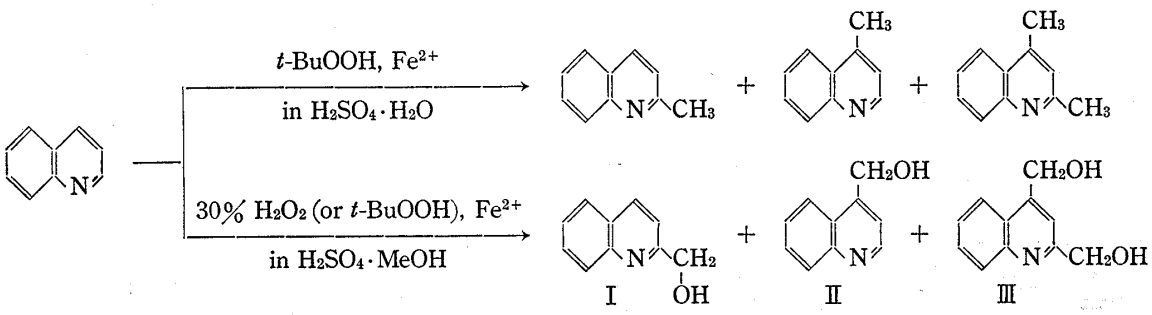

Chart 3

4) *a*) M.H. Palmer and P.S. McIntyre, *Tetrahedron Letters*, **1968**, 2147; M. Hamana and H. Noda, *Chem. Pharm. Bull.* (Tokyo), **17**, 2633 (1969); *b*) N. Hata, I. Ono, and S. Ogawa, *Bull. Chem. Soc. Japan*, **44**, 2286 (1971).

methanol solution at 0°. Reaction product was chromatographed on silica gel by using chloroform-methanol and gave colorless needles at about 53% yield, mp 189—191° (IV). The NMR spectrum (δ in $CDCl_3$) of IV showed the following signals; 5.18 (2H, singlet, aryl-CH_2O-), 2.6 (3H, singlet, aryl-CH_3), 4.47 (1H, broad singlet, -OH) disappeared by D_2O, 7.3—8.1 (5H, aromatic protons), 7.35 (1H, singlet, aromatic proton at C-3). So, IV was estimated as 4-hydroxymethyl-2-methyl quinoline. Mass spectrum (*m/e* 173 (M^+)) and elemental analysis supported this structure.

Also in the case of lepidine, colorless needles was isolated, mp 139—141° (V) at about 55% yield. The NMR spectrum of V showed the presence of aryl -CH_2OH and aryl-CH_3, so V was estimated as 2-hydroxymethyl-4-methylquinoline. Mass spectrum (*m/e* 173 (M^+)) and elemental analysis supported this structure (Chart 4).

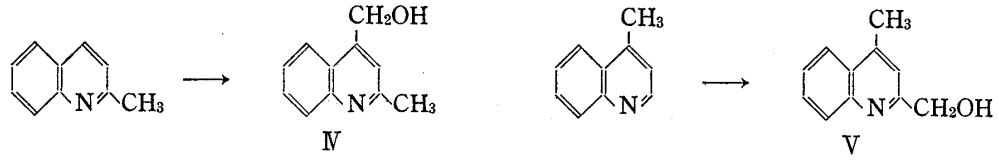

Chart 4

2. The Reaction in Ethanol Solution

From the above result that hydroxymethyl radical was occurred from methanol used as solvent by the redox systems using 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$ in 7% H_2SO_4 in methanol to substitute to quinoline ring from the other solvents which give rise to radicals easily. So, the authors proceeded next investigation using ethanol as solvent. To form redox systems, 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$ were used. In this case, since sulfates of quinolines and $FeSO_4 \cdot 7H_2O$ were not easily soluble in ethanol, 20% ethanol in water was used instead of ethanol solution.

For radical groups formed from ethanol, two processes are possible shown as in Chart 5. That is, a radical eliminated α-hydrogen and the other radical eliminated β-hydrogen. The possibility of the presence of $CH_3CH_2O\cdot$ was very little from that stability.

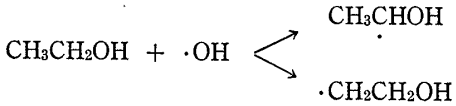

Chart 5

Same as in the case of methanol, quinoline, quinaldine and lepidine were used. The results were that substitution products to be introduced hydroxyethyl group were obtained as expected (Chart 6).

