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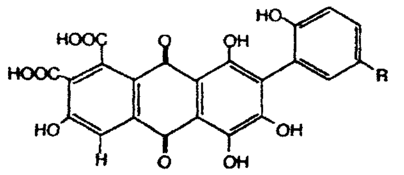
Spectroscopic Investigation of the Interaction of Lac Dyes with Metal Ions

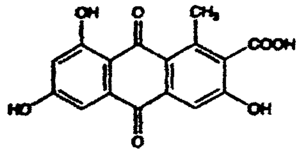
Introduction

Lac, a natural resin of insect origin, is used extensively for natural food additives, cosmetics and as colourant for silk and cotton dyeing. Lac dye, which is the soluble part of stick lac is composed mainly of two major components: laccaic acid A and B [1-7]; the minor components: laccaic acid C, D and E have also been isolated [8,9] (figure1). The UV-Visible spectrum of laccaic acid A had a reported close resemblance to crude laccaic acid in ethanol, with absorption maxima at λ 230, 292, 340, 500 and 530 nm in this solvents; in water, λ_{max} values were at 292 and 490 nm and at 500 in acetone [10]. In the I.R. spectrum of laccaic acid A absorption bands at 1692 and 1715 cm^{-1} were assigned to the carboxylic acid groups and the band at 1626 cm^{-1} to the quinone carbonyl group.

Villagers in northeast Thailand have been using lac dyes extracted from stick lac formed on the Rain tree, *Samanea saman* (Jacq.) Merr. (*Pithecolobium saman*, Mimosaceae) for a long time [11]. In the dyeing process with lac dye on cotton and silk, alum, potassium dichromate, stannous chloride and copper sulfate have been used as mordants to improve colour fastness. While metal ion mordants have also been used by others in dyeing with lac dyes [12-14], there have not been any reports on specific spectroscopic studies involving these components. In an effort to gain a greater understanding of the action of there mordants, a systematic study of the interaction of lac dyes and laccaic acids with some metal ions was undertaken. In particular, metal ion and pH effects on the visible absorption spectra of lac dyes extracted from stick lac from the Rain tree in northeast Thailand, and on laccaic acid A and B, were investigated. The results of this study are reported in this paper.



Laccaic acid A	R=CH2CH2NHCOCH3	M.W. 537
Laccaic acid B	R=CH2CH2OH	M.W. 496
Laccaic acid C	R=CH2CHCOOH NH2	M.W. 539
Laccaic acid E	R=CH2CH2NH2	M.W. 495



Laccaic acid D
M.W. 314

Figure 1. Chemical structures of laccaic acids [6]

Experimetal

2.1 Chemicals

Laccaic acid A [124-04791], laccaic acid B [127-04801], and lac dye [124-04012] were purchased from Wako Company (Osaka, Japan). Analytical grade metal ion salts, $Ni(NO_3)_2 \cdot 6H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ were purchased from Merck Co., Ltd.

2.2 The extraction of lac dye

Stick lac (500.4827 g) from Rain trees in northeast Thailand (Nakhon Ratchasima province) was powdered in a grinding mill and finely ground (18 mesh). The powdered materials was extracted with deionized water (1.5 L) at 60 ^{0}C for 1 hour. The aqueous solution was filtered and then concentrated under reduced pressure (rotary evaporator) to give a crude lac dye extract (38.3287 g), which was then used without further purification. This extract is referred to as Thai lac dye.

2.3 Methods

2.3.1 Measurement of pH and spectra on the visible absorption spectra of lac dyes

The influence of pH on the visible absorption spectra of commercial lac dye from Wako (referred to as Wako) and Thai lac dye was determined using aqueous acetic acid solution in the pH range 2.0-4.5, and sodium hydroxide solution in the pH range 6.0-11.0. The pH values were measured using a pH meter (HACH company, model EC 30). The UV-Visible spectra were recorded using a Cary 1E UV-Vis spectrophotometer. This instrument was used for all UV-Visible absorption spectra in this work.

