*Acta Bot. Gallica, 2007, **154** (1), 43-52.*

Combined dyeing and antioxidative properties of some plant by-products

by Pauline Guinot([1,2]), Ingrid Benonge([1]), Géraldine Nicolet([1]), Annick Gargadennec([1]), Claude Andary([1*]) and Sylvie Rapior([1])

*(1) Laboratoire de Botanique, Mycologie et Phytochimie, UMR CEFE 5175, Faculté de Pharmacie, Université Montpellier 1, 15 avenue Charles Flahault, BP 14491, F-34093 Montpellier Cedex 5; *correspondence: candary@ww3.pharma.univ-montp1.fr*

(2) Pôle de compétence « Productions végétales alternatives », Faculté de Pharmacie, BP 83, F-59006 Lille Cedex

arrivé le 6 février 2006, accepté le 11 avril 2006

Abstract.- Aqueous extracts of plant by-products (carrot, onion, black carrot, sage, spinach and thyme) were investigated for dyeing capacity on fibres and for both colorant and antioxidant potential using colorimetric and chromatographic tools, and FTC assay, respectively. Regarding fibres, classical correlations between measured colours and phytochemical patterns of dyeing extracts were verified. Light fastness of onion, sage and thyme samples, evaluated following a normalised test, was very promising considering industrial restrictions; moreover, antioxidative activities of those aqueous plant extracts were very attractive when compared to the three others and to α-tocopherol used as standard. Our results were of great interest underlining new complementary valorisations for plant by-products, becoming in this way new and inexpensive natural resources for various industries.

Key words : by-products - industrial valorisations - dyes - antioxidants - polyphenols - flavonoids.

Résumé.- Les extraits aqueux de sous-produits végétaux (carotte, carotte noire, épinard, oignon, sauge et thym) ont été évalués pour leurs pouvoirs tinctoriaux sur fibres ainsi que pour leurs propriétés colorantes et antioxydantes par le biais d'outils colorimétrique et chromatographiques et à l'aide du test FTC. Les corrélations classiques entre composition phytochimique de l'extrait utilisé pour la teinture et couleurs résultantes sur fibres ont pu être vérifiées. La stabilité lumière d'échantillons obtenus à partir d'oignon, de sauge et de thym s'est avérée prometteuse au regard des restrictions industrielles. L'activité antioxydante des extraits aqueux de ces mêmes plantes s'est révélée très intéressante par rapport à celle des autres extraits et du standard, l'α-tocophérol. L'ensemble de ces résultats a ainsi permis de proposer de nouvelles voies de valorisations complémentaires dans divers secteurs industriels pour ce type de sous-produits devenant alors de nouvelles matières premières végétales peu onéreuses.

Mots clés : : sous-produits - valorisations industrielles - colorants - antioxydants - polyphénols - flavonoïdes.

I. INTRODUCTION

Insects, minerals, fungi and/or plants are well-known for centuries as raw colouring resources (Hofenk de Graaf, 2004; Rice & Beebee, 1980). Dyeing plants, *i.e. Isatis tinctoria, Reseda luteola, Carthamus tinctorius* and *Rubia tinctorum*, were extensively used for textile industries until 1860, when organic chemistry provided synthetic dyes (Andary *et al.*, 1996; Gilbert & Cooke, 2001; Orska-Gawrys *et al.*, 2003). Regarding to the environmental and health impact of chemicals, natural resources were screened at the end of the 20th century for biological active components (Larson, 1988; Nick *et al.*, 1995; Schmourlo *et al.*, 2005; Katalinic *et al.*, 2006) and natural products as dyes (Angelini, 1999; Jansen & Cardon, 2005; Guinot *et al.*, 2006; *www.spindigo.net*). Dyeing plants traditionally provided from wild resources (Cardon, 2003) or agricultural crops (Angelini *et al.*, 1997, 2003). By-products resulting from plant industrial transformations can also be of a great interest for their dyeing properties (Schieber *et al.*, 2001; Berjoin *et al.*, 2004). Molecular groups generally involved in natural colours as polyphenols, *i.e.* flavonoids, phenolic acid derivatives, anthocyanins and tannins, were reported in plant kingdom (Bruneton, 1999; Macheix *et al.*, 2005). Moreover, polyphenol compounds were investigated for antioxidant activity (Moure *et al.*, 2001; Llorach *et al.*, 2002, Peyrat-Maillard *et al.*, 2003). Nowadays, uses of natural products in various industries are relevant because of their innovative and environmental features in terms of health impact or industrial water pollution (Anliker *et al.*, 1988).