There were obtained four substitution products in the case of quinoline as follows; colorless needles, mp 125—126° (VI), pale brown needles, mp 78—80° (VII),[4b,5] colorless needles, mp 99.5—100° (VIII)[4b,5] and IX in small quantity. The yield of all of them was about 50%, and order of the production ratio was VI>VII>VIII>IX.

From the data of NMR and mass spectroscopy and elemental analysis, the following structures were supported.

VI: 4-(α-hydroxyethyl)-quinoline
VII: 2-(α-hydroxyethyl)-quinoline
VIII: 2-(β-hydroxyethyl)-quinoline
IX: 4-(β-hydroxyethyl)-quinoline

In the case of quinaldine, the products substituted hydroxyethyl groups at C-4, 2-methyl-4-(α-hydroxyethyl)-quinoline (X), mp 115—116.5° was obtained more than 2-methyl-4-(β-hydroxyethyl)-quinoline (XI), mp 119—119.5°, the production ratio was 2:1, the total yield was about 53%.

5) F.R. Stermitz, C.C. Wei, and W.H. Huang, *Chem. Commun.*, **1968**, 482.

In the case of lepidine, the products substituted hydroxyethyl groups at C-2, that is 4-methyl-2-(α-hydroxyethyl)-quinoline (XII), mp 75—76° and 4-methyl-2-(β-hydroxyethyl)-quinoline (XIII), mp 97—98°. The yield of them was about 60%, and the production ratio was about the same (Chart 6).

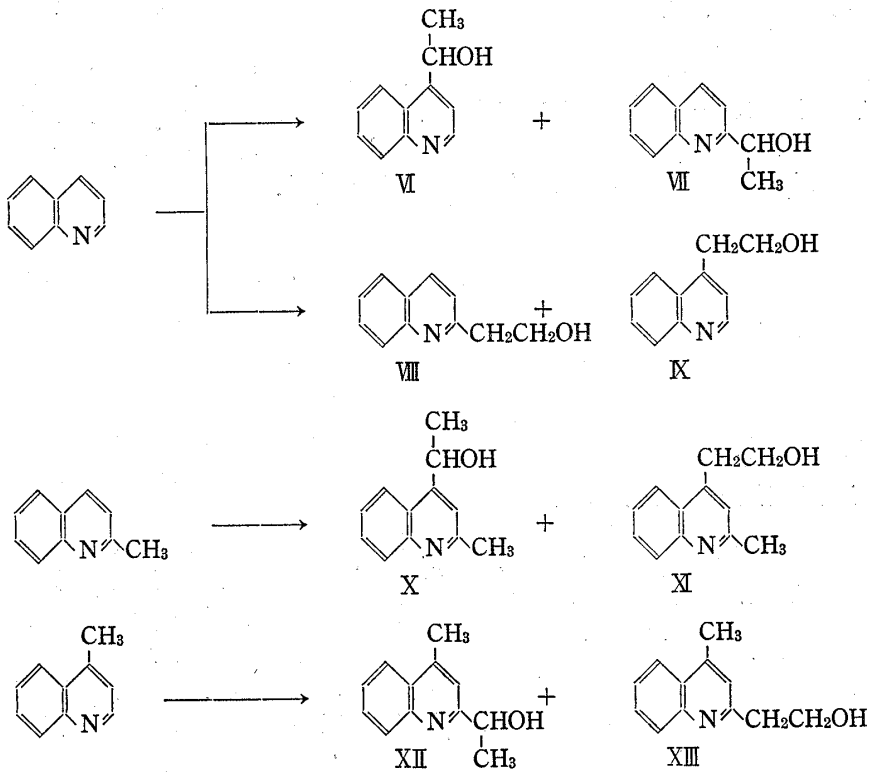

Chart 6

α-Hydroxyethyl and β-hydroxyethyl substituent of quinaldine were apparently differentiated by the NMR spectra. The sites of substitution were easily decided as C-4 from singlet peak (1H) at C-3. They were also differentiated by mass spectroscopy, although β-hydroxyethyl substituent had base peak of quinoline ring, α-hydroxyethyl substituent had base peak of (M^+-15) eliminated CH_3 from $CH_3\underset{|}{C}HOH$.[5,6]

3. The Reaction in *n*-Propanol Solution

Furthermore, *n*-propanol was used as solvent. To form redox systems, 30% H_2O_2 and $FeSO_4 \cdot 7H_2O$ were used same as above mentioned. For radical groups formed from *n*-propanol, three processes are possible shown as in Chart 7. That is, the first is a radical eliminated α-hydrogen and the second is a radical eliminated β-hydrogen and the third is a radical eliminated γ-hydrogen.

