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HPLC-MS identification of two major flavonoids in the textile dye extract from fresh leaves of *Mangifera indica*

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Abstract

Today, scientific research in the field of natural textile dyeing is intensifying with the aim of contributing to the orientation of artisanal and industrial tinctorial practices, and to ensure the protection of the environment from harmful releases of effluents of synthetic dyes but also health of consumers. In this dynamic, physico-chemical, qualitative and quantitative, chromatographic and spectral analyses on the extract from fresh leaves of M. indica were carried out and allowed an informed application of this dye on cotton threads. With an extraction yield of about 9%, M. indica leaves have a total flavonoid content of 400.314±2.221mgEQ/g of dye powder. Hydrolyzable and condensed tanninsrateswere 10.157% and 44.850%, respectively. The HPTLC chromatographic profile of the dye extracted from leaves of M. indica indicated the presence of flavonols and xanthonoids (mangiferin). The vibrations of elongation ν_{O-H}, ν_{C-N} and that of deformation ν_{N-H}respectively of the alcohols, xanthonoids, amines and/or amides in infra-red suggest the presence of flavonic and xanthonoid colouring molecules that, through metal chelators and/or inter and/or intermolecular combinations, are responsible for the final colour shades obtained in tinctorial practice. High-performance liquid chromatography coupled with mass spectroscopy revealed the presence of major flavonoid molecules such as quercetin 3-O-hexose and kaempferol 3-O-hexose. Tinctorial practice techniques applied on cotton threads have allowed to have various shades of colors (champagne yellow, yellow corn, cow tail, vanilla, yellow March ...). In addition to being a natural acid dye, textile dye extracted from M. indica leaves can be classified as a metal dye in terms of the quality of shades obtained with the use of mordants such as alum, hydrated iron and copper sulfates.

Keywords: Aqueous extraction, Flavonoids, Tannins, HPTLC, Infrared, HPLC MS-MS, dyeing practice.

Introduction

The deep link between man and the world of colours has always been at the heart of creativity in fashion, making enormous transformations on his costumes, clothes and linens. But since the advent of synthetic dyes in the early 19th century, the use of natural dyes has decreased considerably. The real limiting factors associated with the use of natural dyes lie in the fairly long dyeing processes, the absence of standard nuance maps and the reproducibility of colour shades[1].

The growing consumer awareness of eco-friendly textiles and the need to preserve the environment has led to the resumption of the old practice of dyeing with natural dyes. Indeed, the global demand for naturally occurring fibres and dyes is increasing due to increased consumer awareness in general in the United States, Europe and Japan (where certain carcinogenic synthetic dyes such as azoic dyes are prohibited) to highly polluting procedures that affect not only the cultivation of fibers, but also their transformation into coloured textiles, as well as the harmful effects of certain synthetic dyes on human health as sources of skin cancer, disorders and allergic contact dermatitis [2]. In recent years, there has been a gradual increase in the effect of UV radiation on human skin due to the destruction of the ozone layer[3]. In the long term, this UV exposure can cause adverse health effects and accelerate skin aging. Today, several approaches are being considered to improve the protection of the skin from the harmful effects of UV rays. Natural dyes absorbing in the UV, their application on cotton would be an alternative to synthetic dyes increasingly decried. It then becomes imperative to develop new coloring techniques and also to standardize these processes using natural dyes so that these dyes can be offered as an effective ecological option to toxic synthetic dyes.

Flora of Burkina Faso, like that of Africa and the world, offers huge and more beautiful adornments for our pleasure and for the particular happiness of the dyeing craftsmen [4]. This multitude of colours offered by flora has always been at the heart of the choices for textile dyeing, especially artisanal, while offering ranges of shades of color according to the taste of consumers.

The mango tree (*Mangifera indica L.*) is a tree of the Anacardiaceae family, native to East India and Burma. However, it was introduced to Africa and Brazil in the 16th century by the Arabs and Portuguese respectively. The leaves of mango trees, the subject of investigation for colouring molecules, have an orange-pink colour at the beginning of their growth and then pass through a bright dark red hue before turning dark green at maturity. This dark green color due to chlorophyll, masks a yellowish dye located in the vacuoles of cells.

Natural dyes for textile use today, through dyeing and these techniques[5], continue to reveal their secrets and are the subject of extensive scientific research able to offer a guarantee of preservation of the health of users and consumers. The various shades of color obtained in natural tinctorial practice are due to the presence of natural organic molecules that are responsible for the pigments of plants in their entirety. *Tamarindus indica* pods, which are used in natural dyeing, contain compounds such as polyphenols and especially proanthocyanidines, a group of compounds formed by condensation or polymerization of flavan-3-ol or flavan-3, 4-diol, commonly known as condensed tannins. Since natural fibres such as cotton have a very low affinity[6] for most natural dyes, tannins play an important role in fixing the dye on the textile. Indeed, the production of quality cotton fibres and the techniques of processing these fibres in Burkina Faso would work in tandem with the mastery of techniques of tinctorial practices especially artisanal.

Fixation the dye on cotton fiber is one of the most important steps in textile dyeing. From this point of view, knowing the structures of molecules responsible for pigmentation and co-pigmentation at the plant level remain a favourable and even unavoidable issue for the understanding and improvement of tinctorial practice protocols[7, 8].

This is why this study aims to identify major polyphenol molecules (by chromatographic and spectral methods) whose structures could explain the shades of color observed in dyeing tests on cotton fibres in dye baths prepared from dye extracted from fresh leaves of *Mangifera indica*.

Indeed, high-performance liquid chromatography coupled with mass spectroscopy which is one of the advanced techniques for identifying the molecular structures of natural substances has been used in the study of the extract of M. indica leaves. Through the phenomena of self-association and/or association[9] with many other molecules (tannins[10], phenolic acids, xanthonoids...) and the use of non-toxic chemical bites (alum, iron sulphates and hydrated copper), these flavonoids contributed to the determination of various color shades in dye made on skeins of cotton threads.

