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Optimization of dyeing processes by compounds isolated from bark of *Myrica esculenta* and their spectroscopy identification

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Abstract

Myrica esculenta **(Myricaceae) commonly known as Kaphal is a small aromatic evergreen tree, abundantly grows in the sub-tropical Himalaya from Kashmir to Bhutan. Commonly associated with Oak and Rhododenderon forests. The bark of the tree is utilized for its astringent, stimulant and resolvent properties. The decoction of the bark along with cinnamone is given in chronic cough and piles. The bark of the plant is used as a dye in ancient Indian traditions and also as a natural mordant. The berries of the plant is one of the richest source of wax, used as a raw material for candle and soap making industries. A number of flavonoids, tannins, Xanthones, terpines and many other anthocyanins have been isolated from the different part of the plant. The present paper deals with isolation and characterization of secondary metabolites namely 2-methyl pyrane 3-O-α-D-glucoside and Flavone 3,'4,' dihydroxy 6-methyl 7-O-α-L-rhamnopyranoside from the plant and optimization of dyeing procedure with isolated compounds on different fibres like silk, wool, cotton etc with and without natural and synthetic mordants. Efforts will be made to check the washing and light fastness properties of dyed samples.**

Introduction

Myrica esculenta (Myricaceae) commonly known as Kaphal is a small aromatic evergreen tree, abundantly grows in the sub tropical Himalaya from Kashmir to Bhutan.Commonly associated with Oak and Rhododenderon forests.

Materials and Method

M.Ps. were incorrected , UV spectra were determined in methanol using $AlCl_3$ as shift reagent. IR recorded in KBr on a Perkin Elmer FT–IR spectrometer. ^{1}H-NMR were run at 300 MHz using TMS as internal standard and C_5D_5N and CD_3OD as solvent. ^{13}C-NMR recorded in 90MHz using CD_3OD as solvent. FAB-MS on a JOEL, JMS 700 Mstaion spectrophotometer.

Plant material:

The bark (2kg) of *Myrica esculenta* were collected from sainti Ghat, Chamoli Garhwal, Uttarakhand India and identified from ethanobotanical plant identification laboratory, Department of Botany HNB Garhwal University Srinagar Garhwal. A voucher specimen was deposited in herbarium of the department.

Extraction and Isolation

The air dried bark of the plant (2) Kg were exhaustively extracted with aqueous ethanol. The concentrated extract after evaporation on water bath was fractionated through column chromatography, using chloroform-methanol as eluting system. Increase in the polarity of methanol affords compounds 1 and 2 respectively. Compound 1 and 2 were identified as 2-methyl pyrane 3-O-α-D glucoside and flavone 3,'4,' dihydroxy 6-

methyl 7-O-α-L-rhamnopyranoside.

Compound 1: It was crystallized from ethyl acetate as yellow amorphous powder, **M.P. 325-327 ^{0}C, Molecular Formula $C_{12}H_{10}O_3$, IR(λ_{max}^{KBr})Cm^{-1}** -1655, 1612 (C=O).

^{1}H-NMR-(C_5D_5N, δppm) 7.17(1H,d,J=8Hz,H-5), 7.19 (1H,d, J=8Hz, H-6), 1.29 (3H, S, CH_3), 5.03 (1H, J=4Hz, H-1) (anomeric proton) 3.31-3.92 (Sugar protons) **^{13}C-NMR (C_5D_5N, δppm)-**132.6 (C-2), 163.0 (C-3), 199.4 (C-4), 131.6 (C-5), 117.2 (C-6), 26.4 (-CH_3), 101.6 (C-1'), 74.9 (C-2'), 77.9 (C-3'),71.2 (C-4'), 78.3 (C-5'), 62.3 (C-6').

Compound 2: It was crystallized from methanol as yellow crystalline solid, **M.P.-240-242 ^{0}C, Molecular Formula- $C_{22}H_{26}O10$, Molecular Weight- 450 amu, IR(λ_{max}^{KBr})Cm^{-1}** -3410, 1650, 1600,1525, 1430.

FAB-MS (M/Z): 489 [M+K], 450 [M+H]$^+$, 307 [M+3H-146], 289 [M+3H-146+H_2O], 273 [M+3H-146+2H_2O]. 242 [M-(146+2OH+OCH_3)]

^{1}H-NMR-(C_5D_5N, δppm): 6.06 (d,J=1.2Hz, H-3), 7.7 (S, H-5), 7.1 (d, J=1.2 Hz, H-5'), 6.9 (d, J=3.2 Hz, H-6'), 7.3 (S, H-5), 6.38 (S, H-2'), 1.72 (rhamnose, 3H), 2.16 (S, OCH_3, 3H), 3.32-3.43 (rhamnose, 5H), 4.2 (S, rhamnose, H-1')

^{13}C-NMR (CD_3OD, δppm): 146 (C-2), 106.1 (C-3), 179.6 (C-4), 122 (C-5), 163 (C-6), 165.8 (C-7), 94.0 (C-8), 148.9 (C-9), 105 (C-10), 121 (C-1'), 116 (C-2'), 158 (C-3'), 159.6 (C-4'), 116.3 (C-5'), 116.9 (C-6'), 53.7 (OCH_3)

Rhamnose: 103 (C-1'), 72.0 (C-2'), 71.9 (C-3'), 73.2 (C-4'), 70.0 (C-5'), 17.6 (C-6')

Results and Discussion

Ethanolic extracts of dried and powdered bark of *Myrica esculenta* after repeated column chromatography afforded compound 1 and 2.

Compound 1: It was crystallized from ethyl acetate as yellow amorphous powder, M.P.-325-327 ^{0}C. It gave positive test with Molish reagent thereby indicating the glycosidic nature of compound. The IR Spectrum displayed a peak at 1655 and 1612 cm-1, which showed the presence of carbonyl function.

^{1}H- NMR spectrum of compound showed two separate doublets each integrating for one proton at ä 7.17 (J=8.0 Hz) and ä 7.79 (J=8.0 Hz) were attributed to the C-5 and C-6, while a singlet appeared at ä1.29 was assigned for a methyl group present in the compound.

The ^{1}H-NMR spectrum further shows a doublet at ä 5.03 (J=4H2) was assigned for C-1' carbon atom of glycosidic linkage. The other suger protons are appeared in between d3.31-3.92 ^{1}H –NMR spectrum.

^{13}C-NMR spectrum of a compound shows presence of twelve carbon atoms. The down field peak at ä 199.4 in ^{13}C-NMR spectrum indicating the presence of á,â un saturated carbonyl group present in the compound. C-5 and C-6 were found to be appeared at ä 133.6 and ä 117.2. Thus on the basis of above observations, it was identified as 2-methyl pyran -3-0- â-D- glucoside. Use of compound as a dye on some fibres (like silk, cotton, wool) proves its excellent deing properties (Results-Table.1)

Compound 2 –It was crystallized as yellow crystals from methanol, M.P 240-242 ^{0}C, Molecular Weight 450 (From FAB-MS). It gave positive Molish reagent test and also test with NaOH, $FeCl_3$, Mg- HCl, which indicates its glycosidic nature. IR absorption bands at 3410,1650,1600,1525,1430 were characteristics for

flavonoid glycoside. FAB-MS provides a peaks at 489 [M+K], 450 [M+H]$^+$, 307 [M+3H-146], 289 [M+3H-146+H_2O], 273 [M+3H-146+2H_2O]. 242 [M-(146+2OH+OCH_3)] shows the loss of one deoxy hexose two Hydroxyl and one methoxyl group respectively.

^{1}H-NMR spectrum displayed doublets of 1.2Hz coupling constant at 6.06 and 7.1 were characteristic for H-3 and H-5', where as singl*et at.,* ä7.3,7.7and 6.38 were assigned for H-2', H-8 and H-5. Further the two singlet at δ1.27 and δ2.16 were assigned for rhamnose and aromatic methoxyl. The position of singlet at δ4.2 indicate a configuration of rhamnose. In ^{13}C-NMR spectrum the down fill peak at δ179.6 assigned for C-4 (Keto group) δ163.4 (C-6), 159.6 (C-4'), 158.0 (C-3') and 165.8 (C-7) support substitution at these positions. Methoxy carbon function resonated at δ53.7 which was assigned at C-6 (δ163.4) in ring A. On acidic hydrolysis (with 7% methanolic HCl) it afford an aglycone identified as 3,'4,' dihydroxy 6-methyl flavone. (Comparison with reported data and authentic sample) and rhamnose (Rf values, PC). Thus on the basis of these observations compound 2 was identified as as flavone 3,'4,' dihydroxy 6-methyl 7-O-α-L-rhamnopyranoside. Compound is used as a yellow dye in dyeing processes. (Table-2).

Optimization of Dyeing processes with isolated compounds from *Myrica esculenta*

Compound 1: A pure yellow amorphous powder. Identified as 2-methyl pyrane 3-O-â-D-glucoside. It imparts yellow colour on wool and greenish yellow colour on cotton samples .The dyed fabrics showed 37% absorption in ultraviolet region in UV Spectrophotometer. Compound showed excellent washing and light fastness properties with and without mordants in different fibres.

References

C.L., Bird, 1972. *Theory and Practice of Wool Dyeing*, Society of Dyers and Colourist, 4 Edn.

Gaur, R.D., 1999. "*Flora of District Garhwal*" 1st edition, Transmedia, Srinagar Garhwal.

M. Mizuno, M. Kato, N. Hosoi, N. Linuma, T. Tanaka, A. Kimura, H. Ohashi, H.Sakai and T. Kajita,1992. ***Heterocycles,*** 31, 1409.

R.H.M.J, Lemmens and N. Wulijarni-Soetijipto 1991. ***Dye and Tannin producing plant.*** Plant Resources of South East Asia, Vol-3.

Sati, S.C., Rawat, U., Sati, O.P., Srivastav, B. 2003. ***Colourage***, 44.

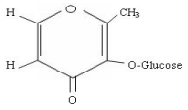
Table:1- Dyeing of Cotton and Wool Samples with Isolated Compound-1

Textile	Wool and Cotton fibres
Ingredients	5 mg compound+100 ml H_2O+2 ml CH_3COOH
Pots	Stainless steel/glass
Water	Tape water enough to cover the yarn.
Mordants	Chrome/Symploccous bark powder
Method of Dyeing	Pre-mordanting
Results	1. Yellow colour on wool fibres. 2. Greenish yellow to brown on cotton.

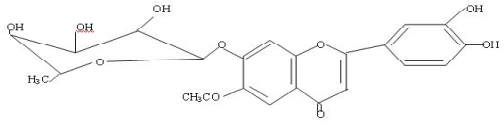
Compound 2: Pure yellowish crystals. Identified as **Flavone 3,'4,' dihydroxy 6-methyl 7-O-α-L-rhamnopyranoside,** produce yellowish grey colour without any mordant with excellent fastness properties toward washing and light. But colour changes was observed from yellow to brown when mordanted with different natural and synthetic mordants. It shows 48% absorption in mordanting stage whereas only 27% absorption without mordant in ultraviolet region.

Table:2- Dyeing of Cotton and Wool Samples with Isolated Compound-2

Textile	Wool and Cotton fibres
Ingredients	5 mg compound+100 ml H_2O+2 ml CH_3COOH
Pots	Stainless steel/glass
Water	Tape water enough to cover the yarn.
Mordants	Chrome/Symploccous bark powder
Method of Dyeing	Pre-mordanting
Results	1. Dark yellow colour on wool fibres. 2. Muddy yellow colour on cotton firbres. 3. Faint yellow colour without mordant.



COMPOUND-1



COMPOUND -2