Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 76 (2008) 207–212

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Ecofriendly sonicator dyeing of cotton with *Rubia cordifolia* Linn. using biomordant

Padma S. Vankar [a,*], Rakhi Shanker [a], Debajit Mahanta [b], S.C. Tiwari [c]

[a] *Facility for Ecological and Analytical Testing, Indian Institute of Technology, Kanpur 208 016, India*

[b] *Arunachal Pradesh State Council for Science and Technology, Vivek-Vihar, Itanagar 791 113, Arunachal Pradesh, India*

[c] *Department of Forestry, Wildlife and Environmental Sciences, Guru Ghasidas University, Bilaspur 495 009, Chhattisgarh, India*

Received 28 March 2006; received in revised form 21 June 2006; accepted 16 August 2006
Available online 11 October 2006

Abstract

Rubia cordifolia (Tamin, local name) produces anthraquinone reddish orange dyes in roots, stem and leaves, which has been used for dyeing textiles since ancient times. Commercial sonicator dyeing with *Rubia* showed that pretreatment with biomordant, *Eurya acuminata* DC var *euprista* Karth. (Theaceae family) [local name, Nausankhee (Apatani tribe), Turku (Nyishi tribe) in 2%] shows very good fastness properties for dyed cotton using dry powder as 10% of the weight of the fabric is optimum. Use of biomordant replaces metal mordants making natural dyeing ecofriendly.

Keywords: *Rubia cordifolia*; Biomordant; *Eurya acuminate*; Commercial dyeing

1. Introduction

A revived interest in the use of natural dyes in textile coloration has been growing and there is pressing need for the availability of natural dye yielding plants. This is a result of the stringent environmental standards imposed by many countries in a response to the toxic and allergic reactions associated with synthetic dyes. Arunachal Pradesh is recognized as one of the hotspot of biodiversity and the indigenous knowledge system particularly associated with extraction and processing of natural dyes from plants. From ancient times some tribes of the state were engaged in natural dyeing. The different tribes mainly the Monpas, Apatanis, Nyishis and Adis, respectively, of West Kameng, Tawang, Lower Subansiri and East and West Siang districts of Arunachal Pradesh have been engaged in extraction, processing and preparation of dyes using barks, leaves, fruits and roots of the plants from time immemorial. Apatani tribe who have traditionally settled in seven villages in the Ziro valley of Lower Subansiri district of Arunachal Pradesh, use *Rubia cordifolia* extensively [11].

In this paper we have shown that the natural dye-stuffs of plant origins, grown in Arunachal Pradesh, used as indigenous systems can be developed scientifically and can be substituted for the chemical dyes. These indigenous dyes can be produced in large scale and could be prepared commercially and economically. The practice of indigenous systems for preparing dye-stuffs and the processes of dyeing has been developed using modern technological methods.

These natural dyes derived from the plants of Arunachal Pradesh are found to be of high quality, and thus these plants need to be protected for conservation of biodiversity of the flora of North Eastern region. People can produce these dyes in large scale, commercially, by establishing processing units and can replace the use of chemical dyes which are hazardous from the environmental point of view. As Arunachal Pradesh amidst its rich diverse flora harbors many dye yielding plant species in abundance, we carried out a study to

* Corresponding author. Tel.: +91 512 2597844; fax: +91 512 2597436.
E-mail address: psv@iitk.ac.in (P.S. Vankar).

0143-7208/$ - see front matter
doi:10.1016/j.dyepig.2006.08.023

revive and restore the traditional dyeing practices using the traditional biomordant – *Eurya acuminata* (Nausankhee, Turku) in place of metal mordant. This work was designed with an aim to focus on the innovative methods of dye extraction, mordant study and by means of application of modern technology to sharpen the skills of tribal traditional dyers of Arunachal Pradesh. Although a lot of work has been done on natural dyeing with rubia [1–6], our approach is towards development of ecofriendly natural dyeing using biomordant and ultrasound energy.

Name: Tamin (*Rubia cordifolia Linn.*)
Habitat: Hispid Climber, Creeper
Color Extracted: Reddish orange.
Parts used: The whole plant mainly roots, Stem and leaves

Name: Nausankhee (*Eurya acuminata*)
Habitat: Shrub
Used as biomordant with Rubia

2. Experimental

2.1. Materials

The cotton fabric used was mill scoured and bleached cotton fabric of 160 g/m^2 was further treated with a solution containing 5 g/l of sodium carbonate and 3 g/l of non-ionic detergent (Labolene) under the boiling condition for 4 h, after which time it was thoroughly rinsed and air dried at room temperature.