Consequently, we investigated plant by-products (*e.g.* distillery wastes, peeling and sorting wastes) for dyeing capacity and antioxidant activity. In order to bring preliminary data on those alternative natural products, representative by-products from distillery and agroalimentary industry were investigated for both properties in order to highlight two fields of valorisation: i) dye application on fibres for textile industry and ii) colouring and antioxidant properties of plant liquid extract for food, cosmetic and/or pharmaceutical industries.

Firstly, the dyeing property of plant extracts were carried out on two fibre models (cellulosic structure, hemp; protein-based structure, wool) and resulting colours were characterized by colorimetry. To consider industrial restrictions, light stability of coloured fibres was evaluated by ISO normalised test. Secondly, plant extracts were directly analysed by colorimetry and assessed for antioxidative activity by ferric thiocyanate assay (FTC assay): those experiments were realised to point out plants which present both properties in order to find the most promising species for industrail purposes. Finally the phytochemical characterization of flavonoids, hydroxycinnamic acid derivatives, anthocyanins and tannins, was carried out by thin layer chromatography; aglycone structures of flavonoids, as luteolin and quercetin widespread molecules in dyeing plants (Cardon, 2003), were assessed using high performance liquid chromatography.

II. MATERIALS AND METHODS

A. Plant materials

Distillery by-products, *i.e. Salvia officinalis* L. (sage; dried leaves and stems) and *Thymus vulgaris* L. (thyme; dried leaves and stems), were provided by the distillery du Chêne (Banon, France). Fresh peeling wastes of *Allium cepa* L. (onion) were obtained from Bonduelle S.A. (Renescure, France) and air-dried. Food products, *i.e.* fresh roots of *Daucus carota* L. (carrot) and fresh leaves of *Spinacia oleracea* L. (spinach), were bought

in supermarket as representative sorting wastes. Both were freeze-dried. Sorting wastes as fresh roots of *Daucus carota* L. var. *nigra* (black carrot) were given by Inosud S.A. (Cruviers-Lascours, France) and freeze-dried.

B. Phytochemical characterization

Extraction: Plant materials were ground using a domestic blender. Extraction was carried out once in distilled water at 100 °C for 10 min under magnetic stirring (Table I). The suspension was then filtered on gauze to obtain a crude extract (CE). Plant extractions were made in duplicate and following phytochemical characterizations were carried out on both replicates.

Table I.- Plant extract concentrations for phytochemical characterization and for dyeing. [1]: concentration in g of dried weight per ml of solution.

Tableau I.- Concentrations des extraits de plantes pour la caractérisation phytochimique et pour la teinture.

Plant	Crude Extract[1] (CE)	Dyeing bath[1]
Allium cepa	0.075	0.10
Daucus carota	0.075	0.10
Daucus carota var. *nigra*	0.075	0.10
Salvia officinalis	0.150	0.10
Spinacia oleracea	0.075	0.05
Thymus vulgaris	0.150	0.10

Hydrolysis of flavonoids: Aliquot (1 ml) of each CE was evaporated to dryness and 5 ml of methanol-water (70:30; v/v) were added to obtain non hydrolysed solution (NHS). The hydrolysis was carried out as follows: 5 ml of HCl 3N were added to 5 ml of CE and laid down in an oven at 100 °C for 3 hours. Then, extraction of aglycones from acidic CE was carried out three times by partition with ethyl acetate (v/v).The three combined organic extracts were evaporated to dryness; 5 ml of methanol-water (70:30; v/v) were then added to obtain the hydrolysed solution (HS).

Thin layer chromatography (TLC): To characterize phytochemical pattern of plants, aliquots (5 ml) of each aqueous CE were evaporated to dryness. The dried extract was dissolved in 2 ml of methanol-water (1:1; v/v) and directly used for TLC analysis (cellulose plates, Merck, ref. 5552). A two-dimensional TLC was developed: mobile phase I as dichloromethane/ acetic acid/ water (50:45:15; v/v/v) and mobile phase II as ethyl acetate/ acetic acid/ water (10:30:70; v/v/v). After drying, plates were observed under UV light at 366 nm before and after Neu's reagent spraying to reveal flavonoids, phenolic acid derivatives and gallic tannins (Dai *et al.*, 1995; Wagner & Bladt, 2001). Condensed tannins were revealed on the same plate (previously treated by Neu's reagent) spraying 4-dimethylaminocinnamaldehyde solution as reagent (Treuter,1989).

For flavonoid aglycone analysis, NHS and HS were compared in mono-dimensional TLC using mobile phase I (cellulose plates, Merck, ref. 5552) in presence of luteolin and quercetin Fluka standards in methanol (0.1%; w/v).

High performance liquid chromatography (HPLC): Confirmation of flavonoid aglycones was assessed using HPLC (ThermoSeparation Products System) coupled to a diode array detector (Spectra System UV 6000LP) as described by Cristea *et al.* (2003) on RP18 Symmetry column from Waters (4.6x250 mm; 5 µm) using HS diluted twice in methanol–water (70:30; v/v). Luteolin and quercetin were used as standards as previously described.

