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Note

Flavonoid glycoside from *Leucas lavandulaefolia* (Rees) aerial parts

K S Chandrashekar*, B J Arun, D Satyanarayana & E V S Subramanyam

Department of Pharmacognosy, N.G.S.M. Institute of Pharmaceutical Sciences, Nanthoor, Mangalore 575 005, India
E-mail: cksbhat@yahoo.co.in

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Chrysoeriol-4′-*O*-α-L-rhamnopyranosyl (1→2) β-D-galacto-pyranosyl (1→6) β-D-glucopyranoside has been isolated from *Leucas lavandulaefolia* Rees aerial parts and its structure has been determined by UV-Vis, IR, ^{1}H and ^{13}C NMR and mass spectroscopic methods.

Keywords: *Leucas lavandulaefolia*, chrysoeriol, takadiastase, β-glucosidase, β-galactosidase

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Leucas lavandulaefolia Rees (family Labiatae) is a herbaceous annual weed found in pastures and waste land throughout India. It has a strong flavour and is reputed for its use as sedative, vermifuge, stomachic, dermatosis and is also useful in the treatment of migraine[1-3]. A literature survey revealed that the presence of acacetin and chrysoeriol from this plant has been reported[4]. This note describes the isolation and characterization of a new compound chrysoeriol-4′-*O*-α-L-rhamnopyranosyl (1→2) β-D-galactopyranosyl (1→6) β-D-glucopyranoside from aerial part of plant material of this species.

Results and Discussion

The compound was found to be a flavone glycoside by its spectral analysis[5] and Molisch test. Upon acid hydrolysis (7% H_2SO_4), the compound yielded D-glucose, D-galactose, L-rhamnose and aglycone. The aglycone was characterized as chrysoeriol on the basis of UV-Vis, ^{1}H and ^{13}C NMR and co-TLC[4]. When UV-Vis spectrum (NaOMe) was compared with that of chrysoeriol, no shift was observed in band-I indicating the glycosylation site at $C_{4'}$. The absence of signal by ^{1}H and ^{13}C NMR at δ 9-9.42 for $C_{4'}$-OH in chrysoeriol clearly indicated the glycosylation at $C_{4'}$. The aglycone gave the characteristic colour reactions of flavonoid. It was confirmed from the red colour with magnesium and hydrochloric acid (Shinoda test)[6]. The inter sugar configurations were deduced from ^{1}H and ^{13}C NMR spectra which confirmed β-D-pyranosyl configuration for glucose and galactose and α-L-pyranosyl configuration for rhamnose. The glycoside completely methylated, was hydrolysed and the resulting methylated sugars were identified as 2,3,4-tri-*O*-methyl-L-glucose, 3,4,6-tri-*O*-methyl-D-galactose and 2,3,4-tri-*O*-methyl-L-rhamnose. Hydrolysis of the glycoside with takadiastase liberated rhamnose. After complete takadiastase hydrolysis, the glycoside was hydrolysed with β-galactosidase and β-glucosidase. The ^{1}H NMR spectrum of the compound showed three anomeric proton signals at δ 5.45 (1H, d, J = 7.1 Hz) assignable to 1-H-β-glucoside proton, δ 5.57 (1H, d, J = 8 Hz) assignable to 1-H-β-galactosyl proton and δ 5.05 (1H, d, J = 2.0 Hz) assignable to 1-H-α-rhamnopyranosyl proton. The remaining sugar protons resonated between δ 3.33-4.50. CH_3 of rhamnose appeared at δ 1.25 (3H, d, J = 6.0 Hz). The ^{13}C NMR pattern of the compound matched with the reported values for chrysoeriol[4]. Anomeric carbons of glucose, galactose and rhamnose appeared at δ 101.3, 104.8 and 100.6 respectively. ^{13}C NMR signals of sugar were similar to their reported values except for a 5.9 ppm downfield shift of C-6″ of glucose and 6.8 ppm downfield shift of C-2″ of galactose. This downfield shift established 1→6 linkage between galactose and glucose and a 1→2 linkage between rhamnose and galactose. Further, the C-4′ site of glycoside resonated at higher field (148.66) as compared to C-5 and C-7. Thus C-4′ of the glycoside exhibited a shielding effect which confirmed that the attachment of sugars was at C-4′ of the glycoside *via* a C-O-C linkage. Based on these evidences, the structure of the compound was assigned as chrysoeriol-4′-*O*-α-L-rhamnopyranosyl (1→2) β-D-galactopyranosyl (1→6) β-D-gluco-pyranoside (**Figure 1**). The isolation and characterization of this flavonoid glycoside has been reported for the first time.

