Research Paper Engineering

Flavonol Glycoside of Jacaranda Mimosifolia D.don

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ABSTRACT

The pinkish fresh flowers of Jacaranda mimosifolia of Bignoniaceae family has been chosen for phytochemical investigation. The flavonol glycoside, isoquercitrin was isolated from the ethyl acetate fraction. The structure of the compound was characterized by modern physical methods like UV, H-1 nmr, C-13 nmr, chemical reactions, chromatographic techniques and hydrolytic studies.

Keywords : Jacaranda mimosifolia, Bignoniacea, quercetin, and isoquercitrin

INTRODUCTION

Jacaranda mimosifolia is a sub-tropical tree native to South America that has been widely planted elsewhere because of its beautiful and long-lasting blue flowers. It is also known as Jacaranda, Blue Jacaranda, Black Poui, or as the fern tree. Older sources give it the systematic nameJacaranda acutifolia, but it is nowadays more usually classified as Jacaranda mimosifolia. In scientific usage, the name "Jacaranda" refers to thegenus Jacaranda, which has many other members, but in horticultural and everyday usage, it nearly always means the Blue Jacaranda. Jacaranda mimosifolia D.DON of Bignoniaceae[1] is cultivated in the Indian gardens and also found in Brazil,Bolivia and Argentina. The Jacarandas are impressive trees when covered with cluster of blue tubular flowers. The flowers are used as a substitute for the Unani herba Gul-e-Gaozabaan in Pakistan[2]. The bark of J.mimosifolia has been used in the treatment of wounds and dermatitis. Astrigent and diuretic properties have also been assigned to the bark extracts[3]. The plant has been attributed with properties to treat syphilis and disease related to urinary tract problems. The ground bark is used as a decoction against veneral diseases or as ethanolic maceration along with a small amount of Cordia alliodora against rheumatism and sciatica[4]. The plant possesses antioxidant[5], antihypertensive[6], antimicrobial [7] and antitumour [8] activities.

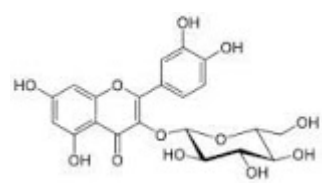
The leaves of J. mimosifolia found to contain jacaranone, verbacoside and the flavonoids scutellarin-7-O-glucosylmethylesters, apigenine-7-O-glucosyl-methylester, luteolin-7-O-glucoside and isovitexin[9]. The flower extract of J.mimosifolia has been found to be potent indicator in all types of acid base titrations,and the activity is attributed to the flavonoids and anthocyanins present in it[10]. With a view to locate additional flavonoids, the fresh flowers of J.mimosifolia have been investigated and the results are presented hereunder.

EXPERIMENTAL

EXTRACTION AND FRACTIONATION :

Fresh flowers of J. mimosifolia collected from Kolli hills of Namakal district during March were extracted with 80% MeOH (4x500 ml)under reflux. The alc. extract was concentrated in-vacuo and the aq. concentrate was successively fractionated with benzene (3x250 ml), peroxide free $Et_2O$and EtOAc (4x250 ml). The benzene and Et_2O fractions did not yield any isolable material.

EtOAc fraction:(flavonol glycoside:Isoquercitrin)



The EtOAc fraction was concentrated in-vacuo and left in an ice chest for 2 days. A yellow solid that separated was filtered and studied. It was recrystallized from MeOH when it afforded yellow crystals, m.p.229-30^{0}C (yield 0.1%). It was freely soluble in EtOAc and MeOH and sparingly soluble in water. It gave an olive green colour with alc.$Fecl_3$,deep pink colour with Mg-HCl, yellow colour with NaOH and appeared deep purple under UV that turned yellow on exposure to NH_3. It did not answered the Horhammer-Hansel test[11] but responded to Wilson's boric acid [12], Gibb's and Molisch's[13]test. The pigment had Rf values as indicated in TableI-1and had λ^{MeOH}_{max} nm 257, 269sh, 299sh, 362; (+NaOMe) 272, 327, 409sh; (+$AlCl_3$) 275, 303sh, 333, 430; (+$AlCl_3$/HCl) 274, 303sh, 353, 401; (+NaOAC) 271, 320sh, 372; (+NaOAC/H_3BO_3)265, 300 sh, 372. The [1] H- and [13]C-NMR of the glycoside were appended (Figs I-1 and I-2). The identity of the glycoside was confirmed by direct comparison with an authentic sample of the same from the seeds of Bauhunia acuminata [14].

Hydrolysis of the glycoside:(flavonol:quercetin)

To a solution of the glycoside (0.1g, 0.2 m mole) in hot aq. MeOH (10 ml, 50%)and an equal volume of H_2SO_4 (10%) was added and the mixture was refluxed at 100^{0}C for 2 h and the hydrolytic products were identified as described below.

