Rare luteolin biflavonoids from leaves of Albizia procerra

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Abstract

Two rare flavonoids from leaves of Albizia procerra (Leguminosae) have been identified as bis-dimethyl chromene (5,6,:5",6')(7-o-7)biluteolin[1] and (7,3":7,7") biluteolin 1, 5-dihydroxy anthraquinone [2] on the basis of chemical reaction , IR, UV, HRMS, NMR, ^{1}H, ^{13}C, and 2D NMR.

Keywords: Albizia procerra, Leguminosae, biflavonoids

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1. Introduction

In the plants belonging to family Leguminaosae polyphenolic derivetives possessing different structure are synthesized and accumulated as phytoalexin in response to infection with pathogenic microbes [1,2] and thus play a corner stone role. Many phenolics compound are being sought for their antioxidant and anthrombic properties as potential agents against Cancer and Cardiac Diseases [3]. In our current investigation on phytochemical we report here the isolation & characterization of two rare luteolin biflavonoids from Albizia procerra .In India genus Albizia is commonly known as, Sirish and used as an astringent to treat boils, cough ,to treat eye flu , lungs problem and used to treat abdominal tumour bank is used to treat inflammation and is also used as psychoactive [4,5]

2. Materials and methods

2.1 plant material

The leaves of Albizia procerra were collected from the CR farm of the Indian Grassland and Fodder research institute Jhansi, identified voucher specimen (IGGS441) has been deposited in herbarium of IGFRI and BBC Jhansi.

2.2 Extraction and Isolation

The air dried powered leaves (4kg) of Albizia procerra were extracted with recetified spirit by cold percolation exhaustively and solvent was removed under vacuum. Dark coloured extractive was subsequently extracted with n-Hexane, Benzene, CHCl3, EtOAC and acetone. The EtOAC extractive (22g) was treated with 0.5% aq NaOH, soluble part was acidified and extracted with EtOAc (1.5g) . The EtOAc extract was chromatographed on Si Gel column (2.5 cm ×30 cm) and eluted with EtOAc and MeOH in different ratio. The eluent from 60:40(EtOAc : MeOH) and 28:72 yielded compound 1 (42mg) and 2 (63mg).

Compound-1 m.p. 204^0 c UV: λmax (MeOH)(log €) 256 (6.28), 268 (6.1), 348 (6.4), NaOMe 272 (6.28, 398 (6.37), $AlCl_3$, 272 (6.12), 298(6.00), 412(6.14), $AlCl_3$/HCl 261 (6.31), 274 (6.32) 292(6.31), 362 (6.12), 380(6.12), NaOAc 265 (6.25), 415 (6.28), NaOAc/H_3BO_3 258 (6.21), 356(6.18)nm. IR KBR 3462,1652, 1360 cm-1, FABMS m/z 767.639$(M+H)^+$ calculated for $C_{44}H_{30}O_{13}$, ^1H and ^{13}C NMR spectral data (DMSO-d6) Table-1.

Compound -2 m.p. 270^0c UV λMeOH max (log€) 255 (6.320, 264 (6.4), 347 (6.5) NaOMe 263 (6.4), 402 (6.7), $AlCl_3$ 270 (6.81), 302 (6.5) 324 (6.12) $AlCl_3$/HCl 273 (6.4), 293 (6.64), 361 (6.31), 380 (6.48), NaOAc 263 (6.71),398 (6.42), NaOAc/H3BO3 255 (6.7) 366 (6.40, 374(6.71)nm, IR Bands KBr max 3421, 1658, 1610cm-1. Positive FABMS m/z 809.502 $(M+Z)^+$, 676 (13), 392(42), 287 (32), 157 (42), 137(100), 107 (86), 1H NMR, 13C NMR (DMSO-d6) data table-2.

