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Juglans nigra: Chemical constitution and its application on Pashmina (Cashmere) fabric as a dye

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ABSTRACT

The shade dried fruit coat husk powder of Juglans nigra (Wall nut) was subjected to column chromatographic separation which yielded 7 fractions. The fractions were then subjected for different spectral (IR, ^{1}H NMR and MS) and chemical analysis. Nine compounds including two 1,4-napthoquinones derivatives, juglone (I) and plumbagin (II), one α-tetralone derivative, (-)-regiolone (III), two sterols, stigmasterol (IV) and β-sitosterol (V), four flavonoids, taxifolin (VI), kaempferol (VII), quercetin (VIII) and myricetin (IX) were isolated from chloroform fraction of aqueous extract of Juglan nigra husk powder. These extracted compounds were subsequently used for dyeing of Pashmina Shawl as natural dye substances which gave promising results. It was inferred that the combined effect of Jugalone and Plumbagin was responsible for the dyeing behaviour of wall nut husk powder.

Key Words: Cashmere, Chemical Constituent, Dyeing, Juglone, Plumbagin.

INTRODUCTION

Walnuts (*Juglans nigra*) are plants in the family Juglandaceae. They are deciduous trees, 10 - 40 metres tall. Walnut has been used in human nutrition since ancient times. The walnut tree is native to central Asia, the western Himalayan chain and Kyrgyzstan [1] and was cultivated in Europe as early as 1000 BC [2]. Walnut kernels have a wide variety of flavonoids, phenolic acids and related polyphenols. These studies have focused on a handful of flavonoids, although thousands of polyphenolics have been identified, and many of them have been attributed anti-

inflammatory [3], anticarcinogenic [4], antitumorigenic [5], good antioxidant, antiatherogenic and antimutagenic properties [6,7]. The present paper deals with the isolation and characterization of chemical constitution of walnut husk grown in J&K. Pashmina which is also known as cashmere wool is a luxurious fibre used for making high quality fabrics. The cashmere fabrics are dyed with natural colours for their further value addition. The present study also attempts to dye the pashmina fabric using the natural dye obtained from walnut husk.

MATERIALS AND METHODS

The walnut husk was collected from Srinagar, Jammu & Kashmir. The husks were dried in shadow and the grinded in to powder using lab model grinding machine.

Purification and Identification of Chemical Constitution

The shade dried fruit coat husk powder (1 Kg) of *Juglans nigra* was exhaustively extracted over a sand bath for 3×12 hours. The resultant extract was concentrated by distilling off the water. The resultant concentrated aqueous solution was extracted with chloroform. The chloroform was removed under reduced pressure and the extract resulted into brown solid mass (200 g) which was subjected to column chromatographic separation and yielded 7 fractions. The fractions were then subjected for different spectral analysis.

IR spectra were recorded on FT-IR Nicolet Magna 550 and Schimadzu 8400 s spectrometers. ^{1}H NMR spectra were measured on JEOL AL 300 MHz FTNMR instrument. Mass spectra (FAB MS) were generated on a JEOL SX-102 spectrometer. Qualitative and quantitative TLC were conducted on aluminium sheets Kieselgel 60F254 (E.Merck). Melting points were determined in soft glass capillaries in an electrothermal melting point apparatus and are uncorrected.

Dyeing of Pashmina Fabric

The fabric used for present study was made of pure hand spun Pashmina yarn with 55-ends/inch and 66-picks/inch. The areal density of shawl fabric was 95 g/m^2.The dyeing of Pashmina fabric with the chemical constituents extracted from walnut husk powder was carried out at pH 4-5 using the following recipe.