Materials and methods

Dye extraction and yield: Fresh leaves of *M. indica* (250g) were ground and the broyat was extracted in water using a soxhlet[11]. Aqueous extraction was justified by the partial preservation of the ways of making dyeing craftsmen in Burkina Faso. The extract was concentrated by evaporation and then frozen and dried with ALPHA 1-2 LD plus brand freeze-dryer.

Fresh leaves of M. indica Shredded material Freeze-dried.

The yield of the resulting dye powder was assessed by Relationship 1 :

$$Yield = \frac{Mass\ of\ Dye\ extract}{Mass\ of\ plant\ material} \text{x } 100 \quad (1)$$

Total flavonoids content: It consisted of adding 60µL of the extract, 150µL of distilled water, 15µL of a solution of sodium nitrite ($NaNO_2$) to 5%, 15L of an aluminum chloride solution ($AlCl_3$) at 10% and 50µL of a soda solution (NaOH) at 1M. Total flavonoid content was determined by reading the absorbance at 510nm using the microplate reader 96-well quartz (MP96 spectrophotometer SAFAS). Absorbance was related to the standard curve obtained from the quercetin taken as standard (relationship 2)[12,13].

$$C(mgEQ/g) = \frac{(\text{Absorbance} - \text{Originally ordained}) \times \text{Volume} \times \text{Dilution Factor}}{\text{Dye mass} \times \text{slope}} \quad (2)$$

C (mg EQ/g): Quercetin equivalent milligram content per gram of dye powder.

Hydrolyzable and condensed tannins rates: Hydrolyzable tannins rate: To 60µL of the extract, was adding a volume of 220µL of a mixture of iron chloride III to 10^{-2}M and hydrochloric acid to 10^{-3}M (50/50 v/v), the absorption reading was made at 660nm using the 96-Well quartz microplate (MP96 spectrophotometer, SAFAS). The absorbentness read is related to the formula of relationship 3[14]:

$$R\ (\%) = \frac{A \times MW \times V \times DF}{\varepsilon_{mole} \times P} \quad (3)$$

A: Absorbance; ε_mole: 2169 of Gallic acid; MW: Molecular weight of gallic acid; V: Extract volume used; P: Sample weight; DF: Dilution factor; R (%): Hydrolyzable tannins.

Condensed tannins rate: To 90µL of the extract was added 190µL of a vanillin solution at 0.01% in concentrated sulphuric acid. The absorption is read at 500nm using a 96-well quartz microplate reader (MP96 spectrophotometer, SAFAS). The rate of condensed tannins is obtained by reporting the absorption read in the formula of relationship 4[15,16].

$$R(\%) = 5{,}2.\ 10^{-2}\ \frac{A \times V}{P} \quad (4)$$

$5{,}2.10^{-2}$: Constant expressed in cyanidin equivalent; A: Absorbance; V: Extract volume used; P: Sample weight; R (%): Condensed tannins rate.

High Performance Thin Layer Chromatography of dye extract: The chromatographic profile of the natural dye was achieved by high performance thin layer chromatography (HPTLC)[17-19]. The principle was to deposit 3µL extract with standard in the form of thin bands 8mm long, on a 20x10cm F_{254} HP silica gel plate using a CAMAG Automatic TLC Auto Sampler 4 device.

After a saturation stage for 20 minutes, plaque development was achieved using the mobile phase acetate of ethyl-formic acid-acetic-water (100:11:11:26 v/v).

To observe polyphenols in general and flavonoids in particular, two specific revelators, successively 2-aminodiphenylborate (1g in 100mL of methanol) and polyethylene glycol (5g in 100mL of ethanol at 96%), were used to spray the plate which is then heated to 110°C for 3 minutes.

Analysis of dye by infra-red to transformed Fourrier: The direct use of raw natural dyes is justified in part by the difficulty of isolating sufficient quantities of dyes for textile dyeing, given the molecular complexity of mixtures at the level of natural substances. For example, infra-red spectra (IR) are often recorded on raw extracts to provide a brief erict of the chemical functions present in the total extracts, which are responsible for observing various final colour shades of dyed textile material[20]. Thus, the total dye extract containing tannins, flavonoids, xanthonoids and other compounds is subjected to an infra-Red spectrometry analysis to Fourrier Transformed (IR-TF) type TENSOR 27 for identification of functional groups present in constituents structures.

HPLC-MS of flavonoids from *M. indica* dye extract: The dye extract from the *M. indica* leaves containing flavonoids, previously filtered using a syringe (type cellulose acetate membrane 25mm and 0.45µm) is characterized by high-performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) at the National Laboratory of Public Health (LNSP) in Ouagadougou (Burkina Faso).

The ions are controlled in MS/MS in positive ionization mode (ESI). The HPLC separation is performed on a Zorbax sb C_{18} column (250x4.6mm; 5µm)[21-23].

The mobile phase consists of two solvents A and B in order to achieve an elity gradient with a flow rate of 0.6mL/min. Solvent A is 5% formic water-acid (v/v), solvent B is made up of 5% formic acetonitrile-acid (v/v). The elion consisted of a 95% to 90% stage of solvent A for 5 minutes and then the gradient was maintained at 90% of A for 10 minutes. Then 90% to 88% A in 10 minutes, to 85% A in 10 minutes, 82% A in 15 minutes, to 75% A in 10 minutes, 70% A in 20 minutes and finally returned to 95% A in 10 minutes (the total run was 90min). The injection volume was 50µL. The mobile phase was then injected into the electrospray ionization source.

