Journal of Molecular Catalysis A: Chemical 157 (2000) 65–72

www.elsevier.com/locate/molcata

Selective catalytic oxidation of naphthol to 2-hydroxyl-1,4-naphthoquinone by hydrogen peroxide over metalloporphyrin catalysts

Yan Yan [a,*], Feng-Shou Xiao [a], Guodong Zheng [a], Kaiji Zhen [a], Chiguang Fang [b]

[a] Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China
[b] The Health and Anti-Epidemic Station of Jilin, Changchun 130021, People's Republic of China

Received 6 August 1999; received in revised form 13 October 1999; accepted 14 December 1999

Abstract

The reactions of 1-naphthol and 2-naphthol were catalytically converted into 2-hydroxyl-1,4-naphthoquinone (HNQ, lawsone) in the presence of H_2O_2 over metalloporphyrin catalysts. The catalytic data showed conversion at 57% and single product of lawsone, which were investigated by UV–Vis, IR, NMR, MS, mp determination, and element analysis. Influences of solvents, amounts of NaOH, H_2O_2, and metalloporphyrins, as well as temperature in the catalytic reaction, were carried out, and a proposed catalytic mechanism based on UV–Vis and EPR measurements was discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metalloporphyrin catalysts; 1-Naphthol; 2-Naphthol; 2-Hydroxy-1,4-naphthoquinone (HNQ, lawsone); Selective catalytic oxidation

1. Introduction

Due to their biological enzyme activities, metalloporphyrins can be used as the intermediate of oxygen carrier to biological systems [1] and they are widely used as catalysts for oxidation reaction of olefin and alkane at room temperature. Meunier [2] and Jogensen [3] had reviewed hydroxylation and epoxidation of hydrogen–carbon compounds, many metalloporphyrins were used as catalysts with different oxygen sources, but they seldom reported the hydroxylation of aromatic compounds, because of low catalytic activities as published in papers concerning hydroxylation of phenylalanine [4] and benzene derivatives [5]. On the contrary, using manganese porphyrin catalyst in the presence of imidazole, high conversions of alkane to ketone and alcohol were obtained [6,7].

On the other hand, it is well-known that the oxidation products of naphthol and 2-hydroxyl-1,4-naphthoquinone (HNQ, lawsone) are important chemicals, and their preparation is generally complex [8–10]. It is reported that lawsone is mainly obtained from the natural plants such as Plumbaginaceae, Juglandaceae, and Ebenaceae [11], and it has important biological

---

[*] Corresponding author.

PII: S1381-1169(99)00440-9

activities and is also used as a redox intermediate material in bioelectrochemical fuel-cell [12] and as hair dyestuff [13] and ultraviolet filter in sunscreen formulations [14]. In this study, we report a catalytic conversion from naphthol to HNQ, and its catalytic mechanism is discussed.

2. Experimental

2.1. Reagents

The metalloporphyrin catalysts are prepared from the methods of Adler et al. [15] and Lindsey et al. [16]. Hydrogen peroxide (30% aqueous solution), methanol, and 1- or 2-naphthol are purchased with purity higher than 99.99%, and other reagents all with purity of 99.9% were used without further purification.

2.2. Catalytic reactions

0.50 g of 1-naphthol (or 0.80 g of 2-naphthol), 5 g of NaOH, and 3.2 mg of TPPFeCl (or 3.0 mg of T(*p*-OCH_3)PPFeCl) was dissolved in 30 ml of MeOH at a temperature of 0°C, followed by addition of H_2O_2 (1.8 or 2.0 ml, 30%) at a rate of 1 drop/6 s. The color of the reaction system is changing from straw yellow to bright orange gradually. After 1 h of reaction, an orange product was obtained. In the present form, the product was sodium salt, which was converted into H-form by the addition of HCl solution (1:1, v/v). The product was extracted by ether three times, and recrystallized in the ether solution.