2.3.2 Metal ion effects on the visible absorption spectra of laccaic acids and lac dyes

2.3.2.1 Effect of metal ion concentration on laccaic acid A and laccaic acid B visible absorption spectra in deionized water

The final concentration of laccaic acid A and B in the measured solutions were 9.31×10^{-5} and 1.05×10^{-4} M respectively. The final concentration of metal ions in the laccaic acid A and B solution were varied as follows : 5.0×10^{-5}, 2.0×10^{-4}, 5.0×10^{-4}, 2.0×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, 3.0×10^{-2}, 3.5×10^{-2}, and 4.0×10^{-2} M. The pH of the final solution in each case was measured using a pH meter (HACH company, model EC 30).

2.3.2.2 Alum solution studies on the visible absorption spectra of Wako lac dye and Thai lac dye

Lac dye solution from Wako and Thai lac dye were freshly prepared prior to each determination. Wako lac dye (0.4978 g) was extracted with deionized water, at 60 ^{0}C, filtered and diluted to 500 mL with deionized in a 500 mL volumetric flask. The Thai lac dye solution was prepared by extracting the dye (1.0026 g) with deionized water at 60 ^{0}C. This solution was filtered and diluted to 1000 mL with deionized water in a 1000 mL volumetric flask. Into two series of eleven 10 mL volumetric flasks were added 2.00 mL of each lac dye solution. To the flasks, was added successively, 0.10, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00 mL of aqueous 5×10^{-2} M $KAl(SO_4)_2 \cdot 12H_2O$. Each flask was diluted to the mark with deionized water and allowed to stand for 30 min. After complex formation was complete, the absorption spectra and the changes in absorbance at 537 nm were recored on Cary 1E UV-Vis spectrophotometer against deionized water as the blank.

The final concentrations of the alum solution in this experiment were as follows: 5.0×10^{-4}, 2.5×10^{-3}, 5.0×10^{-3}, 7.5×10^{-3}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, 2.5×10^{-2}, 3.0×10^{-2}, 3.5×10^{-2}, and 4.0×10^{-2} M.

2.3.2.3 Ni (II) ion solution studies on the visible absorption spectra of Wako lac dye and Thai lac dye

Lac dye solutions were prepared as noted in section 2.3.2.2. Into each series of eleven 10 mL volumetric flask were added 1.00 mL of lac dye solution. To the flasks, added successively, 0.10, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00 ml aqueous 5×10^{-2} M $Ni(NO_3)_2 \cdot 6H_2O$. Each flask was diluted to the mark with deionized water and allowed to stand 30 min. After complex formation was complete, the absorption spectra and the changes in absorbance at 562 nm were recorded on Cary 1E UV-Vis spectrophotometer against deionized water as the blank. The final concentrations of alum solution in this experiment as follow: 5.0×10^{-4}, 2.5×10^{-3}, 5.0×10^{-3}, 7.5×10^{-3}, 1.0×10^{-2}, 1.5×10^{-2}, 2.0×10^{-2}, 2.5×10^{-2}, 3.0×10^{-2}, 3.5×10^{-2}, and 4.0×10^{-2} M.

2.3.3 Determination of the mole ratio for Ni (II) ion – laccaic acid A complex in ethanol

The continuous variation (Job' s) method was used to determine stoichiometry [16]. A series of solutions were prepared by mixing 5×10^{-4} M laccaic acid A and 5×10^{-4}M $Ni(NO_3)_2 \cdot 6H_2O$ and diluting to 5.00 ml with ethanol. The mixtures were allowed to stand for a least 30 min and the changes in absorbance at the λ_{max} were measured using a Cary 1E UV-Vis spectrophotometer.

Results and Discussion

The effect of pH on the longest wavelength absorption band observed of Wako lac dye and Thai lac dye was very similar (figure 2). With both dyes there was substantial bathochromic shift was observed as the pH of the lac dye solution was increased form 2 to 11. This type of behaviour is not uncommon with dye solutions where a lower pH causes a hypsochromic shift in the long wavelength absorption band on dye protonation [15].