The data were provided by Agilent Technologies, Inc. 2012 LC/MS Data Acquisition for 6400 Series Triple Quadripole (version B.06.00 Build 6.0.6025.0). The temperature of the gas (N_2) was 200°C, the gas flow of 10L/min and the pressure of the nebulizer 15 psis. Nitrogen was used as a nebulizer and collision gas. The mass spectrometer scans all ions with a m/z value between 100 and 1100. Comparison of retention times and molecular weights of the observed fragments thus allowed the identification of flavonoid molecules. Indeed, the principle was to inject the sample in solution at a constant flow of about 0.6µL/min into a conductive capillary. A desolvatation gas (N_2 sec) with an approximate flow of 500L/h, surrounds the capillary and promotes the vaporization of the sample. When the potential of the capillary is positively charged, the positive ions generated will be analyzed and vice versa. The ions generated inside the device are drawn to the extraction cone where they will be fragmented. These fragmentations will continue in the collision cell during tandem mass spectrometry analyses [24, 25].

This characterization of flavonoids in ESI-MS/MS was based on generation in the source of ionization of the aglycone patterns of each flavonoid compound. As a result, the tandem MS analysis of molecular ions resulted in different fragmented ions specific to each type of aglycone.

Tinctorial Practice: Unwinding: Its action boils down to ridding textile material (cotton yarn swaths) of wax, pectin and other dirt that influence the fixation of the dye on the textile[26, 27].

Approximately 70g of skein cotton thread was immersed in 700mL of water brought almost to a boil (about 90°C), to which are added 700mg of neutral soap (Marseille soap) and 3.5g of sodium carbonate. After 1 hour of boiling, 0.7mL of acetic acid was added for the neutralization of the base. The skein was then rinsed thoroughly with water and washed with neutral soap and dried in the room.

Mordancing: Several kinds of chemical and plant-based mordants (tannins) are used in natural tinctorial practices. For example, chemical mordants[28,29] such as alum $KAl(SO_4)_2.12H_2O$, hydrated iron sulphate ($FeSO_4.7H_2O$) and hydrated copper sulphate ($CuSO_4.5H_2O$) were used. 140mg of each type of mordant was dissolved in 30mL of hot distilled water. Then, sodium hydroxide (14mg) was added for the revelation of different types of ions and their colors (Al^{3+}: white, Fe^{2+}: pale green, Cu^{2+}: blue). A precise mass of small skeins of yarn (700 mg each) was immersed in each lukewarm mixture and the whole was kept for 12 hours. The skeins were removed and then wrung out heavily and placed in lockdown in plastic bags for 72 hours before dyeing.

Dyeing yarn with *M. indica* dye extract: Two dye baths (acid and basic) were prepared and exploited for the dyeing of cotton yarn skeins. Immersion of non-mordanted and mordanted skeins of yarns (700mg each) in acid and basic baths of the dye from *M. indica* leaves.

The dye rate was set at 4% and so each bath was obtained by dissolving 28mg of the dye in 14mL of distilled water.

After adjusting the pH to 4 for the acid medium and 10 for the basic medium using the mobile pH (826 pH mobile/827 pH lab, Ω Metrohm), each bath was raised to a temperature of about 70°C before skein immersion. To facilitate the homogeneity of the dye, skeins were constantly stirred in each dye bath. After 45 minutes, skeins were removed from the bathing area and spread out in the open air in room, then 10 minutes later they have been rinsed thoroughly and spread out again. An hour later, they are washed with Marseille soap and dried permanently in the room[30-32]. Soap washing is one of the first tests of strength carried out on dyed fibres and fabrics. Other tests such as light, chlorinated water or sweat tests are tests to corroborate test wash results.

The assessment of the homogeneity of the dye was made using a magnifying glass (classical-black magnifying glass, Magnification: 3.5x, 5xØ50mm, Ø60mm, Ø75mm) for careful observation, and this allowed the development of a scale of assessment of the homogeneity of the fixation, ranging from 1 to 4 (1: non-homogeneous; 2: medium homogeneity; 3: fairly good homogeneity; 4: very good homogeneity).

Results and discussion

From the quantitative aspect (Table-1), the leaves of *M. indica*, with an extraction yield of 9%, contain a content of 400,314 ± 2.221mgEQ/g of total flavonoid dye powder, 10.157% and 44.850% respectively of hydrolyzable and condensed tannins (Table-1).

The observation of the chromatographic profile of *M. indica* leaves extract (Figure-2) at the same time as standards and other work done on this extract revealed the presence of a xanthonoid such as mangiferin[33] and flavone derivatives.

In addition, a review of infrared spectral data revealed the presence of essential chemical functional groups characterized by elongation vibrations (Figure-3). Natural dyes, as used in natural dye, are complex mixtures of molecules. Each molecule has chemical functions that give it particular properties. The most information-rich and experimentally accessible part is the medium IR (4000 to 400cm^{-1}). In this area, absorptions corresponding to wave numbers less than 800cm^{-1} form a kind of fingerprint of compounds to recognize them and those greater than 800cm^{-1} are characteristic of the chemical bonds present in the sample, allowing functional and structural analysis[34]. The IR spectrum of the dye extract has characteristic bands corresponding to specific functional groups (Figure-3). Thus, the observed wave number at 3270cm^{-1} characterizes an elongation vibration ν_{O-H} corresponding to the functional hydroxyle OH bound of linked alcohol. Other wave numbers at 1603cm^{-1} and 1036cm^{-1} corresponding to the ν_{C-N} elongation vibration and the ν_{N-H} deformation vibration refers to the presence of functional group C-N in the extract, indicating the functions of amines and/or amides (Figure-3). According to the literature, *M. indica* contains flavonoids belonging to the subgroups of flavonols and xanthonoids[35,36].