Dye	-5%
Acetic acid	- 3gpl
Temperature	- 85°C
MLR	- 1:30
Time	- 1 hr

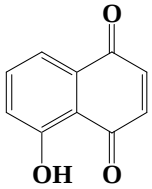
All the dyeing experiments were carried out by exhaustion method in a water bath, keeping material to liquor ratio to 1:30. The scoured Pashmina shawl was introduced into dye bath containing 5% dye (owm) at room temperature and temperature was increased to 85°C with gentle stirring. The dyeing was then continued for one hour. The mordanting with different salts viz aluminium sulphate, stannous chloride and ferrous sulphate of 3% concentration was carried out in the same bath after exhaustion of the dye. The temperature of the bath was allowed to cool below 50°C and the mordant solution of 3% concentration on the weight of the material (owm)

was added to the bath. The temperature was then raised to 85°C and dyeing continued for another one hour. After mordanting, the samples were taken out the bath and thoroughly washed with water, followed by washing with detergent. The washing and light fastnesses of the dyed samples was carried out by standard methods viz. BS 1006 (BO2).

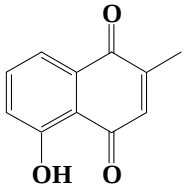
RESULTS AND DISCUSSION

Nine compounds have been isolated from seven fractions of walnut husk powder using column chromatography. The fraction 1 eluted by petroleum ether 100% obtained as red solid mass (70 g) after removal of solvent taken for purification by preparative TLC using petroleum ether: dicholoromethane (4:1) afforded juglone (I), 26 g and plumbagin (II), 25 g. Fraction 2 (5 g) brought out by petroleum ether: chloroform (3:2) as brown solid appeared with brown prisms which were washed with cold petroleum ether and elucidated as (-)- regiolone (III) with the yield of 210 mg. Fraction 3 (10g) turned out by petroleum ether: chloroform (1:4) into pale yellow mass which was purified by preparative TLC using solvent combination petroleum ether: dichloromethane: chloroform (1:2:2) gave 380 mg of stigmasterol (V) and 410 mg of β-sitosterol (V). Fraction 4 (6g) separated out by chloroform 100% as found with colourless powder recrystalized by methanol into white needles analyzed as taxifolin (VI) with the yield of 224 mg. Fraction 5 passed out by chloroform: ethyl acetate (4:1) as a yellow solid followed by preparative TLC separation using chloroform: dichlorofrom: ethyl acetate (2:2:1) yielded 230 mg of kaempferol (VII), and 268mg of quercetin (VIII). Fraction 6 as obtained by chloroform: ethyl acetate (3:2) elution appeared with yellow fibres which were washed with cold benzene to obtain 290 mg of myricetin (IX). The IR, ^{1}H NMR and Mass Spectra results of the separated compounds and the derived structures are given below:

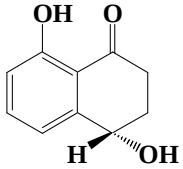
Juglone (I): Orange rosetts; 26 g; m.p. 157-58 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3465 (OH), 1650 (C=O), 1635 (H-bonded C=O); ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 7.02 s (2H, H-2 and H-3), 7.35 dd (1H, J = 7.8, 2.7 Hz, H-6), 7.51 m (2H, H-7 and H-8), 12.1 s (1H, H-bonded OH); MS (*m/z*): 174 $[M]^+$, $C_{10}H_6O_3$.



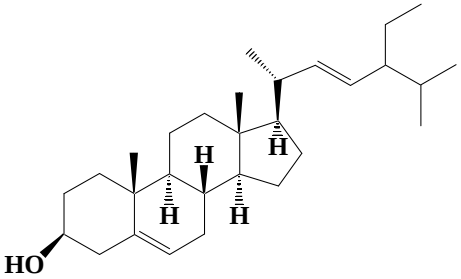
Plumbagin (II): Yellow needles; 25 g, m.p. 78-79 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3468 (OH), 1654 (C=O), 1640 (H-bonded C=O); ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 6.99 s (1H, H-3), 7.36 dd (1H, J = 7.9, 2.6 Hz, H-6), 7.54 m (2H, H-7 and H-8), 11.98 s (1H, H-bonded OH), 1.8 s (3H, CH_3); MS (*m/z*): 188 $[M]^+$, $C_{11}H_8O_3$.



