

Chemical constituent from the stem bark of Samanea saman

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Abstract

New flavonoid glycoside luteolin-7-O-[- β -D-arabinopyranosyl(1 \rightarrow 2)]- β -D-arabinopyranoside **1** have been isolated from the stem bark of *Samanea* saman. The structures have been established on the basis of chemical evidences and spectroscopic method.

Keywords: Raintree, medicinal, flavones.

Introduction

Samanea saman (Mimosaecae) commonly called "Raintree" is a useful medicinal plant distributed from Yucatan Peninsula, Guatemala to Peru, Bolivia, Brazil, throughout the West Indies, in old world tropics and also in Southern Florida¹. It is used as an alcoholic source². It is used for cold, diarrhea, headache, intestine ailments, stomachach³, stomach cancer⁴, sore throat⁵. Earlier alkaloids, lupeol, lupeone, octaconsanolic acid, hexacosanol, flavonoids, kaempferol⁶ have been isolated from the different parts of *Samanea saman*.

In continuation of our research on the chemical investigation of medicinal plants, we report herein isolation and structure elucidation of new flavonoid glycosides from *Samanea saman*.

The water insoluble portion of the hot ethanol extract of the air-dried and crushed stem barks of *S. saman* on column chromatography yield compound **1**.

Result and discussion

Compound 1, $C_{25}H_{26}O_{14}$ ($M^+ 550$), mp 192°C, was also a non-reducing glycoside. On acid hydrolysis it gave an aglycone **1a** and a sugar moiety. The sugar was identified as D-arabinose by co-chromatography with an authentic sample.

The aglycone **1a**, $C_{15}H_{10}O_6 (M^+ 286)$ gave colour reactions characteristic of flavone. The flavone nature of the compound was indicated by its positive Shinoda test⁸. Acetylation of aglycone gave tetraacetate indicated the presence of four hydroxyl groups in the compound. The ¹H NMR spectrum of flavone showed the presence of six protons in aromatic region, indicating that compound is tetrasubstituted flavone which was also supported by ¹³C NMR.

The presence of hydroxy group at 7 and two hydroxy groups at 3' and 4' positions was confirmed by bathochromic shift of 18nm in band II with $NaOAc^9$ and of 38nm in band I with $AlCl_3^{10}$ in



UV spectra, respectively. The compound also gave yellow colour with zirconium oxychloride showing the presence of free hydroxyl group at C-5¹¹, which was also evidenced by its UV spectrum showing a bathochromic shift of 47nm in band I in the presence of AlCl₃ and HCl.¹²

The ¹³C NMR spectrum of the compound showed singlet at 162.2, 166.5, 147.5 and 151.2 which indicated the presence of hydroxyl group at C-5, C-7, C-3' and C-4' respectively.¹³ Thus aglycone is 5,7,3',4'-tetrahydroxy flavone. The site of glycosidation was found to be at C-7 on the basis of UV shift with NaOAc and ¹³C NMR spectral data of **1** and this location is biogenetically favoured.

Quantitative estimation and molecular weight difference suggested the presence of two moles of sugar per mole of aglycone. ¹H-NMR spectrum of compound showed signals of two anomeric protons signal at δ 4.95 (1H, d, J=5.5 Hz) and 5.75 (1H, d, J=7.5 Hz), 3.25-3.80 (m, 10H, sugar protons). This confirmed that glycoside was dissacharide.¹³ The glycoside on permethylation by Hakamori method¹⁴ followed by acid hydrolysis yielded 3,4 di-*O*-methyl-D-arabinose and 2,3,4-tri-*O* -methyl -D-arabinose. This confirmed that interglycosidic linkage was (1→2). From the above evidences, the structure of compound **1** was determined as luteolin-7-*O*-[- β -D-arabinopyranosyl (1→2)] - β -D-arabinopyranoside.

Experimental Section

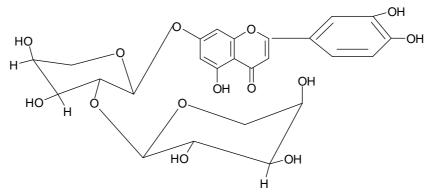
The stem bark of *Samanea saman* was collected in April, 1999 from the Botany Department, University of Allahabad, Allahabad, U.P., India. M.ps measured in open capillary tube and are corrected. TLC was carried out on silica gel G. IR (KBr) and UV spectra were recorded on Perkin-Elmer and Beckman-DK2 spectrophotometer respectively. ¹H NMR spectra of **1** was recorded at 300 MHz in CDCl₃ and ¹³C NMR spectra at 100 MHz in CDCl₃ in FT mode. Mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer.

Extraction and Isolation

The air-dried and finely crushed stem bark (5kg) of *Samanea saman* was repeatedly extracted with boiling EtOH (4x10*l*), concentrated under reduce pressure in a rotatory evaporator and poured into an excess of ice-cold water to give water soluble and water insoluble portion. The water insoluble portion was extracted successively with different solvents of increasing polarity over a sintered column. Elution with different solvents of increasing polarity. On elution with solvent system C_6H_6 : ethyl acetate (8:2, v/v) compound **1** was isolated.



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luteolin-7-*O*-[- β -D-arabinopyranosyl (1 \rightarrow 2)] - β -D-arabinopyranoside.

Compound **1**, mp 192°C, yield 350mg, homogeneous on TLC, $R_f 0.66$ solvent C_6H_6 : CHCl₃ (2 : 8, v/v); Anal. Found: C, 54.53%; H, 4.76%; Calcd. for $C_{25}H_{26}O_{14}$: C, 54.54%; H, 4.72%. UV(MeOH)nm : 275, 374; +AlCl₃ : 257, 389; +AlCl₃/HCl : 265, 409; +NaOAc : 271, 354. ¹H NMR (CDCl₃, 300MHz): \Box 6.72 (s, 1H, H-3), 6.19 (d, 1H, *J*=2.2Hz, H-6), 6.40 (d, 1H, *J*=2.2Hz, H-8), 7.52 (d, 1H, *J*=2.5Hz, H-2'), 6.82 (d, 1H, *J*=7.5Hz, H-5'), 7.68 (dd, 1H, *J*=7.6 and 2.5Hz, H-6'), 12.92 (s, 1H), 4.95(d, 1H, *J*=5.5Hz), 5.75 (d, 1H, *J*=7.5Hz), 3.25-3.80 (m, 10H, sugar

protons). MS : m/z 550^[M⁺] 286, 285, 258, 153, 152, 137, 134; ¹³C NMR data are given in **Table-1**.

С	1	1 a		
2	155.3(s)	155.3(s)	arabinose 1	98.3(d)
3	133.5(d)	133.4(d)	2	76.5(d)
4	177.4(s)	177.4(s)	3	74.6(d)
5	162.2(s)	162.2(s)	4	67.3(d)
6	99.8(d)	99.8(d)	5	74.7(d)
7	166.5(s)	162.3(s)	6	60.5(t)
8	94.4(d)	94.4(d)	arabinose 1	102.29(d)
9	156.8(s)	156.8(s)	2	70.5(d)
10	104.1(s)	104.2(s)	3	73.6(d)
1'	121.2(s)	121.2(s)	4	68.4(d)
2'	115.5(d)	115.5(d)	5	77.1(d)
3'	147.6(s)	147.3(s)	6	61.8(t)
4'	151.2(s)	150.2(s)		
5'	115.9(d)	115.9(d)		
6'	121.8(d)	121.8(d)		

Table 1.¹³C NMR spectra of compounds 1, 1a,



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