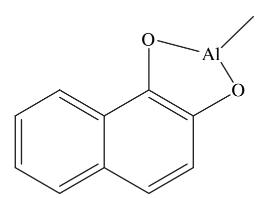
Dye used *Rubia cordifolia* Linn.

Biomordant used *E. acuminata* DC var *euprista* Karth. (Nausankhee, Turku, belonging to the Theaceae family).

All other chemicals used were laboratory grade reagents.

2.1.1. Characterization of the color components

R. cordifolia contains mainly alizarin as well as purpurin, pseudo-purpurin, munjistin, and rubiadin, because anthraquinone dyes have poor affinity for cotton fibers, their fastness was often enhanced by mordants. Mordants, which are metal salts that form an insoluble complex with dye molecules, including potassium aluminum sulfate (alum) and ferrous sulfate. The nature of the mordant–dye complex is well documented in the literature as shown in Structure **I**.

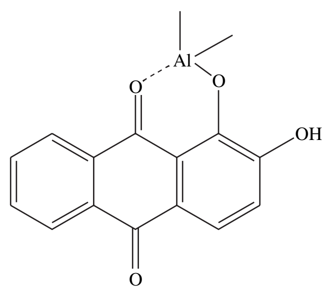


Structure-I

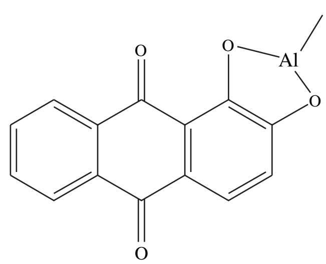
The alizarin molecules are capable of forming six-member chelate rings with aluminum ions. Colored lakes formed by the metal ions and dye molecules resist extraction by water and organic solvents, which readily strip similarly structured acid dyes. The sheer size of the complex may account for some of its insolubility. It is also likely that the large complexes are physically trapped within the fiber. The ortho-dihydroxy structure in the hydroxyl-anthraquinone molecules could greatly enhance the chelation. A similar behavior is envisaged for biomordant as well.

Only a small fraction of plant species takes up high levels of aluminum (Al) in their above-ground tissues. Generally, plants are classified as accumulators if they accumulate at least 1000 mg kg^{-1} in their leaves [7–9]. Our knowledge of Al accumulators is built mainly on the substantial contributions made by Chenery starting some 50 years ago. The extract of *E. acuminata* DC var *euprista* Karth. leaves is found to contain substantial amount of Al. Chenery and Sporne [10] concluded that Al accumulation is a primitive character mainly characteristic of woody and tropical representatives of fairly advanced families (e.g. Anisophylleaceae, Hydrangeaceae, Melastomataceae, Rubiaceae, Theaceae, Symplocaceae, Vochysiaceae).

Atomic absorption spectroscopic analysis (GBC Avanta, model-Sigma, Australia) of *E. acuminata* leaves extract showed 11.767 mg/l of Al content. The high Al content has been suggested to provide useful chelation to the anthraquinone moiety of *R. cordifolia* at two different sites, one with carbonyl and hydroxyl and the other with di-hydroxyl moieties as shown in Structures **IIa**,**b**.



Structure-IIa



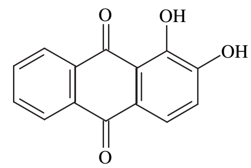
Structure-IIb

The hexane extract from *R. cordifolia* gave one fraction, **III**, while the chloroform extract gave five fractions – **IV**, **V**, **VI**, **VII** and **VIII**. Each of the color components isolated from stems of *R. cordifolia*, showed a characteristic visible spectra for an anthraquinone. As the structures of **III–VII** show vicinal hydroxy as well as carbonyl groups present in most of them, Al in the biomordant shows good chelation.

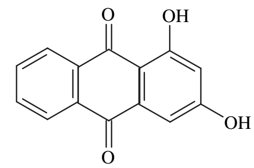
Compound **III** was obtained as red-purple crystals, m.p. 277–278 °C. Vis λ_{max} (MeOH) (nm): 431, UV λ_{max} (MeOH) (nm): 245, 260, 271, 331; IR ν_{max} (KBr) (cm^{-1}): 3338 (–OH), 1662, 1628 (–C=O), 1580 (aromatic –C=C–); MS: *m/z* 240 (M^+). The compound was identified as alizarin based on literature values.