C. Textile dyeing and colour characterization

Mordanting of fibres: Hemp was dipped in aqueous aluminium acetate solution (10%; w/v) for 1 hour. After fibre air-drying, mordant fixing was ended by dipping hemp fibres in aqueous sodium carbonate solution (0.8%; w/v) for 10 min, rinsed in distilled water and air-dried. Wool was dipped in an aqueous sodium carbonate solution (1%; w/v) for 15 min and rinsed in distilled water. Wool was then heated in a mixture of potassium aluminium sulfate (alum) and potassium acid tartrate (20% and 6% of wool weight, respectively) in water (5%, w/v). After 30 min of boiling, wool was then rinsed in water and air-dried.

Dyeing process: Dyeing was realised with an equal weight (w) ratio between dried plant and textile ($w_{dried\ plant} = w_{textile\ to\ dye}$). Dyeing bath was obtained by 10 min decoction of each grounded plant material (5% to 10% in distilled water; w/v; Table I) under magnetic stirring. After filtration, the dyeing bath was added to mordanted fibres of wool and hemp, and heated from room temperature to boiling in 20 min; boiling was maintained for 2 min. Mordanted fibres were then cooled in the dyeing bath for 1 hour, rinsed in distilled water and air-dried at room temperature.

Colorimetric analysis: A spectrophotometer (Mercury, Datacolor) was used to measure ligthness (L*), chroma (C*) and hue (h°) parameters. Lightness increases from 0 (dark colour) to 100 (light colour). Chroma also varies from 0 (drab colour) to 100 (bright colour). Hue is an angular value: 0° (red area), 90° (yellow area), 180° (green area) and 270° (blue area) (Kowaliski, 1990). Measurements on both dyed supports were made in triplicate.

Light fastness: The test was carried out according to ISO standard method 105-B02. The fastness to light was determined by comparing the fading of each sample to that of a normalized blue scale control treated in the same conditions. Stability value ranges from 1 (poor fastness) to 8 (excellent fastness).

D. Colour characterization and determination of antioxidative activity of plant liquid extract

Colorimetric analysis: Aqueous crude plant extracts (CE; Table II) were used to determine lightness (L*), chroma (C*) and hue (h°) parameters. Measurements were made through cell culture flasks (50 ml, Nunclon flask; Nunc) in duplicate as previously described for fibres.

Antioxidative activity: Ferric thiocyanate assay (FTC assay) with some modifications (Benonge, 2005) was used to determine the *in vitro* inhibition of lipid oxidation. Freshly made up reagents and CE prepared as described for phytochemical characterization (Table II) were placed in screw-capped tubes, stirred and incubated in an oven at 50 °C for 16 hours (Inkubator 1000, Unimax 1010; Heidolph) to obtain incubated extracts (IE). Linoleic acid peroxidation (correlated to antioxidative activity) was evaluated after addition of 0.002M ferrous chloride solution in hydrochloride acid-water (3.5:6.5; v/v) in IE by measuring hydroperoxide accumulation in absorbance (abs) at 500 nm using a UV/Vis spectrophotometer (UV2, Unicam). The FTC assay was carried out in triplicate using α-tocopherol as control standard. IC_{50} (concentration of CE to inhibit peroxidation of lino-

Table II.- IC_{50} (antioxidant activity) and colorimetric data of aqueous plant extracts. [1]: concentration in g of dried weight per ml of water; [2]: concentration of CE to inhibit peroxidation of linoleic acid by 50% (µg of dried weight per ml of solution); [3]: concentration in g of dried weight per ml of ethanol-water (70:30; v/v).
Tableau II.- IC_{50} (activité antioxydante) et données colorimétriques des extraits aqueux de plantes.

Plants	Crude Extract[1] (CE)	IC_{50}[2]	L*	C*	h°
Allium cepa	0.0750	314.80 ± 14.48	27.34 ± 0.36	1.34 ± 0.13	288.35 ± 2.90
Daucus carota	0.0600	1275.56 ± 120.04	28.59 ± 0.23	0.74 ± 0.04	26.80 ± 4.35
Daucus carota var. *nigra*	0.0750	537.31 ± 44.93	26.53 ± 1.50	1.29 ± 0.20	279.58 ± 3.03
Salvia officinalis	0.0750	59.95 ± 3.74	22.05 ± 0.27	1.18 ± 0.10	279.69 ± 1.63
Spinacia oleracea	0.0375	2276.25 ± 150.35	27.26 ± 0.19	1.30 ± 0.13	271.79 ± 2.06
Thymus vulgaris	0.1500	105.07 ± 14.48	26.73 ± 0.53	0.52 ± 0.06	322.29 ± 8.22
α-tocopherol (standard)	0.1000[3]	143.00 ± 1.12	-	-	-

leic acid by 50%) was estimated by linear regression while the percentage of inhibition was calculated as [(1- (abs IE/ abs control)] x 100.