For substrate, quinaldine and lepidine were used. The results were that substitution products to be introduced hydroxypropyl group were obtained as expected in Chart 8. However, α-hydroxypropyl substituents were not obtained, because it might be also due to the instability of α-hydroxypropyl radical.

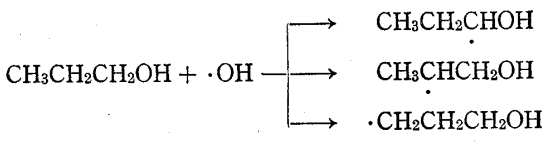

Chart 7

6) W. Burattl, G.P. Gardini, F. Minisci, F. Bertini, R. Galli, and M. Perchinunno, *Tetrahedron*, 27, 3655 (1971).

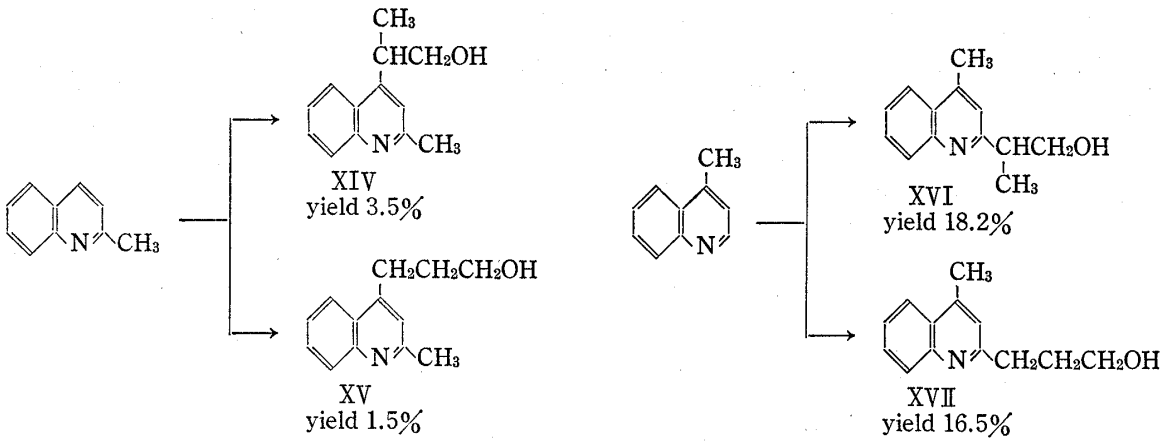

Chart 8

Result and Discussion

The hydroxyalkylation reaction of quinolines with $FeSO_4 \cdot 7H_2O$, 30% H_2O_2 and alcohols in acidic solution proceeds by a radical mechanism. Hydroxyl radical formed from Fe^{2+} and hydrogen peroxide abstracts a hydrogen atom from the alcohols to give hydroxyalkyl radicals, which attack successively C-2 or C-4 position of quinolines. Those products substituted at benzene ring or at C-3 position or at substituted methyl groups were not proved. Therefore, this reaction is nucleophilic to heteroaromatic ring as well as the alkylation of quinolines described by F. Minisci, *et al.*[3,5]

The hydrogen abstraction of the alcohols would be able to occur at the α or β position of ethanol (Chart 5) and the α, β or γ position of *n*-propanol (Chart 7). It has been suggested that the hydrogen abstraction by the hydroxyl radical is similar to that by chlorine radical which occurrs preferentially on the carbon atoms of high electron density.[7] Actually the production ratio of the above hydroxyalkylation reaction is in agreement with the distribution of isomeric products obtained from chlorination of halogenated alkanes.[8]

It is thought that this reaction is very useful to produce synthetic intermediates, since hydroxyl substituent derivatives will be able to get very easily, that is, the reaction proceeds in a short time, and reagents and apparatus are readily available.

Experimental

Reaction of *n*-Hexylmethylketone with Quinoline——To a solution of quinoline (500 mg) in conc. H_2SO_4 (2 ml) and MeOH (50 ml), *n*-hexylmethylketone (1 g) in 30% H_2O_2 (1 ml) at 20—40° dissolved in MeOH (30 ml) with conc. H_2SO_4 (1 ml) was added dropwise with stirring over a period of 20 min at 0°. After completion of the addition, stirring was continued further 10 min. The solution was neutralized with 15% KOH at 0°. The precipitation was filtered through celite, and the filtrate was extracted quickly with $CHCl_3$, after removal of the solvent, gave crude product. TLC ($CHCl_3$–MeOH: 30: 1) revealed 3 components. The product was chromatographed on silica gel using $CHCl_3$–MeOH. I gave colorless needles by recrystallization from Bz, mp 61.5—62°. *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.47; H, 5.66; N, 8.80. Found: C, 74.12, H, 5.57; N, 8.58. NMR (δ in $CDCl_3$): 4.18 (broad s, 1H, $-CH_2-OH$); 4.9 (s, 2H, $-CH_2-$); 7.18—8.12 (m, 6H, aromatic protons). Mass Spectrum *m/e*: 159 (M^+). II have colorless needles from MeOH, mp 92—92.5°. *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.48; H, 5.75; N, 8.72. NMR (δ in $CDCl_3$): 4.88 (broad s, 1H, $-CH_2-OH$); 5.15 (s, 2H, $-CH_2-$); 7.28—8.6 (m, 6H, aromatic protons). Mass Spectrum *m/e*: 159 (M^+). III gave pale yellow needles, mp 136—137°. *Anal.* Calcd. for $C_{11}H_{11}O_2N$: C, 69.84; H, 5.82; N, 7.41. Found: C, 69.10; H, 5.82; N, 7.28. NMR (δ in CMSO-d_6): 4.73 (s, 2H, $-CH_2-$);

7) D.D. Coffman, E.L. Jenner, and R.D. Lipscomb, *J. Am. Chem. Soc.*, **80**, 2864 (1958); W.A. Waters, "Mechanism of Oxidation of Organic Compounds," Methuen & Co., Ltd., London, 1964, pp. 20 —21; G.A. Russell and R.C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).
8) H.C. Brown, A.B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955).

5.00 (s, 2H, $-CH_2-$); 5.4—5.8 (broad s, 2H, $-CH_2O\underline{H}$); 7.35—8.01 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 189 (M^+).

Reaction of Quinoline with 30% H_2O_2 and Fe^{2+} in MeOH——To a solution of quinoline (500 mg) in conc. H_2SO_4 (2 ml) and MeOH (50 ml), $FeSO_4 \cdot 7H_2O$ (1 g) was added. Further, to the solution, 30% H_2O_2 (2 ml) was added dropwise with stirring over a period of 20 min at 0°. This procedure was also carried out with *t*-butyl hydroperoxide instead of H_2O_2. After completion of the addition, stirring was continued 10 min. The solution was neutralized with 15% KOH at 0°. The precipitation was filtered through celite, the filtrate was extracted with $CHCl_3$, after removal of the solvent, gave crude product (400 mg). The product was chromatographed on silica gel, giving I, II, and III (yields: 208 mg, 138 mg, and *ca.* 10 mg respectively).

Reaction of Quinaldine with 30% H_2O_2 and Fe^{2+} in MeOH——The procedure was made as mentioned above. Crude product was obtained, and gave colorless needles (IV) (320 mg) from Bz, mp 189—191°. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 75.48; H, 6.55; N, 7.89. NMR (δ in $CDCl_3$): 2.6 (s, 3H, CH_3); 4.47 (broad s, 1H, $-CH_2-O\underline{H}$); 5.18 (s, 2H, $-CH_2$); 7.35—8.1 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 173 (M^+).

Reaction of Lepidine with 30% H_2O_2 and Fe^{2+} in MeOH——The procedure was made as mentioned above. Crude product was obtained, and gave colorless needles (V) (330 mg) from Bz, mp 139—141°. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 75.96; H, 6.60, N, 8.27. NMR (δ in $CDCl_3$): 2.64 (s, 3H, CH_3); 4.15 (broad s, 1H, $-CH_2-O\underline{H}$); 5.18 (s, 2H, $-CH_2$); 7.2—8.1 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 173 (M^+).

Reaction of Quinoline with 30% H_2O_2 and Fe^{2+} in EtOH——The procedure was made same as MeOH solution. However 20% EtOH in H_2O was used instead of EtOH only, and for neutralization 10% KOH was used. Crude product was separated by chromatography on silica gel, gave four compounds, all of them were recrystallized from Bz, colorless needles (VI), (161 mg), mp 125—126°. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 76.26; H, 6.53; N, 8.14. NMR (δ in $CDCl_3$): 1.57 (d, 3H, CH_3); CH_3

4.4 (broad s, 1H, $-\underset{|}{C}H-O\underline{H}$); 5.6 (q, 1H, $-C\underline{H}-OH$); 7.32—8.62 (m, 6H, aromatic protons). Mass Spectrum $\underset{|}{CH_3}$

m/e: 173 (M^+). Colorless needles (VII) (134 mg), mp 78—80°. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 75.35; H, 6.26; N, 7.55. NMR (δ in $CDCl_3$): 1.55 (d, 3H, CH_3); 4.7 (broad s, 1H, CH_3

$-\underset{|}{C}H-OH$); 5.01 (q, 1H, $-C\underline{H}-OH$); 7.2—8.18 (m, 6H, aromatic protons). Mass Spectrum *m/e*: 173 (M^+). $\underset{|}{CH_3}$

Colorless needles (VIII) (34 mg), mp 99.5—100°. *Anal.* Calcd. for $C_{11}H_{11}ON$: C, 76.30; H, 6.36; N, 8.09. Found: C, 74.87; H, 6.23; N, 8.02. NMR (δ in $CDCl_3$): 3.15 (t, 2H, $-C\underline{H}_2-CH_2-OH$); 3.78 (broad s, 1H, $-CH_2-CH_2-O\underline{H}$); 4.13 (t, 2H, $-CH_2-C\underline{H}_2-OH$); 7.18—8.1 (m, 6H, aromatic protons). Mass Spectrum *m/e*: 173 (M^+). Oily compound (IX) (9 mg) was a small quantity. NMR (δ in $CDCl_3$): 3.5 (broad s, 1H, $-CH_2-CH_2-O\underline{H}$); 3.37 (t, 2H, $-C\underline{H}_2-CH_2-OH$); 4.1 (t, 2H, $-CH_2-C\underline{H}_2-OH$); 7.22—8.6 (m, 6H, aromatic protons).

Reaction of Quinoline with 30% H_2O_2 and Fe^{2+} in EtOH——The procedure was made as mentioned above. Crude product (390 mg) was obtained, and gave two compounds by chromatography on silica gel. Colorless needles (X) (229 mg) from Bz, mp 115—116.5°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 77.01; H, 6.95; N, 7.49. $\underset{|}{CH_3}$

Found: C, 76.54; H, 7.13; N, 7.66. NMR (δ in $CDCl_3$): 1.55 (d, 3H, $-\underset{|}{C}H-OH$); 2.5 (s, 3H, ring-CH_3); 4.3 CH_3 CH_3

(broad s, 1H, $-\underset{|}{C}H-O\underline{H}$); 5.55 (q, 1H, $-C\underline{H}-OH$); 7.3—8.05 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 187 (M^+). Colorless needles (XI) (118 mg), mp 119—119.5°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 77.01; H, 6.95; N, 7.49. Found: C, 76.89; H, 7.14; N, 7.40. NMR (δ in $CDCl_3$): 2.63 (s, 3H, ring-CH_3); 2.8 (broad s, 1H, $-CH_2-CH_2-O\underline{H}$); 3.3 (t, 2H, $-C\underline{H}_2-CH_2-OH$); 4.1 (t, 2H, $-CH_2-C\underline{H}_2-OH$); 7.02—8.05 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 187 (M^+).

Reaction of Lepidine with 30% H_2O_2 and Fe^{2+} in EtOH——The procedure was made as mentioned above. Crude product (400 mg) was obtained, and gave two compounds by chromatography on silica gel using $CHCl_3$–MeOH. Colorless needles (XII) (196 mg) from Bz, mp 75—76°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 77.01; H, CH_3

6.95; N, 7.49. Found: C, 76.15; H, 7.10; N, 7.33. NMR (δ in $CDCl_3$): 1.55 (d, 3H, $-\underset{|}{C}H-OH$); 2.67 (s, 3H, ring-CH_3); 4,73 (s, 1H, broad s, $-\underset{|}{C}H-O\underline{H}$); 4.95 (q, 1H, $-\underset{|}{C}H-O\underline{H}$); 7.15—8.1 (m, 5H, aromatic protons). CH_3 CH_3

Mass Spectrum *m/e*: 187 (M^+). Colorless needles (XIII) (196 mg), mp 97—98°. *Anal.* Calcd. for $C_{12}H_{13}ON$: C, 77.01; H, 6.95; N, 7.49. Found: C, 77.18; H, 7.27; N, 7.51. NMR (δ in $CDCl_3$): 2.61 (s, 3H, ring-CH_3); 3.1 (t, 2H, $-C\underline{H}_2-CH_2OH$); 4.1 (t, 2H, $-CH_2-C\underline{H}_2-OH$); 4.7 (s, 1H, $-CH_2-CH_2-O\underline{H}$); 7.02—8.05 (m, 5H, aromatic protons). Mass Spectrum *m/e*: 187 (M^+).