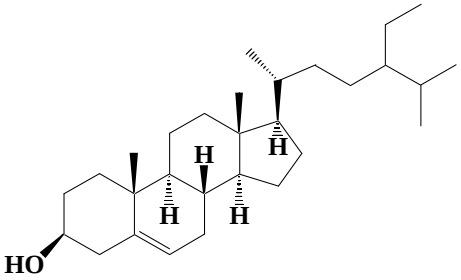
(-)- Regiolone (III): Colourless fibres; 210 mg; m.p. 73-74 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 1640 (H-bonded C=O); 3260-3390 br (H-bonded OH); 735 (aromatic); ^{1}H NMR [300 MHz, solvent $CDCl_3$,δ (ppm)]: 6.88 dd (1H, J = 7.5, 1.5 Hz, H-7), 6.99 dt (1H, J = 7.5, 1.5, 1.1 Hz, H-5), 7.52 t (1H, J = 7.7 Hz, H-6), 12.11 s (1H, 8-OH), 4.89 m (1H, H-4), 2.87 ddd (1H, J = 18.5, 9.0, 5.0 Hz, H-2α), 2.70 ddd (1H, J = 18.5, 9.0, 5.0 Hz, H-2β), 2.32 m (1H, H-3β), 2.16 m (1H, H-3α), 3.04 s (1H, 4-OH)); MS (*m/z*): 178 $[M]^+$, $C_{10}H_{10}O_3$.



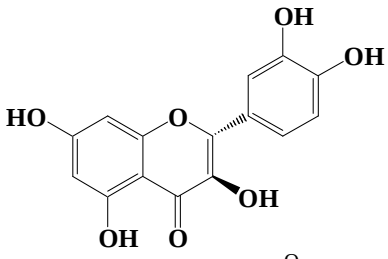
Stigmasterol (IV): colourless needles; 380 mg; m.p. 168-70 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1600, 1460, 1380, 1260, 1050; ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 5.35 brt (H-6), 5.06 dd (J = 16, 10 Hz, H-22), 5.14 dd (J = 16, 10 Hz, H-23), 3.50 m (H-3), 1.00 (J = 7 Hz, H-21), 1.16 s (H-27), 0.93 s (H-19), 0.70 s (3H, H-18); MS (*m/z*): 412 $[M]^+$, $C_{29}H_{48}O$.



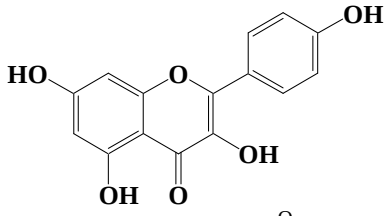
β-Sitosterol (V): Colourless flakes; 410 mg; m.p. 136-37 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1640 (C=C), 1065 (C=O), 1025, 930, 820, 800; ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 5.27 tbr (H-6), 3.50 (H-3), 2.00-0.70 (complex multiplets); MS (*m/z*): 414 $[M]^+$, $C_{29}H_{50}O$.



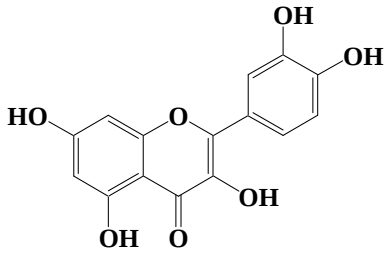
Taxifolin (VI): light brown powder; 224 mg; 232-33 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1635 (C=O), 1530, 1450, 1378, 1255, 1145; ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 4.98 d (1H, J = 10.8, H - 2), 5.80 d (1H, J = 5.9 Hz, 3-OH), 4.51 d (1H, J = 7.0 Hz, H-3), 12.11 s (1H, 5-OH), 5.88 s (1H, H-8), 6.71 s (1H, H-2'), 6.86 s (1H, H-5'), 6.72 s (1H, H-6'); MS (*m/z*): 302 $[M]^+$, $C_{15}H_{10}O_7$.