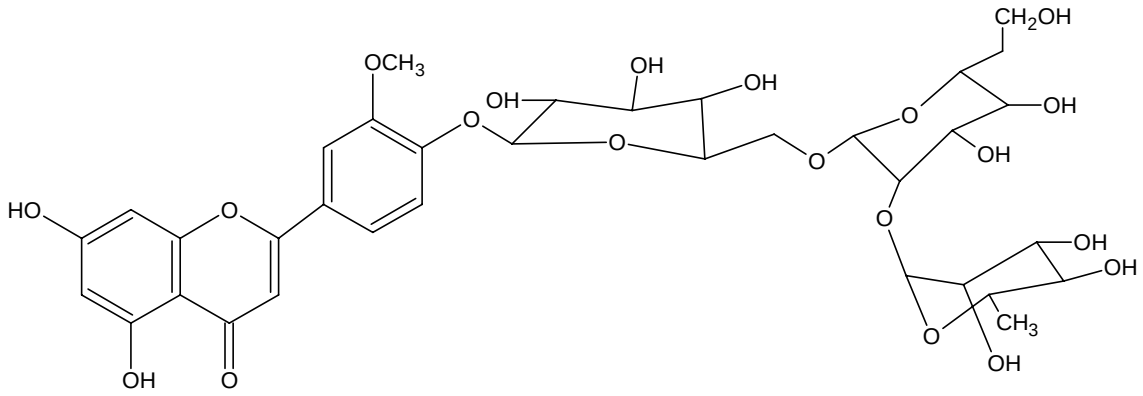

Figure 1

Experimental Section

IR spectra (KBr) were recorded on a Shimadzu 8201 PC FT spectrometer. ^{1}H NMR spectra were obtained on a Brucker WM 400 instrument at 90.56 MHz in DMSO-d_6 using TMS as an internal standard (chemical shift in δ, ppm). TLC were run on silica gel G (Merck). UV-Vis spectra (MeOH) were obtained on a Hitachi 320 spectrophotometer.

Plant material. The aerial parts (including leaves, flowers, stem and branches) of *L. lavandulaefolia* were collected from Udupi, Karnataka, India and its botanical identity was confirmed by Dr. Gopalkrishna Bhat, Department of Botany, Poornaprajna College, Udupi. A voucher specimen has been deposited in NGSM Institute of Pharmaceutical Sciences, Nanthoor, Mangalore.

Extraction and Isolation. The aerial parts of *L. lavandulaefolia* were collected from Udupi, dried under shade and powdered. 1 kg of dry plant material was defatted with petroleum ether in a soxhlet apparatus. The defatted plant material was extracted with hot EtOH to give a solid residue (10 g) which was extracted with EtOAc. The EtOAc fraction on silica gel column chromatography eluting with EtOAc-MeOH (7:4, v/v) yielded compound **1** (200 mg). The compound was then further purified by preparative TLC on silica gel with the same solvent system to get 175 mg of pure compound **1**, m.p. 172-74°C. UV-Vis(nm): (MeOH) 239, 269, 288(sh), 334; (MeOH-NaOMe): 223(sh), 231, 278, 309(sh), 369; (MeOH-$AlCl_3$): 257(sh), 279, 291(sh), 345, 381; (MeOH-$AlCl_3$-HCl): 257, 280, 291 (sh), 342, 381; (MeOH-NaOAC): 232, 275, 310, 350; IR(KBr): 1651, 3355, 1208, 1256, 1033, 1103, 3081, 2907 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 6.54(1H, s, H-3), 3.33-4.50(18H, m, sugar-H), 3.89(3H, s, 1 × OCH_3), 5.05(1H, d, J = 7.5Hz, rha H-1), 5.57(1H, d, J = 7.5Hz, gal H-1), 5.45(1H, d, J = 7.5Hz, glu H-1), 6.42(1H, d, J = 2.5Hz, H-6), 6.53(1H, d, J = 2.5Hz, H-8), 7.18(1Hd, J = 2.5Hz, H-2′), 7.28(1H, dd, J = 2.5 and 9.5Hz, H-6′), 7.39(1H, d, J = 9.5Hz,H-5′), 13.17(1H, s, OH-5); ^{13}C NMR(DMSO-d_6): δ 164.1(C-2), 103.0(C-3), 196.01(C-4), 103.03(C-4a), 163.98(C-5), 97.33(C-6), 163.74(C-7), 106.28(C-8), 166.03(C-8a), 119.44(C-1′), 156.95(C-2′), 98.58(C-3′), 148.66(C-4′), 104.5(C-5′), 126.43(C-6′); glucose 101.3(C-1), 74.3(C-2), 76.7(C-3),70.2(C-4), 77.2(C-5), 67.8(C-6); galactose 104.8 (C-1), 78.1(C-2), 73.7(C-3), 71.2(C-4), 75.2(C-5), 61.9(C-6); rhamnose 100.6(C-1), 71.8(C-2), 72.2(C-3), 73.7(C-4), 68.1(C-5), 18.1(-CH_3); EIMS: m/z 789[M+H]$^+$, 642[M+H-rha], 769[M+H-OMe]$^+$.

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References

1 Anonymous, *Wealth of India*, Vol VI**,** (NISC Publishing Co., New Delhi), **1961**, p 79.
2 Kirtikar K R & Basu B D, *Indian Medicinal Plants*, 2nd edn, (Periodic Experts Book Agency, New Delhi), **1975**, 2020.
3 Nadakarni K M, *Indian Materia Medica*, Vol.1 (Popular Prakashan, Bombay) **1992**, 739.
4 Smith J E , *Acta Pharma Indonesia*, 110, **1985**, 27.
5 Harborne J B, Mabry T J & Mabry H, *The Flavonoids* (Chapman and Hall, London), **1975**.
6 Shinoda J, *J Chem Pharm Soc Japan*, 48, **1928**, 214.