2.3. Instruments

The experimental results were characterized by a Shimadzu UV-240 spectrophotometer (operating conditions: 40 nm/cm, 0.0–1.5 A, wavelength range: 700–350 nm, sample concentration: 0.1–0.0001 mol/dm^3), Nicolet FTIR 5-PC spectrometer (operating conditions: slow scanning speed; resolution power: 4 cm^{-1}; wave number range: 400–4000 cm^{-1}, KBr), VG-Quattro series connection mass spectrometer (operating conditions: laser light source; temperature of ionization source: 200°C; ionization voltage: 70 eV; analytic current: 500 μA; sample feed: DEI (Desorption Electro-Impact), M/z range: 0–300 M/z), UNTY-400 NMR spectrometer (operating condition: 100.57 MHz, standard substance is DMSO), and Shimadzu GC-15A chromatograph with CR 4A chromatpac recorder (operating conditions: SE-54 capillary column; injecting, column, and detecting temperature are 200°C, 150°C, and 200°C, respectively).

2.4. Analysis of product

The GC, ^{13}C and ^{1}H NMR, UV–Vis, IR, MS, melting point measurement and element analysis results show that over TPPFeCl or T(*p*-OCH_3)PPFeCl catalysts, both 1- and 2-naphthol reacting with hydrogen peroxide, form a same and unique product of HNQ [17–21].

Ordinarily, the quantitative analyses of organic substances are performed by means of GC method. 1- or 2-naphthol and their catalytic oxidation product of HNQ were quantitatively analyzed by using the GC method. The GC peaks appeared at $T_r = 0.641$ min, 1.825 min (1.902 min) and 2.068 min are attributed to ether, 1-naphthol (2-naphthol), and HNQ, respectively. At high temperatures such as 50°C, a new peak appeared at 1.144 min, indicating that an over oxidation product of phthalic acid is formed [22]. At a low reaction temperature such as 0°C, HNQ is the only product, which can be determined directly using UV–Vis method.

An alkali aqueous of HNQ, which is present in the form of a sodium salt (HNQNa), has a strong absorption at 452 nm ($\varepsilon = 2.809 \times 10^3$). Meanwhile, other substances in the catalytic system such as NaOH, MeOH, H_2O_2, and 1- or 2-naphthol, have no absorption around 350–700 nm. Therefore, the absorption of HNQNa at 452 nm can be directly used as the characteristic peak to analyze HNQ quantitatively. We also observed that the orange color of HNQNa depends on the amount of NaOH in the aqueous solutions.

An analysis error of HNQ between GC and UV–Vis method is smaller than 2%.

3. Result and discussion

3.1. *Catalytic activities over various catalysts*

A series of TPPM [M = Co(II), Mn(III), Fe(III), Cu(II)] were selected as catalysts for examining their catalytic properties, and the experimental results were listed in Table 1.

Notably, the yield of HNQ is controlled by the variation of catalysts. In case of 2-naphthol, the activities of TPPM were as follows: TPPFeCl $>$ TPPCo $>$ TPPMnCl $>$ TPPCu. The high catalytic activity of TPPFeCl can be accounted for its suitable redox potential of high valence metalloporphyrin [23]. As compared with the corresponding simple metal dichloride, TPPM series catalysts exhibit good catalytic activities.

Table 1
Catalytic activities in naphthol oxidation over various catalysts[a]

Catalysts	Concentration (mol)	HNQ (%)	
		2-naphthol as reactant	1-naphthol as a reactant[b]
TPPCu	3.5×10^{-6}	0.9	
TPPMnCl	3.5×10^{-6}	1.2	
TPPFeCl	3.5×10^{-6}	16.4	
TPPCo	3.5×10^{-6}	4.0	
$CuCl_2$	8×10^{-3}	0.9	
$MnCl_2$	8×10^{-3}	0.6	
$FeCl_2$	8×10^{-3}	0.5	
$CoCl_2$	8×10^{-3}	0.7	
No catalysts	–	0.8	
$T(4\text{-}OCH_3)PPFeCl$	3.5×10^{-6}	20.5	
T(OH)PPFeCl	3.5×10^{-6}	17.3	
TPPFeCl	3.5×10^{-6}	16.4	
TFPPeCl	3.5×10^{-6}	1.0	
$T(NO_2)PPFeCl$	3.5×10^{-6}	0.8	
$T(NO_2)PPCo$	4.5×10^{-6}		–
TPPCo	4.5×10^{-6}		6.7
$TAPPCoI_4$	4.5×10^{-6}		13.1
$T(4\text{-}OCH_3)PPCo$	4.5×10^{-6}		11.9
$T(NO_2)PPFeCl$	4.5×10^{-6}		7.7
TPPFeCl	4.5×10^{-6}		17.5
$TAPPFeI_5$	4.5×10^{-6}		22.1
$T(4\text{-}OCH_3)PPFeCl$	4.5×10^{-6}		21.8

[a] Reaction temperature of 25°C.
[b] Results of GC method.