The HPLC of aqueous extract from *M. indica* leaves presented two (02) essential peaks (Figure-3) in the investigation of flavonoids 1: RT = 44.31min; 2: RT= 45.11min.

The control of the MS/MS molecular ions of compounds 1 and 2, respectively, gives molecular ions m/z to $M+H^+$ 465 u and 449u (Table-2), which would correspond to the masses calculated using the raw formulas $C_{21}H_{19}O_{12}$ and $C_{21}H_{20}O_{11}$. Secondary ions at m/z 303 u and 287 u observed for compounds 1and 2shows the loss of an hexose by the molecular ion of each compound, which could be either glucose or galactose $[M+H-162]^+$. The peak at m/z 465 u of compound 1 would correspond to that of quercetin 3-O-hexose. The one at m/z 449 of compound 2 would correspond to the kaempferol 3-O-hexose.

These flavonic compounds in association with many other phenolic compounds (tannins, xanthonoids...) present in the leaves of *M. indica* such as pentagalloyl glucose, epicatechin, mangiferin, isomangiferin, homomangiferin, mangiferin 6'-0-gallate[37-40], could contribute to the explanation of the different shades of color obtained in tinctorial practice. These hydroxylated compounds, beyond the intermolecular association, often pass through chelator metals (Al^{3+}, Fe^{2+}, Cu^{2+}) for the creation of complexes favorable to the fixation on the monomer unit of the cellulose (D-glucopyranose) of cotton fibers. These complexes are preferred to the hydroxylated sites 6,3 and 2 of D-glucopyranose[41,42]. Thus, the affinity of complexes with cellulosic fiber (cotton fiber), would depend on the acid or basic nature of the dye bath, justifying in part, the diversity of shades of color obtained in tinctorial practice and also their fixation or non-fixation.

Very different shades of colour with a fairly good fixation and fairly good homogeneity were observed at the end of the tinctorial practice with the dye extract from leaves of *M. indica*.

The results of the tinctorial practice (Figure-11 and Table-3) with the extract of the leaves of *M. indica* showed a range of characteristic shades of color (champagne yellow, corn yellow, cow tail, vanilla, yellow March...). In addition, the quality factor (QF) based on the product of the degree of fixation by the degree of homogeneity allowed the obtaining of very appreciable shades of color with the use of alum in acidic environments, hydrated iron sulphate in acid and basic environments, copper sulphate in a basic medium. The fixation

of the molecules of the *M. indica* leaf dye requires the intervention of mordants making it a mordant or metal-bearing dye.

Conclusion

M. indica leaves contain flavonoids that, through intra or intermolecular associations, contribute to shades of colour in tinctorial practice.

With a content of 400.314±2.221mg of EQ/g of dye powder and hydrolyzable and condensed tannins contents, 10.157% and 44.850%, respectively, the natural dye from *M. indica* fresh leaves, in a dying process with alum, iron sulphates and copper mordants provides a variety of colour shades. These shades justifying the homogeneity and fixation of the dye on the cotton fiber, would explain the affinity of flavonols such as quercetin 3-O-hexose and kaempferol 3-O-hexose with the mordants used (alum, iron sulphates and copper). The affinity observed, therefore, justifies the chelation of these compounds by the metal salts (Al^{3+}, Fe^{2+}, Cu^{2+}) already fixed by mordanting on cotton fiber (cellulose) whose monomer unit is D-glucopryranose where hydroxyl groups in positions 2, 3 and 6 (active sites) allow chelation. The dye from *M. indica* leaves, can be classified in the groups of natural mordanting dyes; so, in the group of metal dyes.

Table-1: Yield, Total flavonoids Content (TFC), Hydrolyzable tannins rate (HTR), Condensed Tannins rate (CTR) of *M. indica* leaves extract

Extract	Yield (%)	TFC (mg/g)	HTR (%)	CTR (%)
M. indica	8.99	400.314 ±2.221	10.157 ± 0.055	44.850 ± 0.061

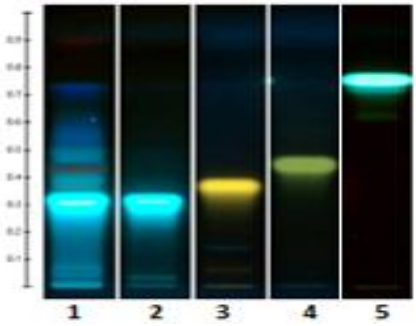

Figure-1: HPTLC flavonoids profile of *M. indica* extract at 366 nm.
1: *M. indica*; 2: Mangiferin; 3: hyperoside (Quercetin3-O-galactoside); 4: isorhamnetine 3-O-glucoside; 5: Kaempferol.

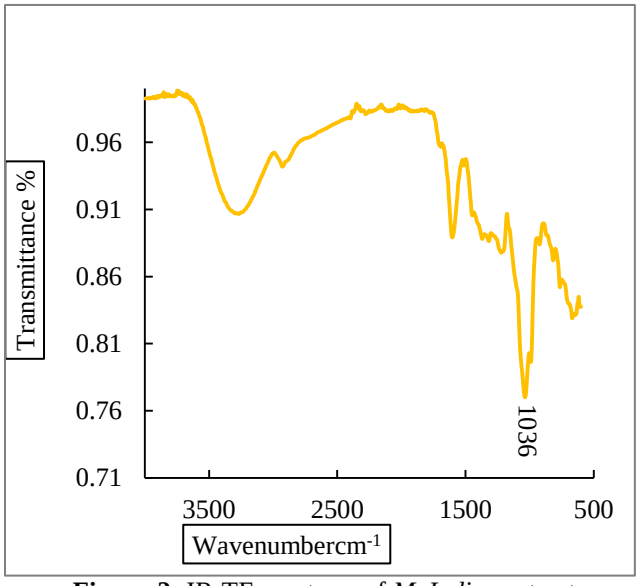

Figure-2: IR-TF spectrum of *M. Indica* extract.

