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Flavone glycoside from the roots of *Fironia limonia*

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ABSTRACT

From the water insoluble part of alcoholic extract of the roots of *Feronia limonia* a new flavone glycoside has been isolated. On the basis of U.V, I.R, N.M.R (^{1}H, ^{13}C) and mass spectral studies the compound was characterized as 5,4'-dihydroxy-7-methoxyflavone-8-O-β-D-glucopyranoside

Key words: *Fironia limonia*, Flavone, Glycoside, Glucopyranoside.

INTRODUCTION

Feronia limonia (syn. *Feronia elephantum*), commonly known as wood apple or *kaitha* in *Hindi*, is a common Indian tree belongs to family Rutaceae. It is widely distributed in India, Ceylon, Bangladesh and Java. All the parts of the plants are prescribed in indigenous system of medicine for the treatment of various ailments. The bark is generally used as remedy for bites and strings of venomous insects and some times it is also prescribed for biliousness. The fruits of the plant are edible and are considered to be used for stomach-ache, as astringent, diuretic, cardio tonic and tonic for the lungs and liver. The leaves are used in carminative mixture for the treatment of indigestion and minor bowel affections in children. The root of the plant is also prescribed by the physicians for the snake bites patients[1-4]. The different parts of the plants have been investigated by several workers and found to contain coumarins, furanocoumarins, lignans, alkaloids, steroids and flavonoids[5-12]. The presence of flavonoids, coumarins, lignans, acridone and steroids derivatives are significant as they exhibit anti-oxidant activity. Flavonoids have exhibited in many ranges of activities including anti-inflammatory, antibiotics, anti-viral and hepatoprotective, which may be due to their activities to seavenge free radicals. Furanocoumarins show photosensitizing effect, xanthotoxin and bergapten are used for the treatment of leucoderma. 8-methoxy psoralen is commonly used in the phytochemotherapy (PUMA - therapy) of hyperpropraliferatives skin diseases such as psoriasis, micosis, fungoids and vitiligo[13-18].

RESULTS AND DICUSSION

The compound was obtained as yellow amorphous powder (mp 243-245°C). The compound gave a purple coloured spot on TLC, when examined under UV light. The compound showed positive test for sugar and flavonoid moiety suggested that the compound may be a flavanoid glycoside. The molecular ion peak at m/z 462 $[M+H]^{+}$ in its electro spray mass spectrum corresponded to the molecular formula $C_{22}H_{22}O_{11}$.

The IR spectrum bands appeared at 3420(OH), 1650(α, β- unsaturated carbonyl group), 1610 (aromatic C=C) cm^{-1}. This together with UV bands at λ_{max} 279, 305 nm confirmed the presence of flavone moiety. The acid hydrolysis of this compound furnished an aglycone, which demonstrated a molecular ion peak at m/z 300 in its mass spectrum, suggesting a flavone bearing three hydroxyl and one methoxy groups. The appearance of mass fragments at m/z 118 and 183 together with UV bands at λ 272.6 and 325.0 of aglycone further supported the presence of flavone skeleton with mono substituted B-ring. The NaOMe shift of band I with increase in intensity in UV spectrum of both glycoside and aglycone, suggested the free para –OH group in ring B. The ortho-coupled protons of ring B resonated as doublet at δ 8.11 and δ 6.94 were assignable to 2^{-2} /6^{-2} and 3^{-2}/5^{-2} protons. The chemical shift values of C-1^{-2}, C-2^{-2}, C-3^{-2}, and C-4^{-2} in ^{13}C NMR of the compound were also compatible with flavone bearing para hydroxyl group in ring B. The acid stable bathochromic shift with $AlCl_3$ in UV spectrum of both glycoside and aglycone suggested a free OH group at C-5. The singlets appeared at ä 6.83 of glycoside and at δ 6.75 of aglycone in this ^{1}H NMR spectra, corresponded to the H-3 proton. The ^{13}C NMR of glucoside showed chemical shift for total twenty two carbon atoms. The appearance of methoxy carbon at 56.4, suggested that at least one ortho position of methoxy group is free. The absence of the shift in band II in UV spectrum of both glycoside and aglycone in the presence of NaOAc fixed the position of $–OCH_3$ at C-7. The remaining one hydroxyl group can be placed either at C-6 or C-8 in aglycone.