Moreover, due to conjugation effect [23,24], either electron-donating or electron-withdrawing groups at the *para* position of four phenyls around porphyrin ring at the positions of 5, 10, 15, and 20 strongly influence the catalytic activities of metalloporphyrins. For getting the information on the catalytic activities, various iron porphyrin catalysts were also examined (Table 1). Their catalytic activities were in a sequence of $T(OCH_3)PPFeCl > T(OH)PPFeCl > TPPFeCl > TFPPFeCl > T(NO_2)PPFeCl$. These experimental data indicate that the electron-donating groups, such as methoxyl and hydroxyl, are favorable for obtaining a higher yield of HNQ, while the electron-withdrawing groups, $\cdot F^-$ and $\cdot NO_2^-$, are unfavorable for HNQ formation. These results could probably be explained by both the stability and low redox potential of the intermediate of high valence metalloporphyrin linked with hydroperoxide. The electron-donating groups around the porphyrin ring give electrons to the metal iron at the center of metalloporphyrin by conjugation, making the iron in the metalloporphyrin easy to be oxidized to high valence, which favors the formation of catalytic intermediates. In contrast, the electron-withdrawing groups, by attracting electrons through conjugation [25], increase the redox potential, making it difficult to get high valence metalloporphyrin intermediates, which leads to low yield of HNQ.

Different amounts of $[T(p\text{-}OCH_3)PPFeCl]$ and TPPFeCl were used for investigating the catalytic activities in the oxidation of naphthol, and experimental data are presented in Table 2. Obviously, in the oxidation of 2-naphthol catalyzed by more than 3.0 mg (3.5×10^{-6} mol) of 5,10,15,20-tetra(4-methoxy)phenyl porphyrin iron chloride (T(*p*-OCH3)PPFeCl) at 50°C, a maximum yield (20%) of HNQ was reached. For the oxidation of 1-naphthol catalyzed by

Table 2
The influences of catalyst amounts

2-Naphthol as a reactant													
T(4-OCH_3)PPFeCl, mg	0.4	0.8	1.1	1.2	1.6	2.0	2.5	3.0		4.0	5.0	6.0	10.0
HNQ, %	3.2	3.8	7.0	14.0	15.8	17.6	20.2	20.8		20.2	20.4	19.8	20.5
1-Naphthol as a reactant													
TPPFeCl, mg	0.4	0.8		1.2	1.6	2.0	2.4	3.2	3.6	4.0	4.4		
HNQ, %	2.6	3.2		7.0	12.5	15.9	16.3	17.1	16.8	17.2	16.9		

TPPFeCl, an optimum amount of catalyst TPPFeCl was 3.2 mg (4.5×10^{-6} mol).

3.2. The influence of the hydrogen peroxide amount

Various amounts of hydrogen peroxide were added into reaction mixture, and catalytic data are shown in Fig. 1. The results indicate that 1.8 ml of H_2O_2 is the most suitable amount with the highest catalytic conversion of 1-naphthol.

3.3. The influence of alkali amount

Sodium hydroxide plays an important role in catalytic oxidation of 1- or 2-naphthol to HNQ. Without sodium hydroxide, only an unknown black tar was produced. When more than 1.0 g of NaOH was added into reaction mixture, the oxidation product was obtained. The dependence of HNQ product on the NaOH amount was shown in Fig. 2. The yields of HNQ were enhanced with the increase of the amount of NaOH. These phenomena indicate the difference of reaction mechanism with or without NaOH. Furthermore, the alkali medium can increase reaction rate, reduce and adjust the redox potentials in the catalytic reaction.