III. RESULTS

A. Phytochemical characterization

According to TLC analysis, condensed tannins and anthocyanins were only found in *Allium cepa* and *Daucus carota* var. *nigra* respectively, while only hydroxycinnamic acid derivatives were detected in *Daucus carota*. Hydroxycinnamic acid derivatives as well as flavonoids were detected in *Salvia officinalis, Thymus vulgaris* and *Allium cepa. Spinacia oleracea* was only characterized by flavonoids.

Using HPLC, it was shown that the main flavonoid aglycone was luteolin for *Salvia officinalis* and *Thymus vulgaris*, and quercetin for *Allium cepa.* As no correlation occurred between aglycone standards (luteolin and quercetin) and hydrolysed aglycone from *Spinacia oleracea*, the flavonoid aglycones were not identified.

B. Colour and stability characterization of dyed textiles

Daucus carota and *Spinacia oleracea* presented the lightest shades ($L^* > 70$) whereas *Daucus carota* var. *nigra* presented the darkest colour ($L^* < 36$) on both hemp and wool fibres (Table III). Other dyed supports were characterized by middle L* value ($40 < L^* < 60$) whatever the fibres. Consequently, L* values were not fibre dependent.

As listed in Table III, we demonstrated that *Daucus carota* var. *nigra* and *Spinacia oleracea* provided drabber colours ($C^* < 16$) on both fibres. The most saturated sample was obtained on hemp and wool with *Allium cepa* extract ($C^* > 50$ and $C^* > 60$, respectively). Regarding *Allium cepa, Salvia officinalis* and *Thymus vulgaris* extracts, hemp fibres gave more saturated colours than wool underlining the influence of support on resulting colours.

Concerning hue (h°), we noticed that yellow, *i.e.* $80° < h° < 100°$, was the most representative colour (carrot, sage, spinach and thyme) whatever the dyed supports. Black carrot provided blue shade ($h°_{hemp} = 268.83°$; $h°_{wool} = 272.01°$) and onion a red hue ($h°_{hemp} = 68.34°$; $h°_{wool} = 64.47°$) (Table III, Fig. 1).

Table III.- Colorimetric data of dyed textiles.
Tableau III.- Données colorimétriques des supports teints.

	L*		C*		h°	
	hemp	wool	hemp	wool	hemp	wool
Allium cepa	44.00 ± 0.39	43.31 ± 0.36	65.31 ± 1.98	51.97 ± 0.59	68.34 ± 0.49	64.47 ± 0.28
Daucus carota	82.16 ± 0.20	73.35 ± 0.15	27.48 ± 0.45	30.95 ± 0.37	99.29 ± 0.19	95.98 ± 0.19
Daucus carota var. *nigra*	35.69 ± 0.56	31.85 ± 0.36	15.58 ± 0.24	15.06 ± 0.23	268.83 ±0.35	272.01 ± 0.41
Salvia officinalis	61.70 ± 0.38	58.28 ± 0.22	52.40 ± 0.66	39.58 ± 0.41	88.91 ± 0.25	85.04 ± 2.40
Spinacia oleracea	83.55 ± 0.15	81.28 ± 0.24	15.31 ± 0.16	12.83 ± 0.41	97.00 ± 0.16	91.11 ± 0.58
Thymus vulgaris	52.10 ± 0.39	50.23 ± 0.30	55.32 ± 3.08	47.32 ± 0.87	84.63 ± 0.41	81.14 ± 0.24

As mentioned in Figure 1, light fastness data ranged as follows:
- on hemp : spinach = thyme = sage > onion > carrot = black carrot;
- on wool : spinach > thyme = onion = carrot > sage > black carrot.

Moreover, regarding light fastness values on Figure 1, hemp fibres showed a better stability than wool fibres.

C. Colour characterization and antioxidative activity of plant liquid extracts

Crude aqueous plant extracts gave dark ($L^* < 30$) and very desaturated ($C^* < 2$) shades whatever the by-products (Table II). Except for carrot that presented a red hue ($h° = 26.80$), coloured extracts appeared in the blue-violet area of colour ($271° < h° < 288°$), thyme extract being more reddish than others ($h° > 320°$).

The antioxidant activity of plant extracts mentioned in Table II as IC_{50}, decreased as follows: sage (59.95) > thyme > onion > black carrot > carrot > spinach (2276.26). It was highlighted that antioxidant activity of sage and thyme extracts were higher than that of α-tocopherol (Table II).