Metal ions also caused a bathochromic shift of the long wavelength absorption band of laccaic acids A and B with increasing ion concentrations, for example with alum (figure 3). It was also observed with alum present these was little change in pH, which remained nearly constant about 4.0 over alum concentration ranges of 200×10^{-5} M to 4000×10^{-5} M. It is propable that the bathochromic shift observed with laccaic acid A and B as with the dyes [15], of a lone pair electrons of donor atoms occures as a result of co-ordination by the lone pair electrons on the N or O donor about with the aluminum site, thus stabilizing the excited state relative to the ground state and lead to longer wavelength absorption maxima [15,16].

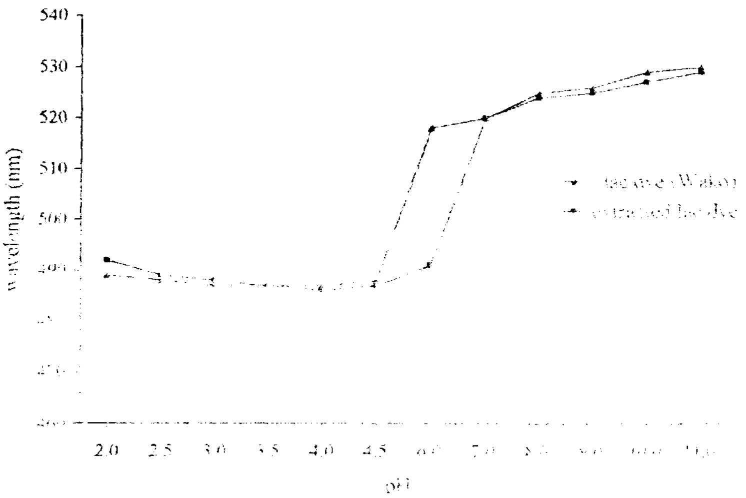


Figure 2. The effect of pH on long wavelength absorption band of Wako lac dye and Thai lac dye

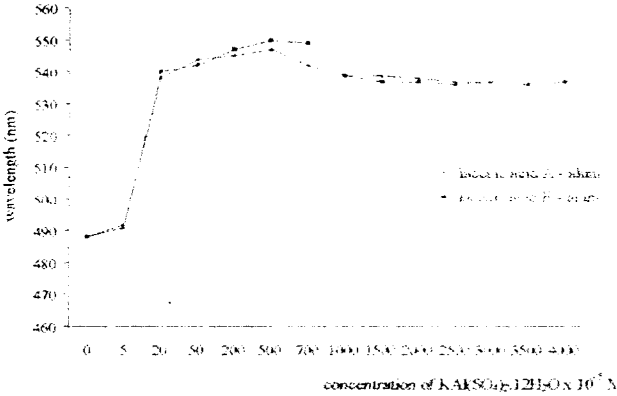


Figure 3. The effect of alum concentrations on a long wavelength absorption band of laccaic acid A and B

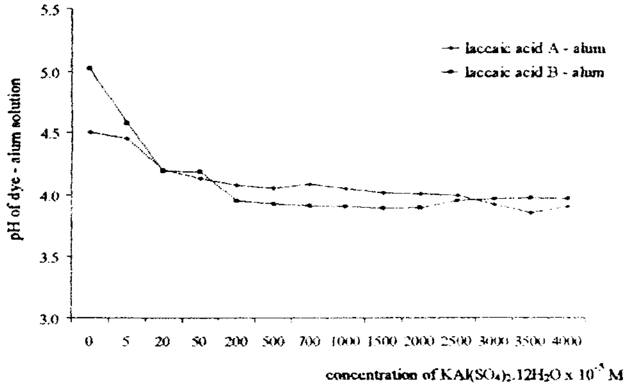


Figure 4. The changes of pH in laccaic acid A – alum solution and laccaic acid B – alum solution