3.4. The influence of reaction temperature

Generally, chemical reactions accelerate with temperature increase. The dissociation of hydrogen peroxide to water and oxygen is also consistent with this rule. For examining the temperature dependence, the catalytic oxidation of

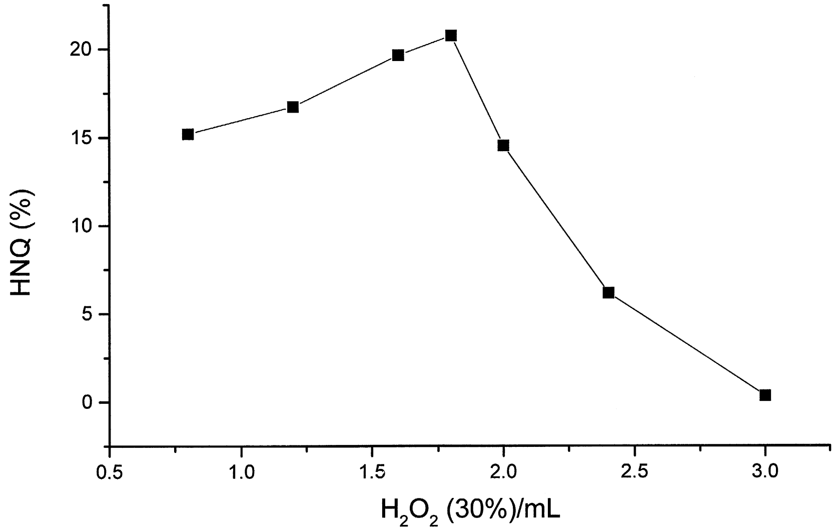


Fig. 1. Influence of H_2O_2 (30%) amount at 50°C.

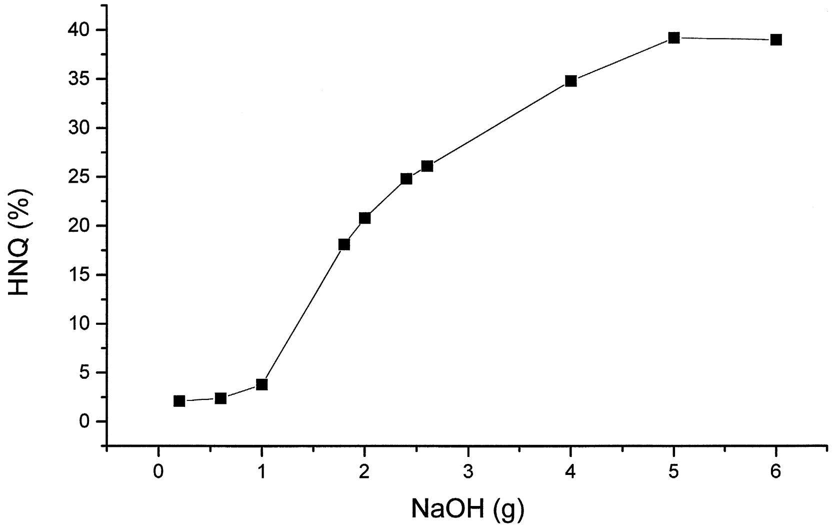


Fig. 2. Influence of NaOH at 25°C.

1- and 2-naphthol was carried out at various temperatures ranging from 0°C to 60°C, and the obtained data are shown in Table 3.

The data listed in Table 3 indicate that both the yield of HNQ and the utilizing ratio of hydrogen peroxide increased with decrease of reaction temperature. These results demonstrated that the catalytic oxidation of 1- and 2-naphthol to HNQ is exothermal, and a low reaction temperature makes the chemical equilibrium shift to the direction of HNQ formation.

The yields of HNQ decreased with temperature increase, and it was worth noting that a linear relationship exists between temperature and the utilizing ratio of hydrogen peroxide. However, the reason for this relationship needs to be further studied.

Table 3
Dependence of temperature on naphthol conversion

Reactant	Catalyst	Temperature (°C)	Conversion (%)
1-Naphthol (0.50 g),	TPPFeCl	0	40.20
30 ml MeOH,	(3.2 mg)	25	24.31
1.8 ml H_2O_2 (30%)		40	19.43
		50	16.68
		60	–
2-Naphthol (0.80 g),	TPPFeCl	0	57.20
30 ml MeOH,	(3.0 mg)	25	38.00
2.0 ml H_2O_2 (30%)		40	27.20
		50	24.06
		60	22.40

3.5. The influence of reacting solvents

The oxidation of 1-naphthol catalyzed by TPPFeCl was carried out in various organic solvents.