IV. DISCUSSION

Among the six plant extracts, *Salvia officinalis, Thymus vulgaris* and *Allium cepa* revealed the best antioxidant activity. This was probably due to the high contents of flavonoids and hydroxycinnamic acid derivatives. In fact, the capacity of flavonoids, luteolin and quercetin derivatives, to act as antioxidants *in vitro* has been the subject of several studies in the past, and structure-activity relationships of the antioxidant activity have been clearly established (Rice-Evans *et al.*, 1996; Pietta, 2000; Dorman *et al.*, 2003). Antioxidant activity of those plant extracts is even more interesting being generally at the origin of therapeutic activities such as anti-inflammatory, anti-tumour or anti-neurodegenerative activities, as well as of protective cardiovascular agents (Andary, 1993; Wang *et al.*, 1998; Aviram & Fuhrman, 2003; Schroeter & Spencer, 2003). Moreover, concerning our extracts, it should be noted that *Salvia officinalis* and *Thymus vulgaris* revealed a higher antioxidant potential than α-tocopherol, worldwide used in food and cosmetic products as natural antioxidant (Asamarai *et al.*, 1996).

Five by-product extracts gave dark blue-violet colours (Table II) while *Daucus carota* developed a red hue, based on its carotenoid content. Whatever the phytochemical patterns of the five former plant extracts, no hue (h°) variation clearly appeared (see § III-A).

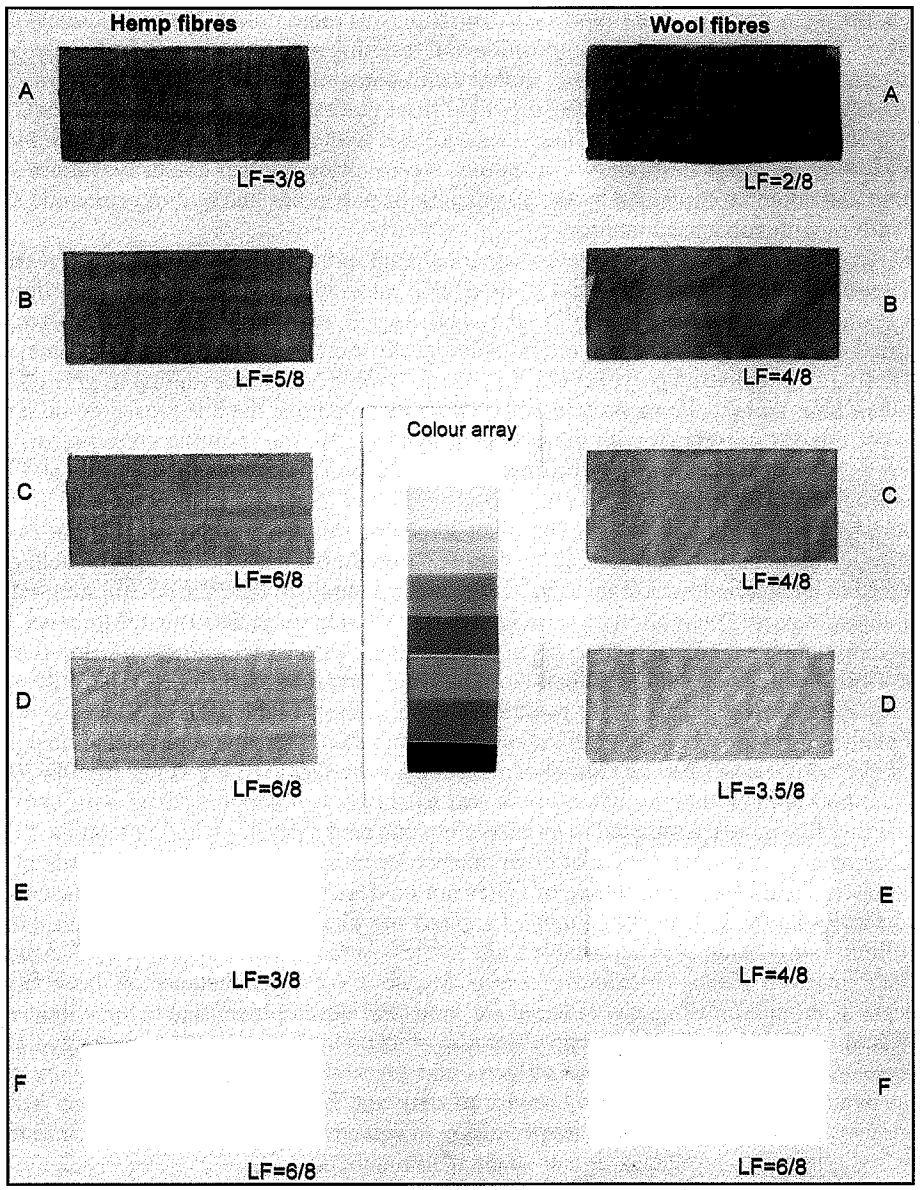

Fig. 1.- Dyed hemp and wool fibres with related light fastness (LF) value. A: *Daucus carota* var. *nigra*; B: *Allium cepa*; C: *Thymus vulgaris*; D: *Salvia officinalis*; E: *Daucus carota*; F: *Spinacia oleracea*. Colour array: normalized colours from Natural Colour System standards. LF = x/8: light fastness values (from 1, poor resistance, to 8, excellent resistance)

Fig. 1.- Supports teints (chanvre et laine) et indice de stabilité lumière (LF). A : *Daucus carota* var. *nigra* ; B : *Allium cepa* ; C : *Thymus vulgaris* ; D : *Salvia officinalis* ; E : *Daucus carota*; F : *Spinacia oleracea*. Règle de couleurs : couleurs standardisées du Natural Colour System. LF = x/8: indice de stabilité lumière (de 1, faible résistance, à 8, excellente résistance).

On the other hand, on fibre models, h° variation was more noticeable and classical correlations between polyphenolic composition and resulting colours were verified. Blue–violet-dyed textiles were obtained from anthocyanin containing extract (*Daucus carota* var. *nigra*) and yellow-coloured supports provided from plant extracts containing hydroxycinnamic acid derivatives without (*Daucus carota*) and with (*Allium cepa, Salvia officinalis* and *Thymus vulgaris*) flavonoids. For onions, the resulting reddish colour was more surprising and could be explained by the association of flavonoids and hydroxycinnamic acid derivatives with condensed tannins.

Differences on hue values between aqueous plant extracts (CE) and coloured textiles indicated the fibre capacity to select some dyeing molecules from the dyeing bath improved by metallic mordanting agents. At the opposite, CE, resulting from hot water extracts of dried plants, contained many others substances (more or less oxidized or damaged) interfering with coloured polyphenols (flavonoids, tannins or anthocyanins) to give observed dark blue-violet colours. As a result, it could be stated that the hue measured on textile is not directly correlated with the colour of dyeing bath; the resulting colour of dyeing fibres is then dependent on physicochemical interactions between the supports and the dyes from the plant extracts.

As previously reported on a dyeing plant screening on wool and cotton (Guinot *et al.*, 2006), correlations between saturation data (C*) on fibres and specific phytochemicals detected in dyeing bath were confirmed in the present study. In fact, the desaturating effect of anthocyanins and their ability to provided darker colours were confirmed. Moreover, the saturation parameter was shown to be fibre-dependent: colours measured on hemp (cellulosic fibres) were more saturated than those on wool (protein-based fibres) especially with flavonoids/ hydroxycinnamic acid-containing plant extracts (Table III).

Finally, correlation between light stability of both dyed fibres and phytochemical patterns, previously described by Guinot *et al.* (2006), were also verified: i) low light fastness with anthocyanin-containing dyeing bath and ii) stability of supports dyed with extracts containing flavonoids associated to hydroxycinnamic acid derivatives and/or tannins. Light fastness of coloured supports are of great interest for industrial applications. In spite of no optimisation neither on mordanting of fibres nor on dyes extraction, five out of the twelve dyed fabrics analysed here (two kinds of support per plant) are in agreement with industrial limit that considers an acceptable light fastness value as equal or upper to 5. Among the six involved plants, *Spinacia oleracea* despite a 6/8 light fastness on both fibres appears as an unpromising raw material for industrial development due to very light and drab colours (Table II; Fig. 1) probably because of its poor phenolic pool according to TLC analysis. *Salvia officinalis, Thymus vulgaris* and especially *Allium cepa* extracts are of a great interest on cellulosic fibres because of dark and bright shades obtained on hemp. Obviously, those kinds of colours are promising in industrial dyeing-formulation since they may be lightened to produce a lighter shade if so required.

V. CONCLUSION

This study highlighted the broad spectrum of industrial uses of some plant by-products (carrot, black carrot, onion, sage, spinach and thyme). In fact our results showed a great interest for dyeing and antioxidative applications. *Salvia officinalis* and *Thymus vulgaris* (both distillery wastes) as well as *Allium cepa* (agroalimentary peeling wastes) appeared as

the most promising species considering their attractive results as textile dyes and antioxidant additives.

Firstly, the great interest of plant by-products was underlined to provide new functionalised extracts as colouring matters and/or antioxidants. Secondly, our data suggest innovative economical features in terms of industrial valorisations for high tonnage of plant by-products (Ghander, 2005): the residual materials become novel natural resources to be developed for textile, food or cosmetic industries.

Toxicity problems in relation to synthetic dyes and antioxidants (Anliker *et al.*, 1988; Saito *et al.*, 2003), evolution of legislation regarding the use of dyestuffs and the processing of by-products (European Directive n°2002/61/CE as well as 1998/04/28 and 2001/06/28 French circulars), increasing consciousness of consumers on food additives and popular request for more natural products are valuable arguments to develop the uses of dyeing plants and alternative antioxidant plant extracts in various industrial formulations.

Acknowledgements - The authors would like to thank Daniel Bocquet from Bonduelle Company (Renescure, France) for providing onion by-products and Michel Garcia from Plantes et Couleurs company (Lauris, France) for providing samples of distilled wastes, and for hemp mordanting. Edwige Lecoeur from Feutrie company (Sailly-sur-la-Lys, France) is gratefully acknowledged for her assistance developing the stability test. Pictural assistance was carried out by Philippe La Fisca from Laboratoire de Botanique, Mycologie et Phytochimie (Faculté de Pharmacie de Montpellier, France).

REFERENCES

Andary C., 1993.- Caffeic acid glycoside esters and pharmacology. *In*: *Polyphenolic Phenomena*. A. Scalbert, Paris, 237-245.

Andary C., S. Prunac & D. Cardon, 1996.- Yellow dyes of Historical Importance: a multi-disciplinary study. II - Chemical analysis of weld and saw-wort. *Dyes in History and Archaeology*, **14**, 33-38.

Angelini L.G., 1999.- Dyeing plants in Italy. *Gützower Fachgespräche: "Fäberpflanzen"*, 209-220.

Angelini L.G., A. Bertoli, S. Rolandelli & L. Pistelli, 2003.- Agromonic potential of *Reseda luteola* L. as a new crop for natural dyes in textiles production. *Industrial crops and products*, **17**, 199-207.

Angelini L.G., L. Pistelli, P. Belloni, A. Bertoli & S. Panconesi, 1997.- *Rubia tinctorum*, a source of natural dyes: agronomic evaluation, quantitative analysis of alizarin and industrial assays. *Industrial crops and products*, **6**, 303-311.

Anliker R., G. Duerig, D. Steinle & E.J. Moriconi, 1988.- List of colorants to be classified as toxic. *J. Soc. Dyers and Colourists*, **104**, 223-225.

Asamarai A.M., P.B. Addis, R.J. Epley & T.P. Krick, 1996.- Wild rice hull antioxidants. *J. Agricult. Food Chemistry*, **44**, 126-130.

Aviram M. & B. Fuhrman, 2003.- Effects of flavonoids on the antioxidant of low-density lipoprotein and atherosclesis. *In*: *Flavonoids in Health and Disease*. C. Rice-Evans & S.L. Packer (eds.), Marcel Dekker, New York, 165-203.

Benonge I., 2005.- *Valorisation d'extraits de végétaux issus d'écarts de triage dans le domaine alimentaire et pharmaceutique*. Rapport de Diplôme de Recherche Technologique, Ingénierie de la Santé, Université Montpellier 1, 129 p.

Berjoin M., C. Raynaud, G. Vilarem, J.M. Bessière & T. Talou, 2004.- Saffron by-products integrated valorisation using agroresource refining concept (ARC). *Acta Horticulturae*, **650**, 355-360.

Bruneton J., 1999.- *Pharmacognosie, phytochimie et plantes médicinales.* Tec & Doc, Paris, 1 119 p.

Cardon D., 2003.- *Le monde des teintures naturelles.* Belin, Paris, 585 p.

Cristea D., I. Bareau & G. Vilarem, 2003.- Identification and quantitative HPLC analysis of the main flavonoids present in weld (*Reseda luteola* L.). *Dyes and Pigments*, **57**, 267-272.

Dai G.H., C. Andary, L. Mondolot-Cosson & D. Boubals, 1995.- Involvement of phenolic compounds in the resistance of grapevine callus to downy mildew (*Plasmopara viticola*). *Eur. J. Plant Pathology*, **101**, 541-547.

Dorman H.J.D., A. Peltoketo, R. Hiltunen & M.J. Tikkanen, 2003.- Characterisation of the antioxidant properties of de-odourised aqueous extracts from selected Lamiaceae herbs. *Food Chemistry*, **83**, 255-262.

Ghander L., 2005.- *Étude du gisement et des possibilités de valorisation des déchets et sous-produits issus de la transformation des légumes en région Nord-Pas de Calais.* Pôle de compétence « Productions végétales alternatives » pour l'ADEME et le Conseil régional Nord-Pas de Calais, 95 p.