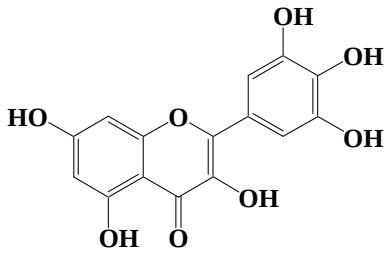
Kaempferol (VII): Yellow powder, 230 mg; 276-77 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3395 and 2930 (aromatic), 1625 and 1450 (quinoid moiety), 1380 (OH); ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 6.20 d (1H, J = 1.5 Hz, H-6), 6.44 d (1H, J = 1.5 Hz, H-8), 6.88 d (2H, J = 9.0 Hz, H- 3', 5'), 8.11 d (2H, J = 8.8 Hz, H-2', 6'); MS (*m/z*): 286 $[M]^+$, $C_{15}H_{10}O_6$.



Quercetin (VIII): Yellow Powder, 268 mg, 314-15 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3400 and 2910 (aromatic), 1628 and 1458 (quinoid moiety), 1370 (OH); ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 6.22 d (1H, J = 2.0 Hz, H-6), 6.42 d (1H, J = 2.0 Hz, H-8), 7.01 d (1H, J = 9.1 Hz, H-5'), 7.44 dd (1H, J = 9.0, 2.5 Hz, H-6'), 7.72 d (1H, J = 2.1 Hz, H-2'); MS (*m/z*): 302 $[M]^+$, $C_{15}H_{10}O_7$.



Myricetin (IX): Yellow powder; 290 mg; m.p. 342-44 ^{O}C; IR ν_{max} (KBr) cm^{-1}: 3390 and 2920 (aromatic), 1625 and 1455 (quinoid moiety), 1368 (OH); ^{1}H NMR [300 MHz, solvent $CDCl_3$, δ (ppm)]: 6.12 d (1H, J = 1.5 Hz, H-6), 6.32 d (1H, J = 1.5 Hz, H-8); 6.84 s (2H, H-2', 6'), 12.19 s (H-bonded OH); MS (*m/z*): 318 $[M]^+$, $C_{15}H_{10}O_8$.



All the identified compounds are matched with the findings of the available literature viz. Juglone [8,9], Plumbagin [8], Regiolone [9], Stigmasterol [10,11], β-Sitosterol [12-14], Taxifolin [15], Kaempferol [15,16], Quercetin [15-17], Myricetin [15-17]. The chemical compounds isolated from the walnut husk dyed the Pashmina fabrics satisfactorily with and without the use

of mordants. The colour obtained on the pashmina fabric using walnut husk dye extract and their fastness properties are given Table 1.

The results showed that the extracted compounds from wall nut husk produced brown colour on Pashmina fabric. The brown colour may be due to fraction I consist on Juglone and Plumbagin which are the major colouring compounds identified from the wall nut husk powder. It is well documented that Juglone is the major colouring compound in wall nut husk powder. However, the present study indicated that Plumbagin also responsible for the colouring ability on textiles. The mordanted fabrics showed coffee brown with aluminium sulphate, reddish brown with stannous chloride and dark grey with ferrous sulphate. The change in colour may be due to difference in coordination complexes between dye and metal ions during mordanting process.

It is also observed that the walnut husk extract dyed the Pashmina wool with bright colours with good fastness properties. The washing fastness results showed that all the dyed samples of walnut extract in acidic condition have good to very good fastness properties on Pashmina fabric with and without the use of mordants. The light fastness of the dyed samples was also good. The washing and light fastness properties of the dyed samples improved after mordanting. However, the shade produced during acidic pH changed to slightly redder hue during washing with detergent. Hence, it is very important to give a soaping treatment for the Pashmina fabric dyed after dyeing to maintain the colour during usage.

CONCLUSION

Nine different chemical constituents were separated and identified from wall nut husk powder. They separated compounds can be used as dye to dye the Pashmina fabric. The combined effect of Juglone and Plumbagin is responsible for dyeing behaviour of wall nut husk powder. The washing and light fastnesses of walnut husk dyed Pashmina fabric was satisfactory. Hence, this process can be considered as a commercially viable process of dyeing Pashmina fabrics. The process enhanced the value of walnut as well as Pashmina wool fabric due to waste utilization and eco friendly dyeing.

Acknowledgement
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