Compound **IV** was obtained as reddish crystals, m.p. 270–273 °C. Vis λ_{max} (MeOH) (nm): 425; IR ν_{max} (KBr) (cm^{-1}): 3310 (–OH), 1660, 1625 (–C=O), 1580 (aromatic –C=C–); MS: *m/z* 240 (M^+). The compound was identified as 1,3-dihydroxy anthraquinone based on literature values.

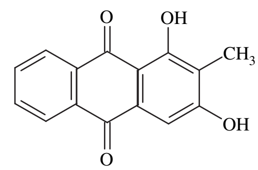
Compound **V** was obtained as yellow needles; m.p. 243–244 °C. Vis λ_{max} (MeOH) (nm): 407, UV λ_{max} (MeOH) (nm): 245, 275; IR ν_{max} (KBr) (cm^{-1}): 3400 (–OH), 1660, 1620 (–C=O), 1585, 1555 (aromatic –C=C–); MS: *m/z* 254 (M^+). The compound was identified as rubiadin based on literature values.



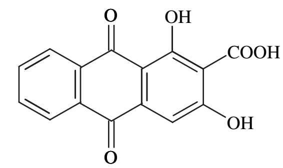
(III)



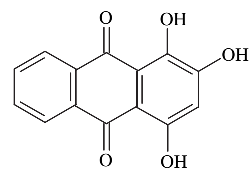
(IV)



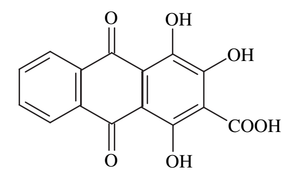
(V)



(VI)



(VII)



(VIII)

Compound **VI** was obtained as yellow needles; m.p. 225–226 °C. Vis λ_{max} (MeOH) (nm): 415, UV λ_{max} (MeOH) (nm): 245, 285; IR ν_{max} (KBr) (cm^{-1}): 3400 (–OH), 1675, 1650, 1630 (–C=O), 1594, 1585 (aromatic C=C); MS: *m/z* 284 (M^+). The compound was identified as munjistin based on literature values.

Compound **VII** was obtained as reddish needles; m.p. 253–256 °C. Vis λ_{max} (MeOH) (nm): 485, 512; IR ν_{max} (KBr) (cm^{-1}): 3400 (–OH), 1675, 1650, 1630 (–C=O), 1594, 1585 (aromatic C=C); MS: *m/z* 256 (M^+). The compound was identified as purpurin (1,2,4-trihydroxyanthraquinone) based on literature values.

Compound **VIII** was obtained as red brown plate like crystals; m.p. 229–230 °C. Vis λ_{max} (MeOH) (nm): 415, UV λ_{max} (MeOH) (nm): 245, 285; IR ν_{max} (KBr) (cm^{-1}): 3500 (–OH), 1675, 1650, 1630 (–C=O), 1594, 1585 (aromatic C=C); MS: *m/z* 300 (M^+). The compound was identified as pseudopurpurin based on literature values.

2.2. Dyeing

Dyeing was carried out in two ways:

(i) Two-step dyeing (in the ratio of 2% biomordant, owf) was used as pretreatment and then dyeing with *Rubia* extract (10%, owf) was carried out for 3 h at temperature 30–40 °C. The dyed fabrics were rinsed thoroughly in tap water and allowed to dry in open air (Fig. 1).

(ii) One-step dyeing (in the ratio of 10% *Rubia* extract and 2% biomordants) was mixed thoroughly in one bath and the moist fabric was dipped for 3 h at temperature 30–40 °C. The dyed fabrics were rinsed thoroughly in tap water and allowed to dry in open air (Fig. 2).

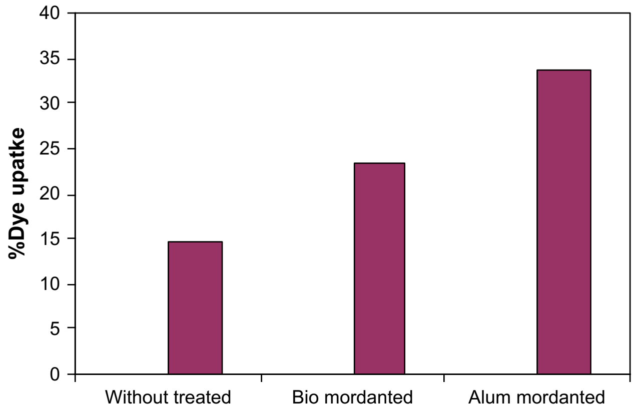


Fig. 1. Dye uptake by different pre-mordanting methods.