Gilbert K.G. & D.T Cooke, 2001.- Dyes from plants: past, present understanding and potential. *Plant Growth*

Regulation, **34**, 57-69.

Guinot P., A. Rogé, A. Gargadennec, M. Garcia, D. Dupont, E. Lecoeur, L. Candelier & C. Andary, 2006.- Dyeing plants screening: an approach to combine past heritage and present development. *Coloration Technology*, **122**, 93-101.

Hofenk de Graaf J.H., 2004.- *The Colourful past.* Abegg-Stiftung and Archetype Publications Ltd, Riggisberg / London, 396 p.

Jansen P.C.M. & D. Cardon, 2005. *Plant Resources of Tropical Africa*, **3** - Dyes and tannins. Backhuys Publishers, Leiden, 238 p.

Katalinic V., M. Milos, T. Kulisic & M. Jukic, 2006.- Screening of 70 medicinal plant extracts for antioxidant capacity and total phenols. *Food Chemistry*, **94**, 550-557.

Kowaliski P., 1990.- *Vision et mesure de la couleur.* Masson, Paris, 255 p.

Larson R.A., 1988.- The antioxidants of higher plants. *Phytochemistry*, **27**, 969-978.

Llorach R., J.C. Espin, F.A. Tomàs-Barberàn & F. Ferreres, 2002.- Artichoke (*Cynara scolymus* L.) by-products as a potential source of health promoting antioxidant phenolics. *J. Agricult. Food Chemistry*, **50**, 3458-3464.

Macheix J.J., A. Fleuriet & C. Jay-Allemand, 2005.- *Les composés phénoliques des végétaux.* Presses polytechniques et universitaires romandes, Lausanne, 192 p.

Moure A., J.M. Cruz, D. Franco, J.M. Dominguez, J. Sineiro, H. Dominguez, M.J. Nunez & J.C. Parajo, 2001.- Natural antioxidants from residual sources. *Food Chemistry*, **72**, 145-171.

Nick A., T. Rali & O. Sticher, 1995.- Biological screening of traditional medicinal plants from Papua New Guinea. *J. Ethnopharmacology*, **49**, 147-156.

Orska-Gawrys J., I. Surowiec, J. Kelh, H. Rejniak, K. Urbaniak-Walczak & M. Trojeanowicz, 2003.- Identification of natural dyes in archeological Coptic textiles by liquid chromatography with diode array detection. *J. Chromatography* A, **989**, 239-248.

Peyrat-Maillard M.N., M.E. Cuvelier & C. Berset, 2003.- Antioxidant activity of phenolic compounds in 2,2'-azobis(2-amidinopropane)dihydrochloride (AAPH)-induced oxidation: synergistic and antagonistic effects. *J. Amer. Oil Chemists's Soc.*, **8**, 1007-1012.

Pietta P.G., 2000.- Flavonoids as antioxidants. *J. Natural Products*, **63**, 1035-1042.

Rice M. & D. Beebee, 1980.- *Mushrooms for color.* Mad River Press, Eureka, 146 p.

Rice-Evans C.A., J.M. Miller & G. Paganga, 1996.- Structure-antioxidant activity relationships of flavonoids and phenolic acids. *Free Radical Biology and Medicine*, **20**, 933-956.

Saito M., S. Hiroshi & S. Fujisawa, 2003.- Cytotoxicity and apoptosis induction by butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT). *Anticancer Research*, **23**, 4693-4701.

Schieber A., F.C. Stintzing & R. Carle, 2001.- By-products of plant food processing as a source of functional compounds; recent developments. *Trends in Food Science and Technology*, **12**, 401-413.

Schmourlo G., R.R. Mendonça-Filho, C. Sales Alviano & S.S Costa, 2005.- Screening of antifungal agents using ethanol precipitation and bioautography of medicinal and food plants. *J. Ethnopharmacology*, **96**, 563-568.

Schroeter H. & J. Spencer, 2003.- Flavonoids: neuroprotective agents? Modulation of oxidative stress-induced MAP kinase signal transduction. *In*: *Flavonoids in Health and Disease.* C. Rice-Evans & S.L. Packer (eds.), Marcel Dekker, New York, 233-272.

Treuter D., 1989.- Chemical reaction detection of catechins and proanthocyanidins with 4-dimethylaminocinnamaldehyde. *J. Chromatography*, **467**, 185-193.

Wagner H. & S. Bladt, 2001.- *Plant drug analysis, A thin layer chromatography atlas.* Springer-Verlag, New York, 384 p.

Wang H.K., Y. Xia, Z.Y. Yang, S.L. Natschke & K.H. Lee, 1998.- Recent advances in the discovery and development of flavonoids and their analogues as anti-tumour and anti-HIV agents. *Adv. in Exper. Medicine and Biology*, **439**, 191-225.