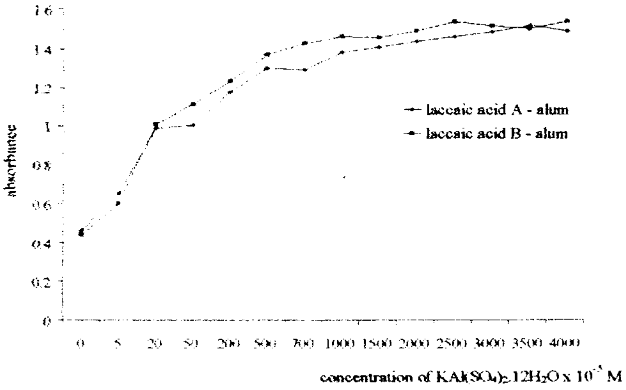


Figure 5. Laccaic acid A and B absorption dependence on concentration of alum at λ = 537 nm

The effect of varying alum concentrations on Thai lac dye and Wako lac dye absorption spectra is presented in Figure 6 and a the similar bathochromic shift of the lac dye band was observes as for the laccaic acids. This result is consistent with these acids being the major components of the dyes. A greater difference between the dyes was observed on monitoring at λ_{max} 537 nm (Figure 8). Furthermore, the pH of the Thai lac dye solution was consistently lower than Wako lac dye at all alum concentrations (Figure 7).

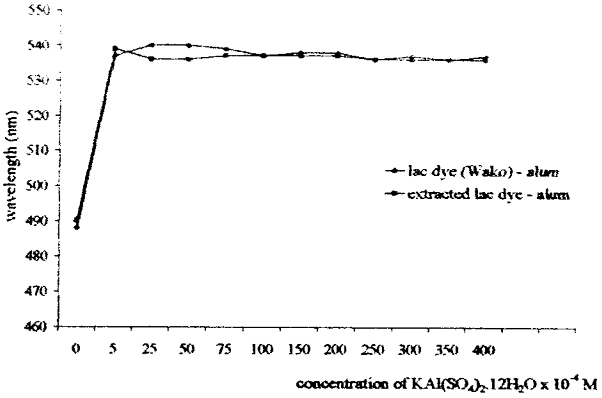


Figure 6. The effect of alum concentrations on the long wavelength absorption band of Wako lac dye and Thai lac dye

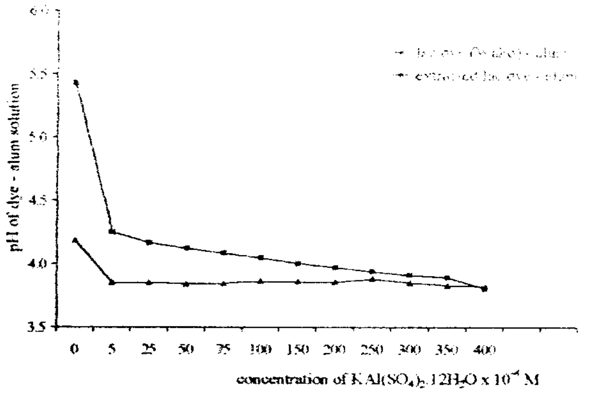


Figure 7. The changes of pH in Wako lac dye) - alum solution and Thai lac dye- alum solution

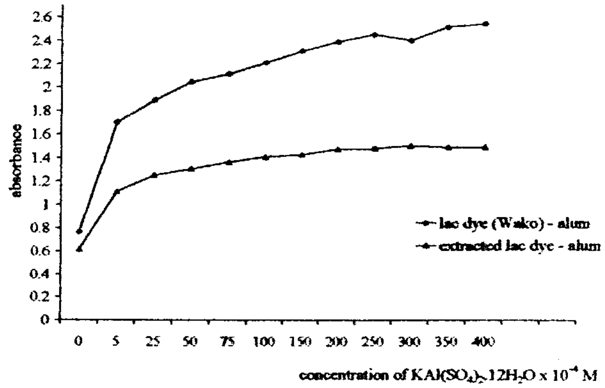


Figure 8. Wako Lac dye and Thai lac dye absorption dependence on concentration of alum at $\lambda = 537$ nm

The study of Ni(II) ion with lac dye and laccaic acid A and B were presented in Figure. 9 and 12 which indicated the larger bathochromic shift of laccaic acid A and B as the metal ion concentration increased. This behavior was also observed in Wako lac dye and Thai lac dye. The higher metal concentration will caused stronger

interaction with dyes stabilizing extracted state and lead to lesser energy in transition from ground state.

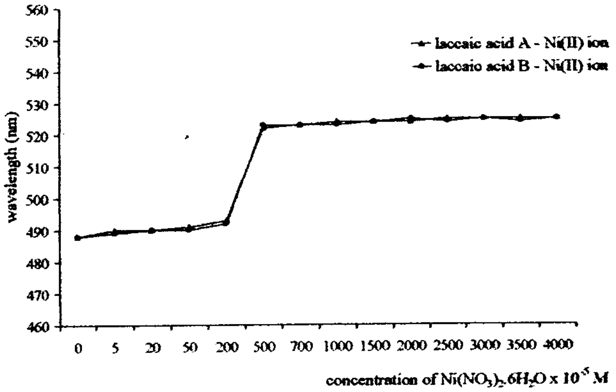


Figure 9. The effect of Ni(II) ions concentrations on the long wavelength absorption band of laccaic acid A and B

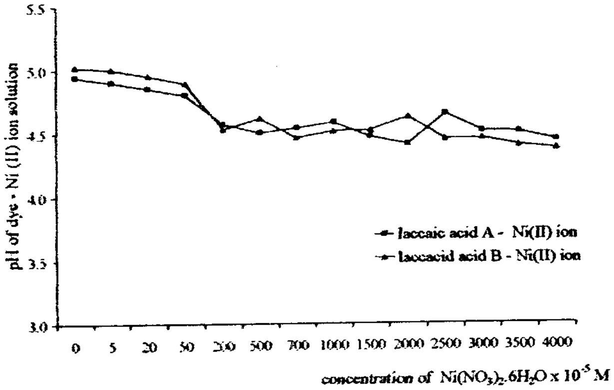


Figure 10. The changes of pH in laccaic acid A – (II) solution and laccaic acid B – Ni(II) solution

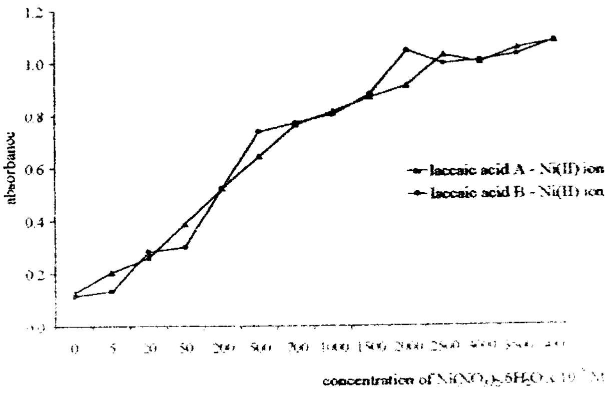


Figure 11. Laccaic acid A and B absorption dependence on concentration of Ni(II) ion at $\lambda = 562$ nm

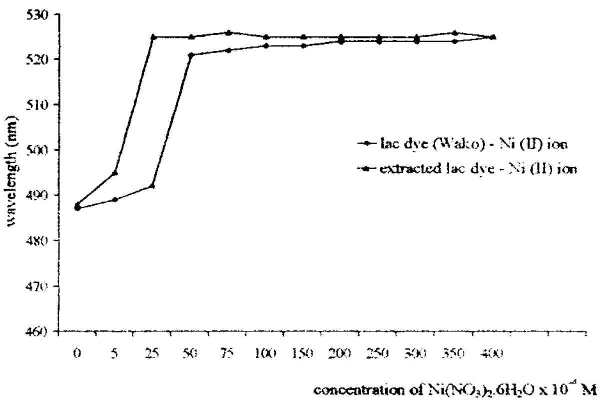


Figure 12. The effect of Ni(II) ion concentrations on the long wavelength absorption band of Wako Lac dye and Thai lac dye