The GC analytic results indicate that either MeOH or EtOH is favorable for forming HNQ, and their yields of HNQ are similar (at 50°C, with conversions of 17.1% and 15.5%, respectively). No HNQ is produced when reactions were carried out in other solvents, such as water, non-aqueous solvents soluble in water (CH_3CN and $(CH_3)_2CO$) and insoluble in water[$(CH_3CH_2)_2O$, CH_2Cl_2, $CHCl_3$, C_6H_6, and $C_6H_5CH_3$]. These results indicate that polarity of solvent controls the catalytic mechanism, and either methanol or ethanol is the best one of the solvents for obtaining higher yield of HNQ due to their suitable polarities.

Accordingly, we optimized the catalytic reaction conditions as follows: 30 ml of MeOH, 5.0 g of NaOH, 3.2 mg of TPPFeCl [or 3.0 mg of

T(p-OCH_3)PPFeCl], 0.50 g of 1-naphthol (or 0.8 mg of 2-naphthol), 1.80 ml (or 2.0 ml) of hydrogen peroxide (30%), and temperature at 0°C.

3.6. Reaction mechanism

TPPFeCl can react with H_2O_2 to form a high valence metalloporphyrin complex, forming an active catalytic intermediate for the oxidation of naphthol to HNQ, and the absorption spectra are shown in Fig. 3.

In Fig. 3, the absorption peak of TPPFeCl appeared at 416 nm (Sorret band). By adding H_2O_2 into this solution, an in situ determination revealed a new absorption peak at 465 nm, meanwhile the Sorret band of TPPFeCl weakened gradually with an isobestic point emerging at 425 nm. This is followed by adding 1-naphthol into the reaction system; the absorption at 465 nm assigned to the new species of metalloporphyrin disappeared gradually owing to the formation of HNQ (Fig. 4). These evidences

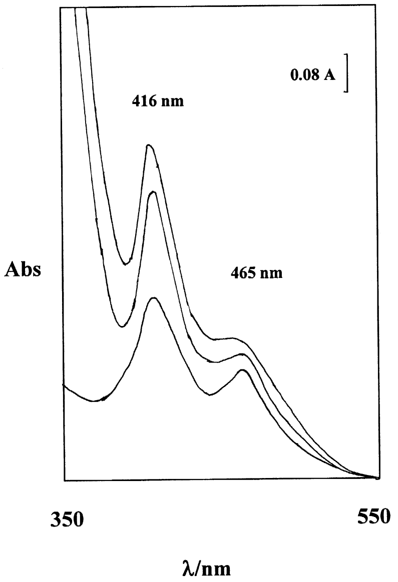


Fig. 4. The varying spectra of high valence ferro-porphyrin complex of TPPFeCl reacting with 1-naphthol.

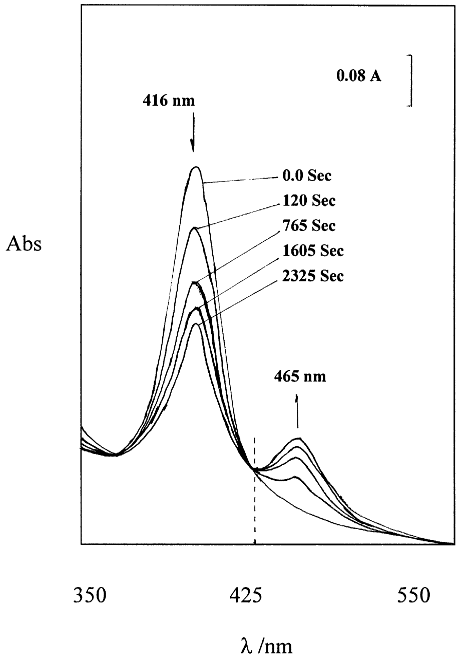


Fig. 3. In situ determination of high valence ferro-porphyrin complex in the solution of 2.7 ml of methanol containing NaOH (0.38 mmol/l), TPPFeCl (5×10^{-3} mmol/l), and H_2O_2 (3.78 mmol/l).