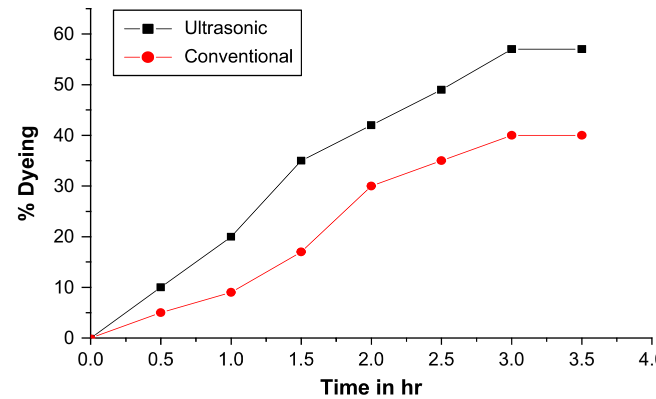


Fig. 3. Ultrasonic dyeing with *Rubia* with *E. acuminata* DC var *euprista* Karth. as biomordant.

2.3. Methods

2.3.1. Effect of ultrasound

Generally, the sonochemical activity arises mainly from acoustic cavitation in liquid media. The acoustic cavitation occurring near a solid surface will generate microjets; the microjet effect facilitates the liquid to move with a higher velocity resulting in increased diffusion of solute inside the pores of the fabric. In the case of sonication, localized temperature raises and swelling effects due to ultrasound may also improve the diffusion.

The stable cavitation bubbles oscillate which is responsible for the enhanced molecular motion and stirring effect of ultrasound. In case of cotton dyeing, the effects produced due to stable cavitation may be realized at the interface of leather and dye solution. Dye uptake was studied during the course of the dyeing process for a total dyeing time of 3 h with and without ultrasound. About 58% exhaustion of dye (*Rubia*) can be achieved in 3 h dyeing time using ultrasound while compared to only 40%, in the absence of ultrasound in stationary condition for this natural dye was observed as shown in Fig. 3.

2.4. Measurements and analysis

2.4.1. Color measurements

The relative color strength of dyed fabrics expressed as *K*/*S* was measured by the light reflectance technique using the Kubelka–Munk equation. The reflectance of dyed fabrics was measured on a Premier Colorscan.

$$K/S = (1 - R)2/2R$$

where *R* is the decimal fraction of the reflectance of dyed fabric. *K*/*S* was measured for one-step dyeing process as well as for two-step process (Figs. 4 and 5).

The CIELab values were ascertained with and without biomordant for *R. cordifolia* (Table 1).

2.4.2. Effect of mordanting conditions

It was observed that the pre-mordanting technique with biomordant and metal mordants imparted better fastness properties to the cotton fabric compared simultaneous mordanting techniques. Therefore, pre-mordanting technique was applied in our case; the dyed fibers were mordanted with biomordant, $CuSO_4$, $FeSO_4$ and Alum.

The mordant activity of the four cases followed the sequences.

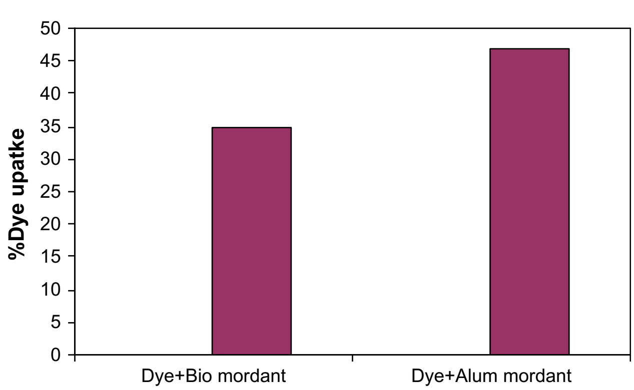


Fig. 2. Dye uptake by different simultaneous mordanting methods.