The sugar was identified as D-glucose when compared with authentic sample by Co-PC. The appearance of an anomeric proton at δ 4.83(d, J=6Hz) proved the β linkage of D-glucose. The anomeric carbon signaled at δ 106.0 in its ^{13}C NMR spectrum indicating the 8-O-β-D-glucopyranoside structure of the compound, where as H-6 appeared at ä 6.56 in ^{1}H NMR and C-6 carbon at ä 96.2 in ^{13}C NMR. The position of sugar was concluded to be at C-8-OH based on comparison of ^{1}H and ^{13}C NMR spectral data with a known compound 5,7,8-trihydroxyflavone-8-O-β-D-glucopyranoside.

Thus on the basis of the above spectral evidences the structure of the isolated compound was finally concluded to be 5,4'-dihydroxy-7-methoxyflavone-8-O-β-D-glucopyranoside. This compound is first time reported from *Feronia limonia.*

EXPERIMENTAL

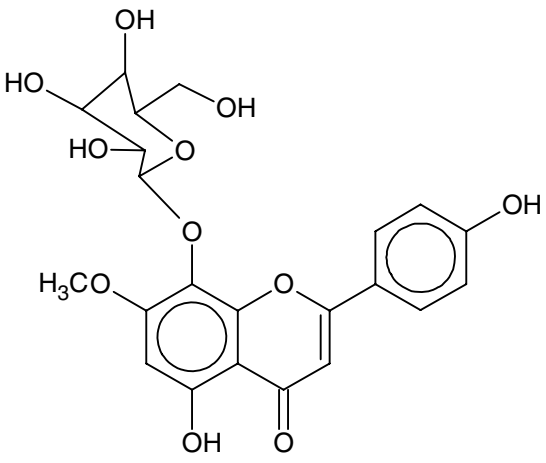
Ultra violet absorption spectrum was recorded on Perkin-Elmer Lambda Bio 20 UV spectrometer. I R spectroscopy was performed on Perkin-Elmer 1710 infrared fourier transformation spectrometer. NMR spectra were recorded on Bruker AVANCE DRX- 300(300 Hz). FEBMS was recorded on JEOLSX 1021/DA-6000 mass spectrometer.

Plant material

The roots of *Feronia limonia* were collected from the rural areas of district Shahjahanpur in the month of April and a specimen sample was preserved in the department of botany.

Extraction

Air dried roots of *Feronia limonia* were first defatted with petrol (3lt × 5 times) to obtain 20 gm of petrol-extract on distillation under reduced pressure. The marc was then extracted with C_2H_5OH (3lt × 5 times). The solvent was evaporated under vacuum on rotatory evaporator below 50°C temperature to yield 90 gm of alcoholic extract. The



Scheme 1: (5,4'-dihydroxy-7-methoxyflavone-8-O-β-D-glucopyranoside)

alcoholic extract thus obtained was poured in 500 ml distilled water to get water soluble and insoluble portions. The water insoluble part (ppt) after partitioned with C_6H_6 was dissolved in MeOH to provide 15 gm of methanolic extract. A well-stirred suspension of silica gel (100 -150 g in pet-ether 60-80°) was poured into column (150 cm long and 50 mm in diameter). When the absorbent was well settled, the excess of petrol was allowed to pass through column. Slurry was made to methanolic extract with 5 gm of silica gel in pet-ether and was digested to well setelled column. The column was successely eluted with the solvents and solvent mixtures of increasing polarity. Elution with $CHCl_3$: MeOH (7:1) afforded a yellow powder.

Compound (glycoside)

m.p.	: 243-245 °C
R_f	: 0.42(MeOH: $CHCl_3$ 10:90)
UV λ_{max} (nm)	: (MeOH) 279, 305, 326 (sh): (MeOH- NaOMe) 281.0, 374.9, (MeOH: $AlCl_3$) 285.3,320.1(sh) , (MeOH-$AlCl_3$- HCl)290.0, 318.2(sh), 348.0, (MeOH-NaOAc) 278.1, 308.6, 38 2.7 (sh),(MeOH-NaOAc-H_3BO_3)279.4, 307.9, 326(sh),
IR (KBr)	: 3616, 3420, 2790(-OMe) 1650, 1610 cm^{-1}
^{1}H NMR (DMSO-d_6) δ	: 6.83(1H, s, H-3), 6.56 (1H, s, H-6), 8.11(2H, d, J=9Hz, H-2' 6'), 6.94(2H, d, J=9Hz, H-3', 5'), 12.90 (1H, s, C-5 OH), 3.90 (3H, s, C-7 OCH3), 4.83 (1H, d, J=6Hz, H-1") 3.40-4.50 (6H, m, Sugar)
^{13}C NMR	: 165.2, (C-2), 103.3(C-3), 183.1 (C-4), 158.6 (C- 5), 96.2(C-6), 159.2 (C- 7),126.5(C-8),105.3 (C- 10), 122.4(C-1')117.0 (C-2', 6'),129.8(C-3', 5'), 162.9(C-4'), 56.6(C-7-OCH_3), 106.0 (C-1"), 76.1 (C-2"), 78.9(C- 3"), 71.7(C-4"), 78.4 (C-5"), 62.8 (C-6")
MS m/z	: 462[M+H]$^+$ $C_{22}H_{22}O_{11}$