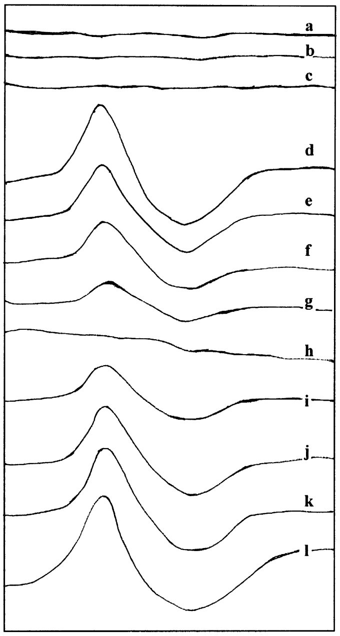
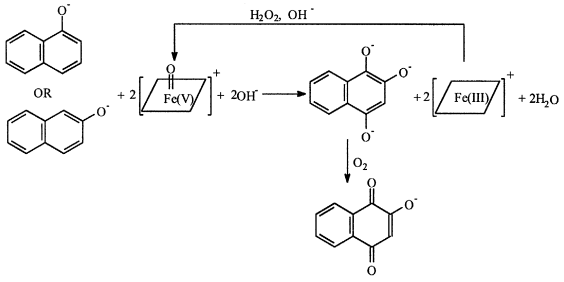


Fig. 5. The EPR spectra of the catalytic oxidation of 1-naphthol (a) H_2O_2 + NaOH + MeOH; (b) 1-naphthol + MeOH; (c) H_2O_2 + NaOH + 1-naphthol + MeOH; (d) TPPFeCl + NaOH + MeOH; (e–h) H_2O_2 + (d), 10, 20, 35, and 45 min; (i–l) 1-naphthol + (h), 5, 10, 15, 25, and 30 min.



Scheme 1.

indicated that the new species of metalloporphyrin appearing at 465 nm is possibly an active catalytic intermediate.

EPR spectra (Fig. 5) of the catalytic oxidation has confirmed this suggestion. We observed that only the catalyst TPPFe(III)Cl possessing paramagnetic property gave a signal appearing at $g = 2.225$ (Fig. 5d), other substances, including MeOH, H_2O_2, 1-naphthol, and HNQ, did not give any paramagnetic signal (Fig. 5a–c). When H_2O_2 was added to the solution of MeOH containing TPPFe(III)Cl, the signal of TPPFe(III)Cl disappeared gradually (Fig. 5e–h). By adding 1-naphthol into this solution, the paramagnetic signal appeared again due to reaction of the high valence coordinated metalloporphyrin reacting with 1-naphthol (see Fig. 5h–l).

The high valence of TPPFeCl is paramagnetic, but it belongs to ‘‘EPR-inert’’ one giving a broad spectrum, and hence, is difficult to be detected [26].

According to Meunier’s review [2], a probable catalytic mechanism of naphthol oxidized to produce HNQ was proposed as shown in Scheme 1.

By the heterolytic mode, the large amount of hydroxyl species in the catalytic system promoted the formation of a high valence iron-oxo porphyrin complex and water molecule. The high valent oxo-metalloporphyrin repeatedly reacted with naphthol to generate 1,2,4-trihydroxyl naphthalene, which could be easily oxidized to HNQ ($E° = 0.218$ V vs. SCE [27]) by oxygen generated from dissociation of hydrogen peroxide.

4. Conclusions

By using hydrogen peroxide as an oxidant, the 1- and 2-naphthol have been catalytically converted into HNQ over metalloporphyrin catalysts. This catalytic process exhibits obvious features in the following: (1) low reaction temperature is convenient to get high selectivity and activity; (2) strong alkali medium is necessary; (3) the suitable solvents are methanol and ethanol; (4) it is easy to operate for getting high purity of HNQ.

Acknowledgements

We are thankful for financial support from The Young Researcher Fund of Science and Technology Committee in Jilin Province, China, and National Natural Science Foundation of China.

References

[1] R.D. Jones, D.A. Summerville, F. Basolo, Chem. Rev. 79 (2) (1979) 139–179.
[2] B. Meunier, Chem. Rev. 92 (1992) 1411–1456.
[3] K.A. Jorgensen, Chem. Rev. 89 (3) (1989) 432–459.
[4] T. Shimidru, T. Iyoda, N. Kanda, J. Chem. Soc., Chem. Commun. (1981) 1206–1207.
[5] M.A. Brook, L. Castle, J.R. Linsay Smith, R. Higgins, K.P. Morris, J. Chem. Soc., Perkin Trans. 2 (1982) 687–692.
[6] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Antiles, M. Fort, D. Mansey, J. Am. Chem. Soc. 110 (1988) 8462–8470.
[7] P. Battioni, J.P. Renaud, J.F. Bartoli, D. Mansuy, J. Chem. Soc., Chem. Commun. (1986) 341–343.
[8] D.M. Martine, C. Sylvio, T. Cecile, H. Michel, J. Bernard, O. Esther, M. Marie-Therese, Tetrahedron 48 (10) (1992) 1869–1882.
[9] L. Synoradzki, A. Sernika-Poluchowicz, H. Hajmowicz, K. Bujnowski, Pol. PL 167, 196 (Cl. C09B13/02), 31 Aug 1995, Appl. 296, 545, 10 Nov 1992, 2 pp. (Pol.).
[10] E. Rutkowaka-Olma, W. Piwonski, J. Zimnicki, Pol. PL 167,265 (Cl. C09B13/02), 31 Aug 1995, Appl. 297,210, 29 Dec 1992, 2 pp. (Pol.).
[11] A. Marston, K. Hostettmann, J. Chromatogr. 295 (1984) 526–529.
[12] K. Tanaka, R. Tamamushi, T. Ogawa, J. Technol. Biotech. 35B (1985) 191–197.

[13] M. Christian, Fr. Demande FR 2, 543, 434 (Cl. A61K7/13), 05, Oct. 1984, Appl. 83/5, 414, 01 Apr 1983, 16 pp.

[14] A.C. Watkinson, K.R. Brian, K.A. Walters, J. Hadgraft, Int. J. Cosmet. Sci. 14 (6) (1992) 265–275.

[15] A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korakoff, J. Org. Chem. 32 (1967) 4761.

[16] J.S. Lindsey, I.C. Schreiman, H.C. Hsu, P.C. Kearney, A.M. Marguerettaz, J. Org. Chem. 52 (1987) 827–836.

[17] R. Morris, J. Nagarkatti, J. Heaton, C. Lane, in: Aldrich Catalog Handbook of Fine Chemical 1996–1997 Aldrich Chemical, 1996, p. 829, H4,680-5, CA: 83-72-7.

[18] Sadtler Research Laboratories, Inc., in: Sadtler Standard Spectra of Nuclear Magnetic Resonance, Editors & Publishers, USA, 1970, p. 19857M.

[19] Y.X. Zhao, in: Spectrum Analysis and Structure Identification of Organic Compounds (Chinese), 1st edn., Press of Univ. Science & Technology of China, Itefei, China, June 1992, pp. 315–325.

[20] C.J. Pouchert, in: The Alderich Library of Infrared Spectra, 3rd edn., Aldrich Chemical, Inc., Milwaukee, Wisconsin, USA, 1981, p. 897A.

[21] R.M. Silverstein, G.C. Bassler, T.C. Morrill, in: Spectrometric Identification of Organic Compounds, 3rd edn., John Wiley & Sons Inc., Canada, 1974, p. 52.

[22] C. Sotirou, W. Lee, R.W. Giese, J. Org. Chem. 55 (1990) 2159–2164.

[23] J.T. Groves, T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 5786–5791.

[24] O. Botolini, B. Meunier, J. Chem. Soc., Chem. Commun. (1983) 1364–1366.

[25] G.D. Zheng, Y. Yan, S. Gao, S.L. Tong, D. Gao, K.J. Zhen, Electrochim. Acta 41 (1) (1996) 177–182.

[26] G. Palmer, in: The Porphyrins, D. Dolphin (Ed.), Phys. Chem., Part B Vol. IV Academic Press, New York, 1979, p. 313.

[27] S.A. Petrova, M.V. Kolodyazhuy, O.S. Ksenzhek, J. Electroanal. Chem. 277 (1990) 189–196.