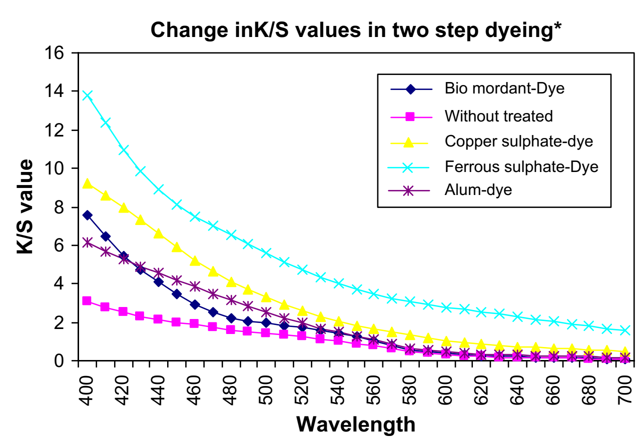


Fig. 4. Pre-mordanting with metal and biomordant.

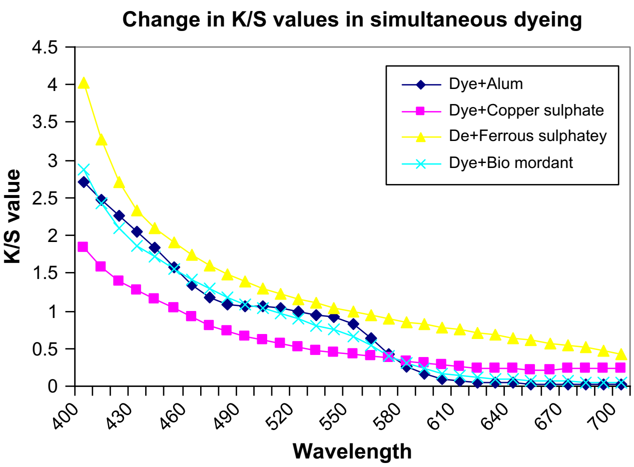


Fig. 5. Simultaneous mordanting.

Fe → Cu → Al → biomordant in cotton for *R. cordifolia*, the absorption of color by cotton fabric was good for both metal mordants and biomordant. This might be due to the maximum absorption and easy formation of metal-complexes with the fabric.

2.5. Dyeing and fastness tests

Dried stems, leaves plus roots of *Rubia* ground into fine powder were used to dye cotton, using a sonicator dyeing apparatus (Julabo, Germany). The fabric to be colored was previously washed with mild soap solution (Labolene) at 40 °C for 30 min. Then they were mordanted with 2% (weight/commercial weight) of *E. acuminata* DC var *euprista* Karth. at 40 °C for 60 min. The ground powder (30% weight/commercial weight) was mixed with water (powder–water = 1:5), stirred for 60 min at a temperature of 40 °C and then filtered. This extract was used for filling the dyeing system, in which the substrate was placed. The dyeing process took place at 30 °C for 60 min and at atmospheric pressure. Finishing consisted of several rinsing with water.

2.5.1. Fastness testing

The dyed samples were tested according to Indian standard methods. The specific tests were color fastness for light, **IS-2454-85** by a xenotest to measure resistance to fading using a laboratory apparatus (Xenotester – Alpha, Germany) under the following conditions: light-exposure system featuring an air-cooled Xenon arc discharge lamp simulating outdoor global radiation; irradiation on sample level λ 300–400 and 400–700 nm; test chamber temperature: 25 °C; and relative humidity 65%. A light fastness rating from 1 (severely fading) to 8 (fast) was made by comparing the resistance to fading of each sample to that of eight different blue tones, color fastness to rubbing, **IS-766-88**, color fastness to washing, **IS-687-79**, wash fastness rating from 1 (fading) to 5 (excellent fastness) was used, color fastness to perspiration, **IS-971-83** (Table 2).

Table 2
Fastness properties of dyed cotton fabrics under conventional heating and ultrasonic conditions of biomordant and *R. cordifolia*

Dyeing methods	Wash–perspiration–rubbing–light					
	WF	Per_{acidic}	Per_{basic}	Rub_{dry}	Rub_{wet}	LF
Conventional	4	4	3–4	3–4	3–4	4
Ultrasonic	5	4–5	4–5	4	4	4–5

WF, wash fastness; LF, light fastness. Light fastness accordingly: 1, severely fading; 2, fading; 3, fairly fading; 4, quite good fastness; 5, good fastness; 6, very good fastness; 7, excellent fastness; 8, exceptional fastness. Wash fastness accordingly: 1, fading; 2, fairly fading; 3, medium fastness; 4, good fastness; 5, excellent fastness.