Acid hydrolysis

The compound (10 g) was hydrolysed under reflux condition for 4 h with 5% methanolic HCl (4 mL).Reaction mixture after usual work up provided aglycone (5.0 mg) and aqueous portion. This on subsequent neutralisation followed by evaporation yielded sugar. The sugar was identified as D-glucose by Co-PC with authentic sample.

Aglycone

It was obtained as dark yellow needles, recrystallized with methanol. It showed a purple spot under UV light.

m.p.	:	305-307 °C
R_f	:	0.59 (MeOH: $CHCl_3$ 10:90)
UV λmax (nm)	:	(MeOH) 272.6, 301(sh), 325, (MeOH- NaOMe) 271.6, 381.0, (MeOH -$AlCl_3$)279.1,308.3(sh), 345.8 ,(MeOH- $AlCl_3$-HCl) 278.9, 306.9(sh), 341.4, (MeOH- NaOAc) 272.1, 383.7(sh), (Me OH-NaOAc- H_3BO_3) 272.3, 301(sh), 328.
IR (KBr) λ_{max} 2362,	:	3750, 3420, 2871,
1652,1608,1454,771 cm^{-1}		
^{1}HNMR (DMSO-d_6)	:	6.75(1H, s, H 3), 6.56 (1H, s, H-6), 8.00(2H, d, J=9Hz, H- 2', 6^2), 6.92(2H, d, J=9Hz, H-3', 5'), 12.51(1H, s, C-5 OH), 3.89(3 H, s, C-7 OCH_3)
EIMS m/z (%)	:	300 $[M]^+C_{16}H_{12}O_6$ [100], 285 $[M-15]^+$, 254, 182 $[C_8H_6O_5]^+$, 173,136,118 $[C_8H_6O]^+$

REFERENCES

1. Hooker, J.D., *The Flora of British*. India. L. Reeva and Co.London (1879)
2. Kirtakar,K.R., Basu.B.D: An I.C.S., *Indian Medicinal Plants*. India (1993).
3. Yusuf,M., Chowdhury,J.U., Wahab,M.A., Begum,J. *Medicinal plants of Bangladesh*. BCSIR Lab. Bangladesh (1994).
4. Perry, L.M., *Medicinal plants of east and southern Asia*. MIT press,Cambridge Massachusetts (1980).
5. Agrawal, A., Siddiqi, I.R., Singh, J., *Phytochemistry.* **28**: 1229 (1989).
6. Talpatra, S.K., Chaudhuri, M.K., Talpatra, B., *Phytochemistry*. **12**: 236 (1973).
7. Gupta, S.R., Seshadri, T.R., Sharma, C.S., Sharma,N.D.1979.*Planta medica*,**36**,95
8. Chopra, R.N., Chopra, I.C., Verma, B.S., Eds. *Supplement to Glossary of Indian Medicinal Plants*.P-**29**, Pub.And Inf.Directorate, Delhi (1969).
9. Chakraborty, D.P., *J. Sci. Ind. Res*. **18 B**: 90 (1959).
10. Banerji, J., Ghosal, N., Sarkar, S., Kumar, M., *Indian J.Chem.* **21B**: 496 (1982).
11. Shukla, J., Shrirama. Tiwari, R.D., *Ind. J. Chem*. 287 (1971).
12. Rahman, M.N., Gray, A.I., *Phytochemistry*, **59**: 73 (2002).
13. Soine, T.O., *J. Pharm. Sci*. **53**: 231 (1964).
14. Elmofty, A.M. 1968. Vitiligo and Psoralen PP-**1-221**, Pergamon Press,Oxford
15. Parrish,J.A.,Fitzpatric,T.B.,Tannenbaum, L., Pathak, M.A. *Eng. J. Med*. **291**: 1209 (1974).
16. Gilchrest, B.A., Fitzpatric, T.B., Tannenbaum, L., Hayenes, H.A., Parrish, J.A., *Cancer*, **38**: 683 (1976).
17. Besson. T., Ruiz, N., Coudert, G., Guillaumeat, G., *Tetrahedron*, **51**: 3197 (1995)
18. Muuay, R.D.H., Mendez, J., Brown, S.A., *The Natural Coumarins* PP.**31**.Wiley-Interscience, New York (1982).