CHEMICAL CONSTITUENTS FROM THE BARK OF
QUERCUS LEUCOTRICHOPHORA

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ABSTRACT

From the bark of Quercus leucotrichophora β- Sitosterol, Kaempferol 7-O- methyl ether and 3-α (rhamnopyranosyl (1-4) α-L rhamnopyranosyl (1-6)- β-D glucopyransosyl quercetin were isolated. All constituents were identified by spectral studies.

Key words: Chemical Constituents, Bark, Quercus leucotrichophora

INTRODUCTION

Quercus leucotrichophora belongs to family Fagaceae to family fagaceae, is an evergreen tree up to 40 meter height with pale grey or blackish bark. It founds most abundantly on North East slope of submontane to montane Himalaya of Garhwal region or otherwise usually associated with Rhododendron and Myrica species (1). The gum of the plant is diuretic and used to treat gonorrhea and diarrhea. The seeds are used as a tonic and its seed oil is used for massage in the treatment of arthritis and rheumatism (1)

MATERIAL AND METHODS

Collection of Plant Material

The bark Quercus leucotrichophora was collected from the forests of Nagdev, Pauri Garhwal Uttarakhand in the month of October. The identity of the Plant was confirmed from Ethano-Botanical Plant identification Laboratory, Department of Botany H.N.B. Garhwal University, Srinagar Garhwal. A voucher specimen is available in the Plant identification Laboratory.

Extraction and Isolation

The air dried bark of the plant were finely powdered and defatted with light petroleum in soxhlet. The defatted mass was exhaustively extracted with 90% EtOH repeatedly until the extractive became colourless. All the extract were mixed together and concentrated under reduced pressure using vacuum evaporator. The extract was
then fractionated through column chromatography using Chloroform: Methanol as eluting solvent. The polarity of solvent was gradually increased by addition of methanol. The repeated column chromatography afforded Compound 1 and 2 together with β-Sitosterol (Direct comparison with authentic sample).

RESULTS AND DISCUSSION

It was crystallized from MeOH as pale yellow needles

M.P. - 226-228°C
Molecular Formula - C_{16}H_{12}O_{6}
Molecular Weight - 300 amu
UV (\gamma_{\text{Max}}^{\text{MeOH}})\text{nm} - 270, 275, 280, 373, 390
IR (\gamma_{\text{Max}}^{\text{KBr}})\text{cm}^{-1} - 3480, 3260, 1650, 1600, 1500, 1420, 1350, 1340, 1280, 1220.

\text{\textsuperscript{1}H-NMR (CD_{3}OD, \delta \text{ ppm})}

3.83 (3H, s, OMe), 6.23 (1H, d, J= 2.5 Hz, H-6), 6.49 (1H, d, J= 2.5 Hz, H-8), 6.87 (2H, d, J= 8.7 Hz, H-13, 15), 8.06 (2H, d, J= 8.7 Hz, H-12, 16)

\text{\textsuperscript{13}C-NMR (CD_{3}OD, \delta \text{ ppm})}

148.3 (C-2), 137.4 (C-3), 177.4 (C-4) 162.1 (C-5), 98.5 (C-6), 167.0 (C-7), 92.7(C-8), 158.1(C-9), 105.4(C-10), 123.6 (C-11), 130.7 (C-12,16), 116.3 (C-13, 15), 160.6 (C-14), 56.4(OMe).