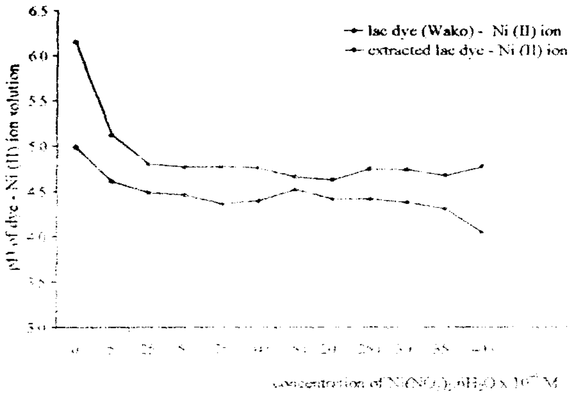


Figure 13. The changes of pH in Wako lac dye – Ni(II)ion solution and Thai lac dye – Ni (II) ion solution

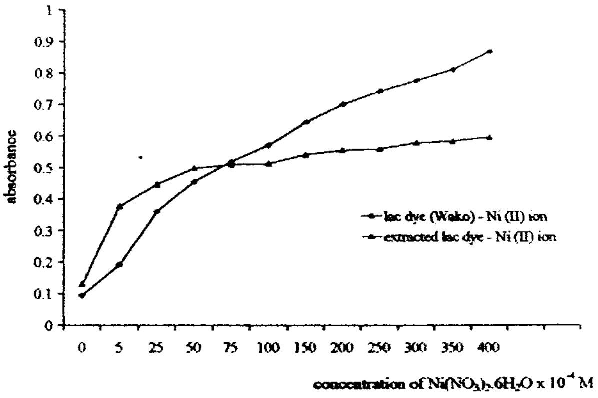


Figure 14. Wako Lac dye and Thai lac dye absorption dependence on concentration of Ni(II) ion at λ = 562 nm

From the results presented in Figure 5, 8 and 14 it was apparent that when the concentration of the metal salts increased within the range of concentrations studied, the intensity of the long wavelength absorption band of laccaic acid A, B and lac dyes (both Wako and Thai lac dye) increased accordingly. The similar pattern of this behavior of laccaic acid A, B and lac dyes again indicated similar chromophores for these substances. These visible absorbance results differ in some respects from the interactions of other dyes with metal ions [12] where increased absorption intensity was observed only up to some higher concentrations.

The effects of Ni(II) on wavelength, pH and absorbance values for the lac dyes and the laccaic acids are given in Figure 9, 10 and 11 respectively for the dyes, as well as Figure 12,13 and 14 for the acids.

The mole ratio of Ni : laccaic acid A as determined by Job method (Figure 15) was 1:1 and it is likely that the rest of the coordination sites of Ni(II) would be occupied by solvent molecules.

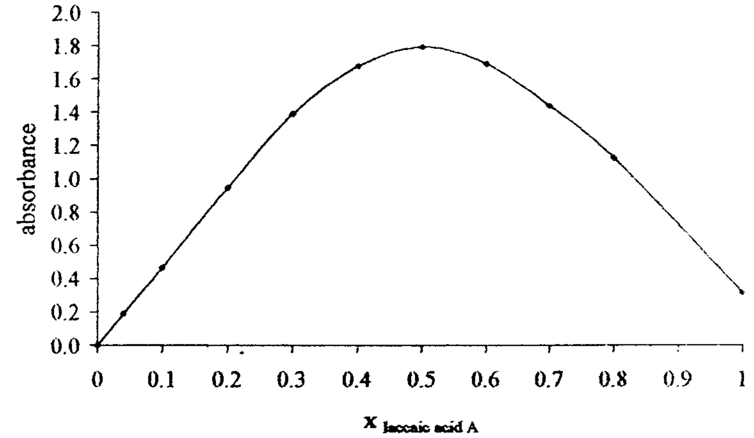


Figure 15. Determination of the mole ratio for Ni (II) ion – laccaic acid A complex in ethanol