2.5.2. Dye exhaustion

The dye exhaustion percentage (%*E*) was calculated according to the following equation:

$$\%E = [A_0 - A_r/A_0]100$$

where A_0 and A_r are, respectively, the absorbance of the dyebath before and after dyeing at λ_{max} of the dye used. The absorbance was measured on a Perkin Elmer Lambda 40 UV/vis spectrophotometer at λ_{max} of the dye used.

3. Results and discussion

The one-stage and the two-stage dyeing of cotton fabric with and without biomordant by the natural dye *R. cordifolia*, show that two-stage process with biomordant showed very good results. The dye uptake in case of two-step dyeing is 14.8%, 23.5% and 33.5% for without mordant, biomordant and alum mordant. In the case of one-step dyeing, the dye uptake is 38% and 47% for dye–biomordant and dye–alum simultaneous mordanting methods. The effectiveness of biomordant–*R. cordifolia* in better dye uptake may appear to

Table 1
Effect of *E. acuminata* (Nausankhee) biomordant and metal mordant (alum) on the colorimetric data obtained for *Rubia cordifolia* dye

Experiment	*L**	*a**	*b**	C	H
Without mordant	59.851	15.246	23.401	27.929	56.892
With biomordant	59.915	19.560	32.493	37.926	58.929
With alum mordant	64.372	17.043	34.088	38.111	63.411
With $CuSO_4$ mordant	63.685	7.069	31.338	32.125	77.257
With $FeSO_4$ mordant	59.613	4.700	21.879	22.378	77.845
With biomordant + dye	68.130	18.129	27.387	32.844	56.474
With alum mordant + dye	61.848	20.774	26.726	33.850	52.121

be slightly less as compared to metal mordanting, however, the reduction in effluent pollution as well as improved fastness properties outweighs its benefit as observed during the course of this study. The pH of *R. cordifolia* extract is 5.7 whereas the pH of *E. acuminata* DC var *euprista* Karth. (Nausankhee) extract is 7.67. Thus it can be said that the two extracts are complimentary to each other and that causes the better dye adherence. The suitability of specific biomordant *E. acuminata* (Nausankhee) for this particular natural dye was evaluated on the basis of the traditional information collected from the tribal people.

4. Conclusion

R. cordifolia was found to have good agronomic potential as a dye crop in Arunachal Pradesh. Biomordant – *E. acuminata* DC var *euprista* Karth. (Nausankhee) when used in conjunction with *R. cordifolia* was found to enhance the dyeability due to the Al contents present in the leaves. Enhancement of dye uptake was 23.5% with biomordant, 33.5% with alum and 14.8% without any mordant. Use of biomordant not only enhances the fastness properties but also gives good colorimetric data on dyeing. Even the fastness properties in this case show good results. The two-step biomordant–dye, developed for the ease of industrial application offers an ecofriendly process which should be popularized as an alternate method to the metal mordant–dye method.

Acknowledgement

The authors express their sincere thanks to Department of Biotechnology, Government of India, New Delhi for financial support.

Appendix A. Supplementary information

Supplementary information for this manuscript can be downloaded at doi: 10.1016/j.dyepig.2006.08.023.

References

[1] Angelini LC, Pistelli L, Belloni P, Bertoli A, Panconesi S. Industrial Crops and Products 1997;6:303.
[2] Asada H, Nakamura R, Torimoto N, Takaoka A. Kagaku to Kyoiku 1993;41(5):339.
[3] Sasahi K. Sen'i Kako 1971;23(10):721–9.
[4] Endo M, Sakata K, Katayama A. Nippon Sanshigaku Zasshi 1997;66(2):107–12.
[5] Singh S, Jahan S, Gupta KC. Colourage 1993;40(8):33–6.
[6] Bhuyan R, Saikia CN. Bioresource Technology 2005;96(3):363.
[7] Robinson WO, Edgington G. Soil Science 1945;60:15–28.
[8] Jansen S, Watanabe T, Smets E. Annals of Botany 2002;90:53–64.
[9] Chenery EM. Annals of Botany 1948;12:121.
[10] Chenery EM, Sporne KR. New Phytologist 1976;76:551.
[11] Pal GD. Journal of Economic and Taxonomic Botany, Addl. Series 1992;10:198–203.