Table-2: HPLC-MS/MS of major flavonoids.

Peaks	Retention Time (min)	Formula	Molecular ions $M+H^+$ (m/z)	Secondary ions (m/z)	Proposed compound
1	44.25	$C_{21}H_{19}O_{12}$	465	303	Quercetin 3-O-hexose
2	45.12	$C_{21}H_{20}O_{11}$	449	287	Kaempferol 3-O-hexose

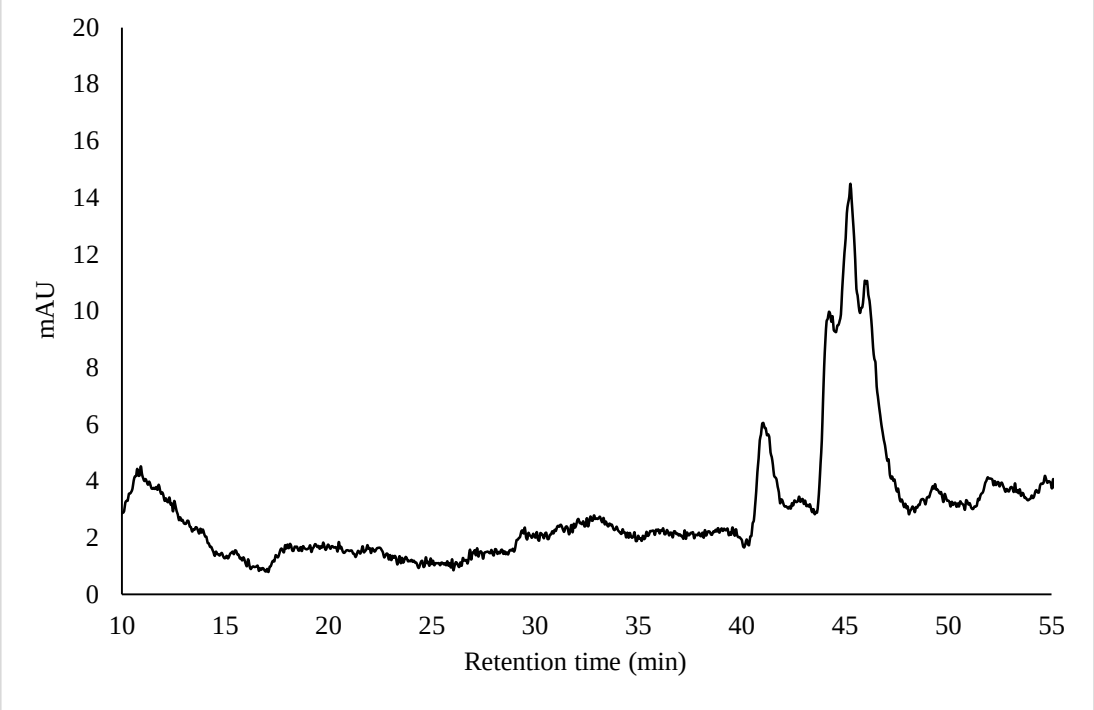

Figure-3: Chromatogram of flavonoids *M. indica* extract.

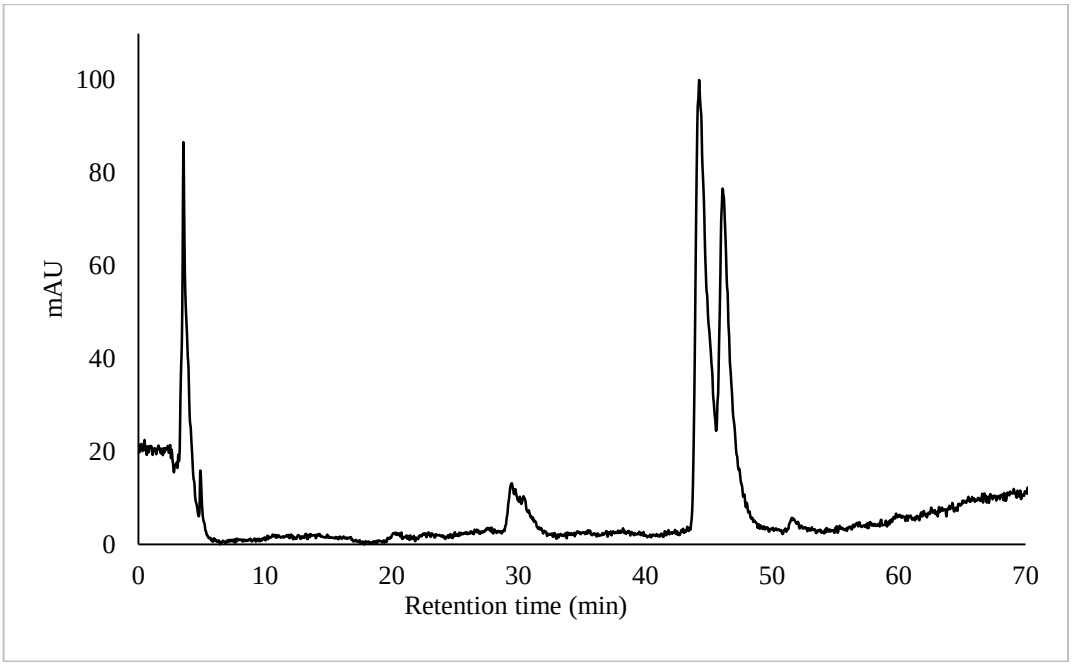

Figure-4: Chromatogram of molecular ion à m/z 465 (compound-1).