Conclusions

When the pH of the lac dye solution was increased from 2 to 11, a substantial bathochromic shift of the lac dye visible absorption band was observed in both Wako and thai lac dyes. Also increasing the metal ion concentration, for both alum and Ni (II) ion, caused a bathochromic shift of the lac dye absorption bands in the visible region in both the laccaic acids and the dyes. The bathochromic shifts in observed are consistent with the lone pair electrons in the donor atoms (N and O in the lac dyes/laccaic acids) participating in co-ordination and stabilizing the excited state relative to the ground state.

Acknowledgement

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References

1. Pandhare, E. D., Rama Rao, A. V., Srinivasan, R., and Venkataraman, K. Lac pigments. **Tetrahedron (Suppl.)** (1996), 8: 229-239.
2. Pandhare, E. D., Rama Rao, A. V., and Shaikh, I. N. Lac pigments : Part III*- Isolation of laccaic acids A & B & the constitution of laccaic acid A. **Indian Journal of Chemistry** (1969), 7: 977-986.
3. Pandhare, E. D., Rama Rao, A. V., Shaikh, I. N., and Venkataraman, K. The constitution of laccaic acid B*. **Tetrahedron Letters** (1996), 26 : 2437-2440.
4. Bhide, N. S., Pandhare, E. D., Rama Rao, A. V., Shaikh, I. N., and Srinivasan, R. Lac pigments: Part IV*- Constitution of laccaic acid B. **Indian Journal of Chemistry** (1969), 7 : 987-995.
5. Burwood, R., Read, G., Schofield, K., and Wright, D. E. The pigments of stick lac . Part II The structure of laccaic acid A_1. **J. Chem. Soc.** (1967), 842-851.
6. Oka, H., *et al.* Separation of lac dye components by high-speed counter-current chromatography. **Journal of Chromatography A** (1998), 813: 71-77.
7. Oka, H., *et al.* Identification of lac dye components by electrospray high performance liquid chromatography - tandem mass spectrometry. **J. Mass Spectrom. Soc. Jpn.** (1998), 46(1): 63-68.
8. Rama Rao, A. V., Shaikh, I. N., and Venkataraman, K. Laccaic acid C, the first natural anthraquinone with an amino acid side chain. **Indian J. Chem.** (1968), 7: 188-189.
9. Mehandale, A. R., Rama Rao, A. V., Shaikh, I. N., and Venkataraman, K. Desoxyerythrolaccin and laccaic acid D*. **Tetrahedron Letters** (1968), 18: 2231-2234.
10. Prasad, N., Prasad, K. M., Ghosh, A. K., and Khanna, B. B. Spectrophotometric studies on laccaic acid. **J. Oil Colour Chem. Assoc.** (1984), 67(5) : 117-118.
11. Moeyes, M. **Natural dyeing in Thailand** (1993), Bangkok : White Lotus.
12. Rastogi, D.; Gulrajani, M.L.; Gupta, P. Application of lac dye on cationized cotton. **Colourange** (2000), 47(4), 36-40.
13. Saxena, S.; Iyer, V.; Shenai, V.A. Dyeing of cotton with lac dye **Colourange** (1997), 44(11), 23-28.
14. Nakamura, T.; Matumoto, K. A studey of lac dyeing with tin mordant. **Kaseigaku Zasshi** (1980), 31(1), 19-23.
15. Beck, M.T. **Chemistry of complex equilibrium** (1970), London: Van Nostran Reinhold Co.
16. Christie, R. M. **Colour chemistry** (2001), United Kingdom: Royal Society of Chemistry.