Reaction of Quinaldine with 30% H_2O_2 and Fe^{2+} in *n*-PrOH——The procedure was made same as EtOH

solution using quinaldine 500 mg. Crude product was separated by chromatography on silica gel, gave two compounds. Recrystallization from Bz, pale yellow plates, identified as β-hydroxypropyl substituent of quinaldine at C–4 (XIV) (25 mg), mp 105°. *Anal.* Calcd. for $C_{13}H_{15}ON$: C 77.61; H, 7.46; N, 6.96. Found: C, 76.67; H, 7.52; N, 6.90. NMR (δ in $CDCl_3$): 1.41 (d, 3H, –CH–C<u>H</u>$_3$); 2.39 (s, 3H, ring–CH_3); 2.95 (m, 1H, –C<u>H</u>–CH_3); 3.95 (broad S, 1H, –CH_2–O<u>H</u>); 4.04 (d, 2H, –C<u>H</u>$_2$–OH); 7.10 (S, 1H, ring proton at C–3); 7.25—8.24 (m, 4H, benzene ring). Mass Spectrum *m/e*: 201 (M^+). Pale yellow plates, identified as γ-hydroxypropyl substituent of quinaldine at C–4 (XV) (11 mg), mp 130°. *Anal.* Calcd. for $C_{13}H_{15}ON$: C, 77.61; H, 7.46; N, 6.96. Found: C, 77.61; H, 8.01; N, 6.60. NMR (δ in $CDCl_3$): 1.90 (m, 2H, –CH_2–C<u>H</u>$_2$–CH_2–OH); 2.49 (s, 3H, ring–CH_3); 2.89 (t, 2H, –C<u>H</u>$_2$–CH_2–CH_2–OH); 3.56 (t, 2H, –C<u>H</u>$_2$–OH); 4.41 (broad s, 1H, –CH_2–O<u>H</u>); 7.00 (s, 1H, ring proton at C–3); 7.10—7.90 (m, 4H, benzene ring). Mass Spectrum *m/e*: 201 (M^+).

Reaction of Lepidine with 30% H_2O_2 and Fe^{2+} in *n*-PrOH——The procedure was made same as above method using lepidine 500 mg. Crude product was separated by chromatography on silica gel, gave two compounds. Recrystallization from Bz, colorless plates, identified as β-hydroxypropyl substituent of lepidine at C–2 (XVI) (128 mg), mp 100°. *Anal.* Calcd. for $C_{13}H_{15}ON$: C, 77.61; H, 7.46; N, 6.96. Found: C, 77.22; H, 7.56; N, 6.98. NMR (δ in $CDCl_3$): 1.39 (d, 3H, –CH–C<u>H</u>$_3$); 2.59 (s, 3H, ring–CH_3); 3.14 (m, 1H, –C<u>H</u>–CH_3); 4.01 (d, 2H, –C<u>H</u>$_2$–OH); 5.00 (broad s, 1H, –CH_2–O<u>H</u>); 7.10 (s, 1H, ring proton at C–3); 7.20—8.10 (m, 4H, benzene ring). Colorless plates, identified as γ-hydroxypropyl substituent of lepidine at C–2 (XVII) (116 mg), mp 46°. *Anal.* Calcd. for $C_{13}H_{15}ON$: C, 77.61; H, 7.46; N, 6.96. Found: C, 77.61; H, 8.39; N, 6.48. NMR (δ in $CDCl_3$): 2.10 (m, 2H, –CH_2–C<u>H</u>$_2$–CH_2–OH); 2.62 (s, 3H, ring–CH_3); 3.10 (t, 2H, –C<u>H</u>$_2$–CH_2–CH_2–OH); 3.80 (t, 2H, –C<u>H</u>$_2$–OH); 5.20 (broad s, 1H, –CH_2–O<u>H</u>); 7.10 (s, 1H, ring proton at C–3); 7.25—8.20 (m, 4H, benzene ring). Mass Spectrum *m/e*: 201 (M^+).

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