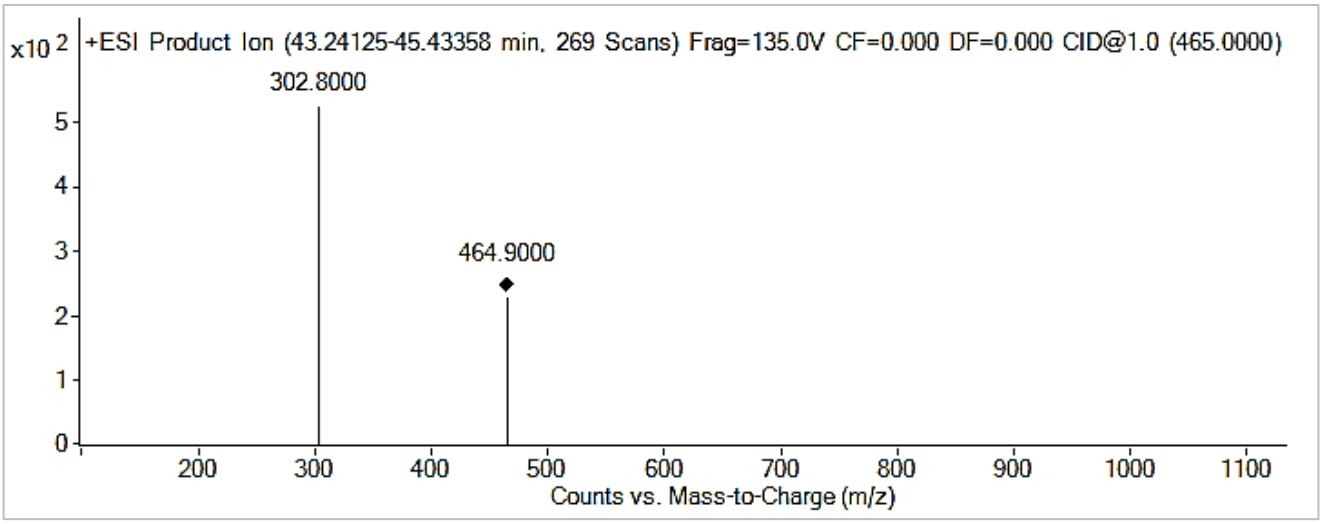

Figure-5: ESI^+ MS/MS spectrum of compound 1.

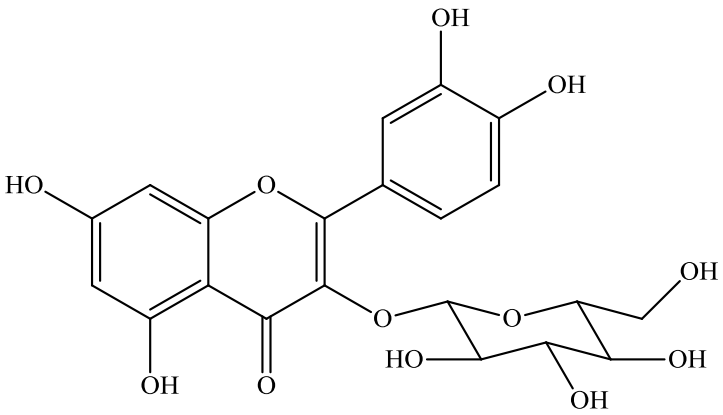

Figure-6: Proposed structure for compound 1.

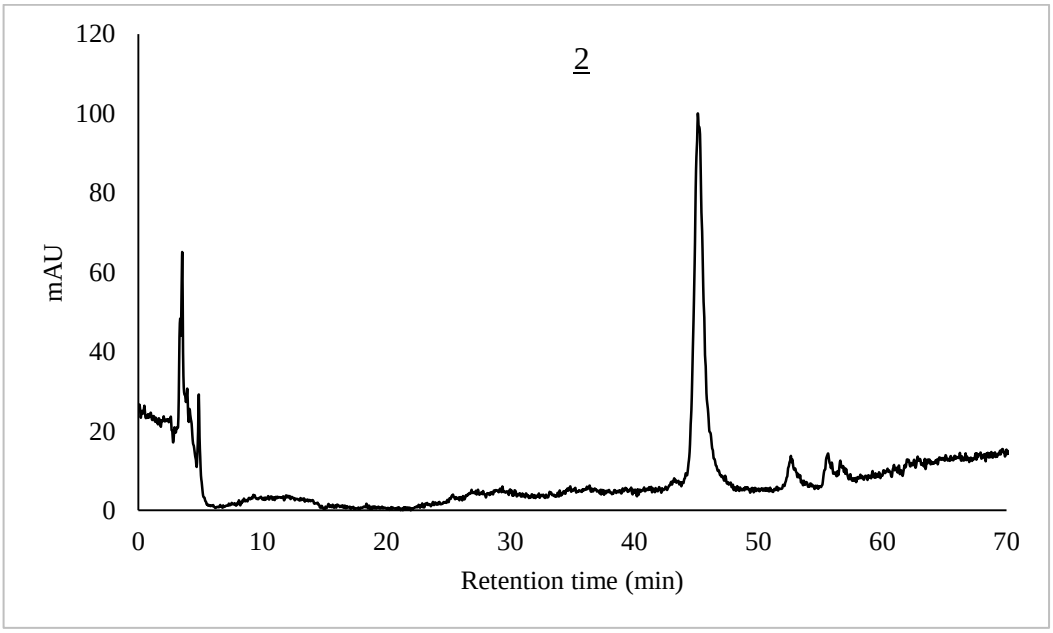

Figure-7: Chromatogram of molecular ion à m/z 449 (compound 2).

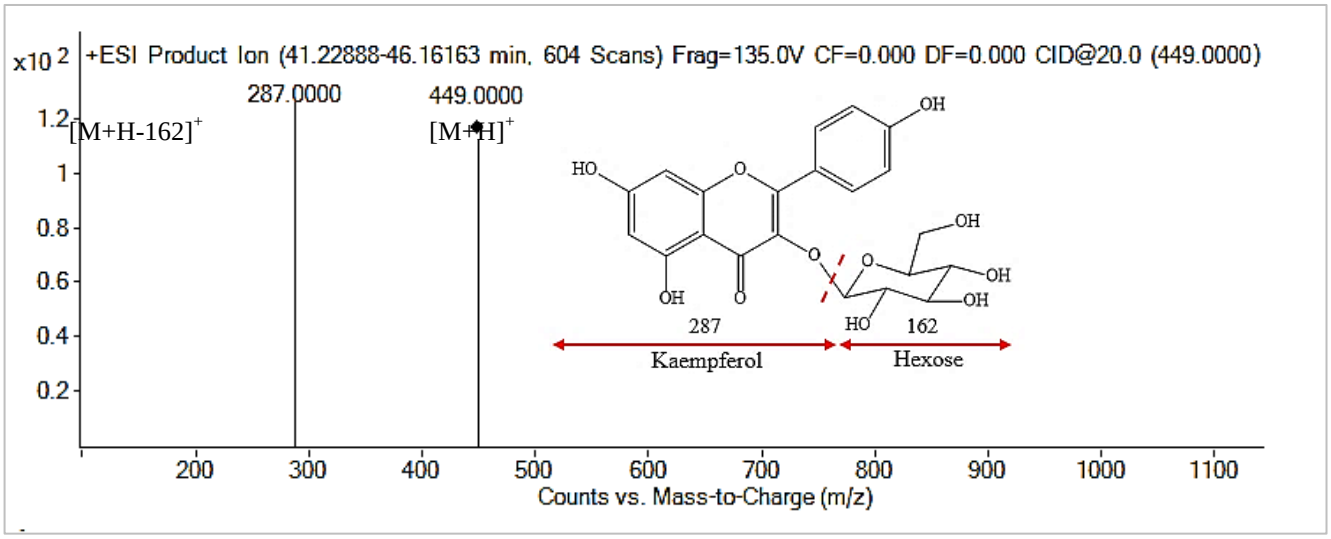

Figure 8: ESI^+ MS/MS spectrum of compound 2.

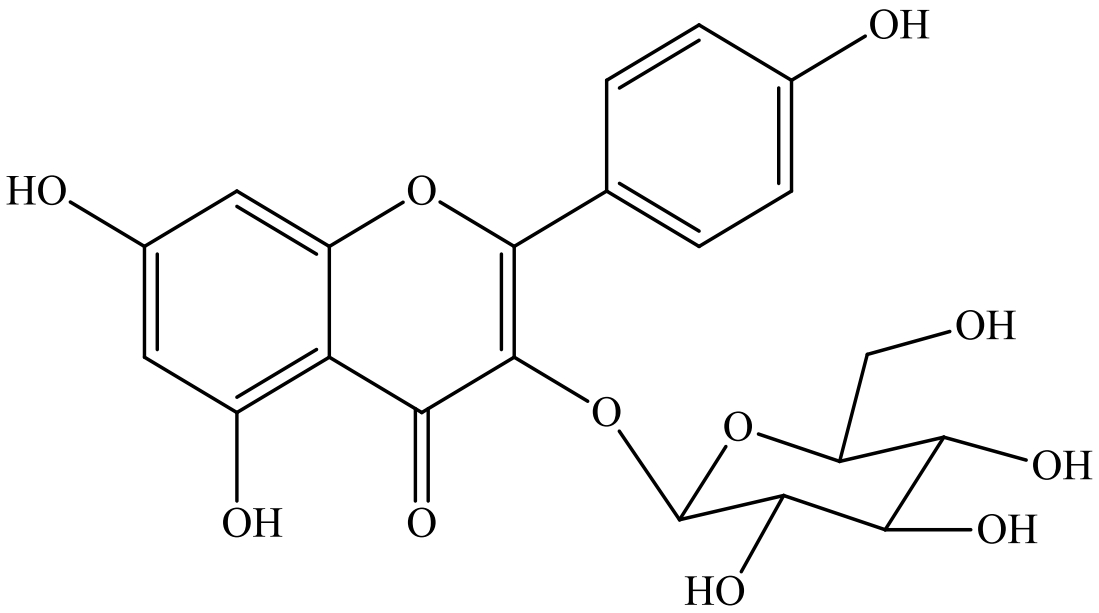

Figure-9: proposed structure for compound 2.

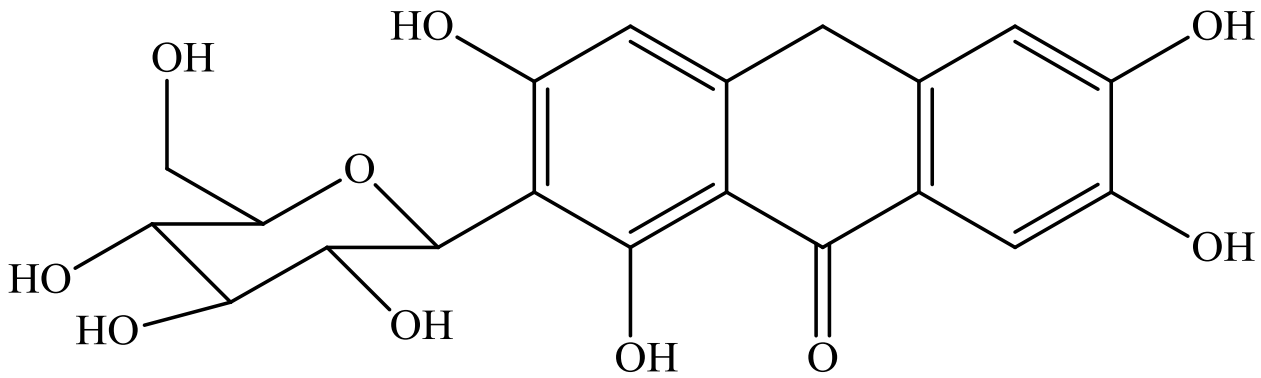

Figure-10: Structure of mangiferin.

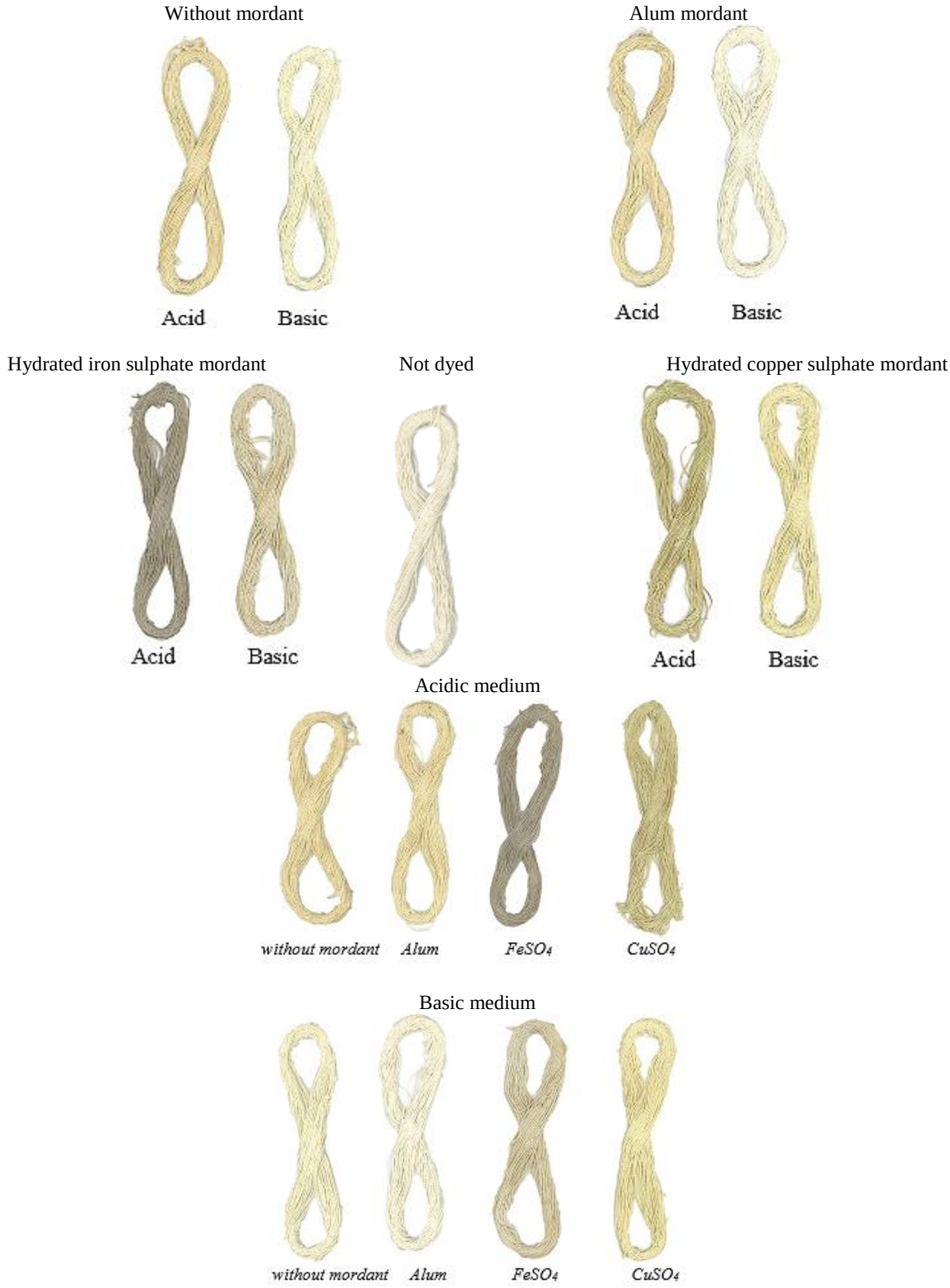

Figure-11: Cotton fibers dyed with *M. indica* leaf extract.

Table-3: Results of tinctorial pratice with *M. indica* dye extract.

	Without mordant		Alum ($KAl(SO_4)_2,12H_2O$)		Hydrated iron sulphate ($FeSO_4,7H_2O$)		Hydrated copper sulphate ($CuSO_4$, $5H_2O$)	
Bath of dye	Acid	Basic	Acid	Basic	Acid	Basic	Acid	Basic
Fixation	2	2	3	3	3	3	2	3
Homogeneity	3	3	3	3	3	2	2	4
QF=CFxCH	6	6	9	9	9	6	4	12
Quality	Good	Good	Very good	Very good	Very good	Good	Very fair	Excellent
Shades of colors	Champagne yellow	Naples yellow	Corn yellow	Light champagne yellow	Cow's tail	Vanilla	March yellow	Nanking yellow
Not dyed								
Skeins dyed								

Legend: Fixation (Scale 1 to 3): 1: non fixation; 2: medium fixation; 3: fairly good fixation, Homogénéité (Echelle de 1 à 4): 1: non-homogeneous; 2: medium homogeneity; 3: fairly good homogeneity; 4: very good homogeneity. FQ: quality factor de; CF: coefficient of fixation; CH: coefficient of homogeneity – FQ≤ 3: bad quality. QF∈3; 6: very fair quality; FQ = 6: good quality; FQ ∈ 6; 9: very good quality; FQ∈ 9; 12: excellent quality.

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