Identification of the aglycone:

The Et_2O fraction from the hydroslysate was concentrated in vacuo and left in an ice chest for about a week. A yellow solid that separated was filtered and studied. It came out as pale yellow needles m.p.316-18^{0}C on recrystallisation from MeOH.

It was soluble in organic solvents and sparingly in hot water. It gave a red colour with Mg-HCl, olive green with NH_3 and NaOH, yellow solution with a pale green fluorescence with conc. H_2SO_4 and appeared yellow under UV and UV/NH_3. It answered Wilson's boric acid, Horhammer-Hansel and Gibb's tests but did not respond to Molisch's test. It had λ^{MeOH}_{max} nm 255, 269 sh, 301 sh, 370; (+NaOMe) 247 sh, 321 (dec); (+$AlCl_3$) 272, 304 sh, 333, 458; (+$AlCl_3$/HCl) 265, 301 sh, 359, 428; (+NaOAc) 257sh, 274, 329, 390; (+NaOAc/H_3BO_3) 262, 304 sh, 388 and had Rf values as depicted inTable I-1. The ^{1}H and ^{13}C-NMR of the flavonol were appended.. It was identified as quercetin and the same was confirmed by co-PC and mixed-PC and m.m.p with an authentic sample of quercetin from Physalis minima [15]

Identification of the sugar:(glucose)

The aq.solution from the above hydrolysate was neutralized with BaCO3 and filtered. The concentrated filtrate on chromatographic examination (PC) gave Rf values corresponding to those of glucose. The running properties of the glycoside were in favour of a monoside. The identity of the sugar was also confirmed by direct comparison with an authentic sample of glucose.

TABLE –I-2

^{13} C-NMR SPECTRAL DATA AND THEIR ASSIGNMENT FOR THE GLYCOSIDE FROM THE FLOWERS OF J.mimosifolia

Compound	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
Isoquerctrin (from literature) (δppm)	156.5	133.7	1776.	161.3	98.8	164.2	93.6	156.5	104.2	121.4	115.3	144.8	148.5	116.5	121.6
Glycoside (δppm)	156.385	133.383	177.518	161.303	98.724	164.164	93.568	156.385	104.055	121.666	115.274	144.868	148.519	116.281	121.2

Compound	$C_{1''}$	$C_{2''}$	$C_{3''}$	$C_{4''}$	$C_{5''}$	$C_{6''}$
Isoquerctrin (from literature) (δppm)	101.4	74.3	76.8	70.3	77.5	61.3
Glycoside (δppm)	100.920	74.154	76.555	69.984	77.620	61.031

RESULTS AND DISCUSSION

The fresh flowers of **J.mimosifolia** have been found to contain isoquercitrin. The UV spectrum of the glycoside showed two major absorption peaks at 362 nm (band-I) and 257 nm (band-II) showing a flavonol skeleton. A bathochromic shift of 47 nm in band –I observed in its NaOMe spectrum indicated the prescence of a free 4'-OH group. The $AlCl_3$–HCl spectra of the glycoside as well as its aglycone showed 3 absorption peaks and a shoulder indicating a free 5-OH group in both. The glycoside as well as its aglycone did not exhibit any intense UV fluorescence, ascertaining the presence of a free hydroxyl group at C-5 in both. A bathochromic shift of 39 nm and 58 nm respectively in $AlCl_3$-HCl spectra was yet another evidence for the same. The presence of an ortho di hydroxyl group in the B-ring could be inferred from a shift of +10 nm noticed in the glycoside and +18 nm noticed in case of the aglycone on the addition of H_3BO_3. In the $AlCl_3$ spectrum, an absorption peak was noticed at 430 nm (band-I) which on addition of HCl reduced by 29 nm. This was another evidence for the presence of a catechol type di-OH group in the B-ring.

In the ^{1}H-NMR spectrum (400 MHz,DMSO-d_6,TMS)of the glycoside, the protons at C-6 and C-8 appear at δ 6.18 and 6.42 ppm respectively. The C-5' proton appears as a doublet at δ 6.81 ppm. The 5-OH proton resonates at δ 12.64 ppm as distinct singlet. The OH protons at C-7,C-3' and C-4' show upto δ 9.7, 9.45 and 9.22 ppm respectively. The H-1'' signal of the flavonol-3-O-glucoside was found at δ 5.45 ppm. The remaining glycosyl protons appear in the range δ 3.4 to 3.8 ppm.

Supporting evidence for the structure of the glycoside was provided by the analysis of ^{13}C-NMR (400 MHz, DMSO-d_6, TMS) data and a complete assignment was given (TableI-2). Due to glycosylation at 3-position,C-2 and C-4 carbons absorb at δ 156.3 and 177.2 ppm respectively. C-1", absorbs at δ 100.9 ppm. The rest of the carbons of the sugar unit appear between δ 69.9 ppm and 77.6 ppm. Based on this the glycoside has been characterized as quercetin-3-O-glucopyronoside).

Acknowledgements:

The authors thank S.I.F. of I.I.Sc. Bangalore, for their assistance in recording the nmr spectra.

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