Result and Discussion

compound [1] was isolated as brown amorphous solid m.p. 204^0, it responded positive tese for flavonoid[6]. The UV spectrum showed absorption maxima and shift with various conventional reagents indicated its hydroxylation pattern, similar to luteolin [7]. The spectrum showed absorption bands at 3462 (OH), 1652(chelated carbonyl) and 1360 cm^{-1} (gem dimethyl grouping). The high molecular ion peak m/z 767.639 $(M+H)^+$ corresponding to molecular formula $C_{44}H_{30}O_{13}$.

The ^{13}C NMR and DEPT showed 22 resonance lines consisting of 2 methyl, 6 methine, 14 quaternary C atom. The 300 MHz (Table-1) in DMSO- d6 of compound [1] displayed the chemical shifts for a luteolin skelton, without any substitution in ring A because of an upfield shift of C-6 & C-8 at δ99.1 and δ94.2 [8]. On reviewing the literature, the remaining six signal were matched with chromene moiety[9]. Since there were no signals for 5'6' protons in HMQC the chromene ring could be assigned at 5'6' and confirmed by the 2D NMR. More surprisingly this compound contains an antiaromatic butadiene ring yet this compound is stabilized by a type of resonance called captodative effect [10]. The chemical shifts with multiplicity of the signal, absolute values of the coupling constant and the magnitude in the ^1H NMR , ^{13}C as well as HMQC, HMBC data led to conclude the presence of two luteolin

molecules each one with chromene moiety linked together on C-7 with ethereal linkage . On the basis of all these results the compound (1) was established as bis2”2” dimethyl chromene (5’6’: 5”6”) [1-7-O-II-7] biluteolin (Fig-1).

TABLE-1: IH and 13C NMR chemical shifts of compounds (1) (300 MHz, DMSO,-d6)

Cposition	δC	δH(splitting)	HMQC,HMBC
2	164.8		
3	103.7	6.76(d)	
4	181.8		
5	161.6		
6	99.1	6.42(d)	C-7,C-5
7	164.1		
8	94.2	6.46(d)	C-7,C-9
9	157.5		
10	103.7		
1’	119.2		
2’	113.4	7.46	C-3’
3’	146.0		
4’	150.1		
5’	121.5		
6’	139.8		
1”			
2”	79.1		
3”	116.2	7.41(d)	C-2”,C-4”
4”	119.2	6.92(d)	C-5”,3”
5”	121.5		
6”	157.5		
7”	29.2	1.22(s)	C-2”
8”	29.2	1.22(s)	C-2”

TABLE-2: 1H and 13C NMR chemical shifts of compound (2) (300MHz, 75 MHzDMSO-d6)

Cposition	δC	δH(splitting)	NOESY
2	165.2		
3	104.3	6.57(S)	
4	181.8		
5	163.4		
6	99.8	6.24(d)	H-4”
7	165.0		
8	94.8	6.5(d)	H-2”
9	158.9		
10	105.4		
1’	120.2		
2’	114.2	7.57(S)	
3’	146.6		
4’	150.2		
5’	116.7	7.40(S)	
6’	123.8	7.51(S)	
1”	163.4		
2”	129.3	7.09(d)	
3”	152.6		
4”	123.5	6.98(d)	
5”	163.4		
6”	129.3	7.09(d)	H-8
7”	152.6		
8”	123.5	6.98(d)	H-6
9”	184.2		
10”	184.2		

Compound-2 was obtained as a yellow substance responding to positive Shinoda test[4] as well as reaction for anthraquinone [11]. The UV spectrum exhibited characteristic bands of a luteolin flavone with various shift reagents [5] similar to compound (1). The HR FABMS of (2)showed the $[M+Z]^+$ at m/z 809.502 suggested the molecular formula $C_{44}H_{24}O_{16}$.

^{I}H NMR of compound 2 (Table -2) displayed the highly deshielded chemical shift as sharp singlet for chelated hydroxyl at δ13.08 and δ12.29 integrating for 4 protons. The two protons of A ring resonating at δ6.24[H-6] and δ6.5 [H-8] and a disubstituted benzene ring B protons at δ7.57 at and δ7.40 for 2'6' and 5' respectively . The integration confirmed presence of two luteolin unit. Besides this there were chemical shift observed for the two meta coupled proton at δ7.09 (H-2", 6") and upfield shift at δ6.981 [H-4",8"] confirming presence of 1,3,5,7, substituted anthraquinone[12].

The ^{13}C NMR spectra showed signals for all 22 carbons in aromatic region, out of these 15 shifts were for C showing close resemblance to those of luteolin [8] and remaining 7 signals corresponding to 14C . These observation were indicative of the existence of C2 symmetry in compound 2 [13]. The luteolin unit was connected to anthraquinone via an ether bridge at C-3 as evidenced by NOESY difference spectroscopy data. On the basis of the above evidence the compound 2 could be assigned as biluteolin [7-3"] [7-7"]1,5 dihydroxy anthraquinone(Fig- 2)

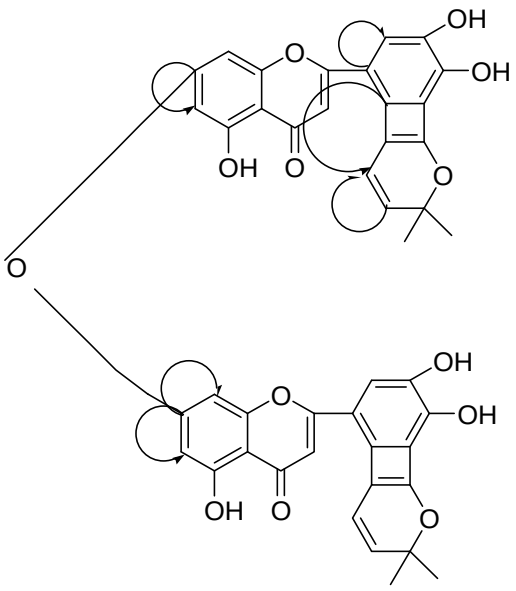

Fig-1: HMBC Correlation of compound-1.

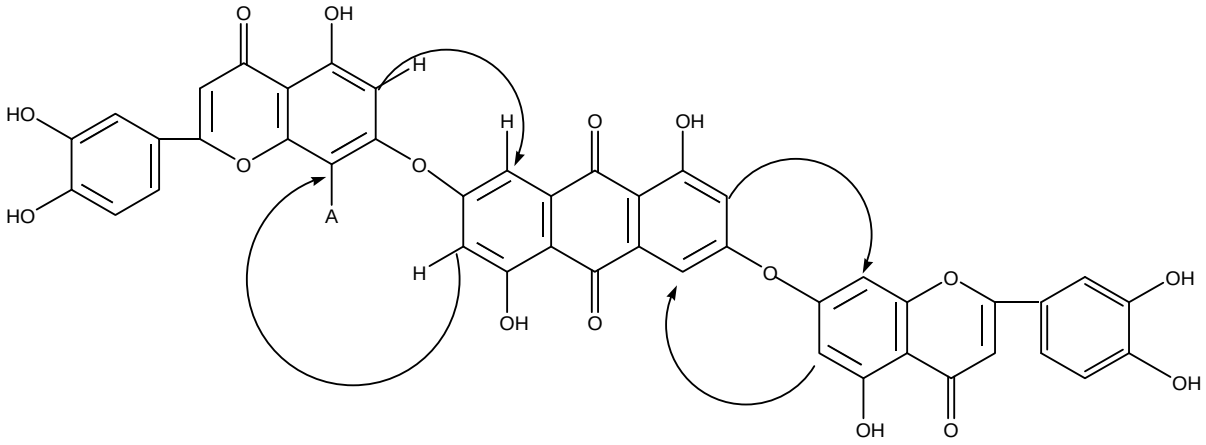

fig 2 Important NOE correlation of compound 2

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