It was crystallized from methanol as pale yellow needles. It gave green colouration with FeCl\textsubscript{3} and positive test with Mg/HCl thereby indicating the flavonoid nature of compound (2). The IR spectrum of compound furnished two absorption bands at 3480cm\textsuperscript{-1} and 3260cm\textsuperscript{-1} for chelated and non -chelated OH functions, the other IR absorption bands were observed at 1650cm\textsuperscript{-1} and 1600cm\textsuperscript{-1} for αβ unsaturated carbonyl and 1500cm\textsuperscript{-1}, 1420cm\textsuperscript{-1} for ether function. \text{\textsuperscript{1}H-NMR spectrum of compound 1 displayed two meta coupled doublets each for 1H at }\delta 6.23 (J=2.5Hz, H-6) and \delta 6.49 (J=2.5Hz, H-8) \text{ and two ortho coupled }A_{2}B_{2} \text{ type doublets each with } J \text{ value 8.7 Hz at }\delta 6.87 \text{ and }\delta 8.06 \text{ assigned for H-13, H-15, H-12 and H-16 respectively, suggested a tetra substituted nature of the compound 1. It was further supported by its }\text{\textsuperscript{13}C-NMR data appeared at }\delta 130.7 (C-12, 16) \text{ and }\delta 116.3 (C-13, 15) \text{ which were corresponded with hydrogen bearing carbon of p-cresol (3). The }\text{\textsuperscript{13}C-NMR spectrum showed other peaks at }\delta 177.4 \text{ for C=O}
at C-4 a benzylic carbon at δ 148.3 and an oxygen bounded ethylenic carbon atom at δ 137.4 (C-3). On the basis of all these data the structure of compound 1 was identified as Kaempferol 7-O - methyl ether, which was further supported by reported data of rhamnocitrin (4).

**Compound 2**

It was crystallized from EtOH as pale yellow crystals.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>M.P.</td>
<td>232-234°C</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>756 amu</td>
</tr>
<tr>
<td>FAB-MS (m/z)</td>
<td>755[M-H]-, 609[(M-H)-146]-, 463[M-H]- 2x146]-, 301 [(M-H) - 2x146 + 162] -</td>
</tr>
</tbody>
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$^1$H-NMR (CD$_3$OD, δ ppm)

4.4 (1H, d, anomeric of rhamnose), 4.6 (1H, d anomeric of rhamnose), 5.3 (1H, d, J= 6.5 Hz, anomeric of glucose).

$^1$H-NMR (CD$_3$OD, δ ppm) (Aglycone)

160.7 (C-2), 149.6 (C-3), 177.4 (C-4), 160.9 (C-5), 149.2 (C-6), 165.1 (C-7), 92.3 (C-8), 157.7 (C-9), 133.6 (C-2'), 156.3 (C-5'), 97.3 (C-6').

(Glycone)

Glu-104.96 (C-1'), 73.58 (C-2'), 71.15 (C-3'), 78.0 (C-4'), 73.05 (C-5'), 65.65 (C-6').

Rham-102.28 (C-1''), 70.90 (C-2''), 72.18 (C-3''), 70.50 (C-4''), 70.40 (C-5''), 17.77 (C-6'').

Rham-100.21 (C-1''), 70.00 (C-2''), 70.00 (C-2''), 68.57 (C-3''), 68.24 (C-4''), 68.15 (C-5''), 17.60 (C-6'').

It was crystallized from EtOH as pale yellow crystals. It gave characteristic test for flavonoids and also a Molish's test for carbohydrate, thereby indicating the flavonoidal glycosidic nature of compound 2. The molecular ion peak observed at m/z 755 [M-H] in its FAB-MS, which conclude the molecular weight of compound is 756 amu. Other fragmentation peaks appeared at m/z 609 [(M-H)-146], 463 [(M-H)-2x146] and m/z 301 [(M-H) -2x146+162] - corresponding the sequential loss of two deoxy hexosyl and one hexose unit from molecular ion peak. Acidic HOH of the compound gave an aglycone identified as quercetin (by direct comparision with authentic sample) and a mixture of mono saccharide identified as glucose and rhamnose (PC with suger samples). On
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Compound-1

Compound-2

per methylation compound 2 afforded 2,3-di-O methyl D-glucose and 2,3,4-tri O- methyl L-rhamnose. The types of linkage at the glycosidic points were found to be D-glucose-β and L-rhamnose-α by 1H-NMR and 13C-NMR data. The anomeric signals corresponding to D-glucose unit was observed, at δ 5.3 (1H, d, J= 6.5 Hz) and 1H of rhamnose was observed at δ 4.6 (brd).

From above spectral studies compound 2 was identified as and 3-O {α L-rhamnopyranosyl (1-4) α-L-rhamnopyranosyl (1-6) β-D-glucopyranosyl quercetin.

REFERENCES: