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A FLAVONE GLYCOSIDE FROM THE STEM OF *IXORA ARBOREA*

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Key Word Index—*Ixora arborea*, Rubiaceae, stem, chrysin 5-*O*-β-D-xylopyranoside

Abstract—A new flavone glycoside isolated from the stem of *Ixora arborea* has been characterized as chrysin 5-*O*-β-D-xylopyranoside on the basis of spectral data, colour reactions and degradation studies

Ixora arborea was selected for phytochemical investigation because of its reputed medicinal importance [1, 2] The new glycoside (**1**) was isolated from an ethanolic extract of the stem The purified compound was found to be homogeneous Hydrolysis with 7% ethanolic sulphuric acid afforded a water insoluble aglycone and an aqueous hydrolysate The aglycone (**2**) was crystallized from hot ethanol and was characterized as chrysin [3] (5,7-dihydroxy flavone) on the basis of colour reactions, UV and IR data and degradation studies Xylose was identified from the aqueous hydrolysate by osazone formation (xylosazone mp 157°) and co-chromatography with an authentic sample (R_f value 0 27 in BAW, 4 1 5, top layer) Enzymatic hydrolysis [4] showed the aglycone and the sugar to be β-linked Periodate oxidation [5] revealed the presence of only one xylose unit in the pyranose form

The next task was to locate the position of the xylose on the aglycone The sugar moiety can be linked at either of the two free hydroxyls at positions-5 and -7 of chrysin The actual point of linkage was determined by comparing the properties of the glycoside with those of the aglycone The positive tests with vanillin–hydrochloric acid [6], ethanolic aluminium chloride [7], zirconium oxychloride [8, 9] and with Dimroth's reagents given by the aglycone and not by the glycoside indicated that the 5-position was free in the aglycone and not in the glycoside Both aglycone and glycoside gave bathochromic shifts of 10 nm and 9 nm (λ_{max} 260 nm to λ_{max} 270 nm and λ_{max} 262 nm to λ_{max} 271 nm), respectively on addition of a 1% ethanolic solution of fused sodium acetate This confirmed the presence of a free hydroxyl group at position-7 in both Thus as position-5 is not free in the glycoside it must be involved in the glycosidic linkage Failure of the glycoside to reduce Fehling's solution, Tollen's reagent and a negative test with aniline hydrogen phthalate reagent showed that the reducing group of the sugar is not free and must therefore be involved in the glycosidic linkage

On the basis of all this evidence the glycoside was identified as chrysin 5-*O*-β-D-xylopyranoside

EXPERIMENTAL

Isolation and purification Air-dried and powdered stem (5 kg) of *Ixora arborea*, procured locally and identified by the Botanical Survey of India, Allahabad, was extracted with EtOH for 120 hr and filtered hot On keeping in a refrigerator overnight the hot filtrate left a small amount of yellowish brown material which was filtered off and the filtrate concd to half its vol It left no residue when kept in a refrigerator for two days The clear soln was again concd to a small vol and poured into excess distilled H_2O with vigorous stirring An H_2O insoluble fraction separated out, which was purified and extracted consecutively with increasingly polar solvents The EtOH fraction afforded **1**, which was purified over basic alumina, eluted with MeOH and crystallized from EtOAc–MeOH (1 4), mp 120–122° (Found C = 25 21%, H = 3 49%, required C = 25 29%, H = 3 55%)

Acid hydrolysis of **1** Compound **1** (1 g) was hydrolysed with 7% ethanolic sulphuric acid (50 ml) for 1 hr Compound **2** was crystallized from hot EtOH as yellow crystals, mp 273–275° (Found C = 70 79%, H = 3 87%, $C_{15}H_{10}O_4$ required C = 70 86%, H = 3 93%) The aq hydrolysate after neutralization with $BaCO_3$ gave xylose

Acetylation of **2** The acetyl derivative, mp 190°, obtained by acetylation of **2** (45 mg) with Ac_2O (6 ml) and pyridine (20 ml) was crystallized from EtOH (Found $COCH_3$ = 25 38%, required for $C_{15}H_8O_4$ $(COCH_3)_2 - COCH_3$ = 25 44%)

Methylation of **2** Compound **2** (40 mg) was methylated with dimethyl sulphate (2 ml) and dry K_2CO_3 (2 g) in dry Me_2CO (30 ml) for 8 hr The dimethyl ether melted at 188–190°

Potassium permanganate oxidation Compound **2** (40 mg) was oxidized by the usual method The product obtained after oxidation was identified as benzoic acid, mp 120°, and confirmed by mmp Compound **1** also gave benzoic acid under similar conditions

Potassium hydroxide degradation Alkaline degradation of **2** (50 mg) was carried out as usual [10] The product obtained from the first and third fractions were identified as benzoic acid, mp 120°, and phloroglucinol, mp 217°, respectively by their mp and mmp

Enzymatic hydrolysis of **1** Compound **1** (20 mg) was hydrolysed with emulsin at 30–40° for 6 hr to ensure complete hydrolysis and only xylose was detected

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ISOFLAVONES OF *IRIS SPURIA*

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Key Word Index—*Iris spuria*, Iridaceae, isoflavones, iristectorigenin A, iristectorin A

Abstract—A new isoflavone, 5,7-dihydroxy-6,2′-dimethoxyisoflavone, together with iristectorigenin A and iristectorin A were isolated and characterized from the methanol extract of *Iris spuria*

Iris spuria is a rhizomatous herb growing wild in Kashmir (2000–2700 m) Chemical investigation of this plant is reported here for the first time A defatted methanol extract of the rhizomes on repeated CC over silica gel furnished compounds **1**–**3** Compound **1**, mp 194°, $C_{17}H_{14}O_6$, was assigned the structure 5,7-dihydroxy-6,2′-dimethoxyisoflavone—a new isoflavone The substitution pattern of ring A was deduced from the UV spectrum by the application of diagnostic shift reagents, and of ring B by the chemical shifts and multiplicity of signals in high field ^{1}H NMR which allows the identification of two (H-4′, H-5′), two *ortho* and one *meta*-coupled, and two (H-3′, H-6′), one *ortho* and one *meta*-coupled aryl-protons ^{13}C NMR chemical shifts for C-2 and C-3 are in good agreement with the values reported for isoflavones [1–4] In the mass spectrum the $[M]^+$ is the base peak and $[M-Me]^+$ the next highest peak This provides justification for putting the methoxyl at C-6 for in 8-methoxy-5-hydroxyflavones the order is generally reversed and the $[M-Me]^+$ is the predominant peak The retro-Diels–Alder fragments at *m/z* 182 and 132, and a peak at 283 $[M-31]^+$ further support the assigned substitution pattern

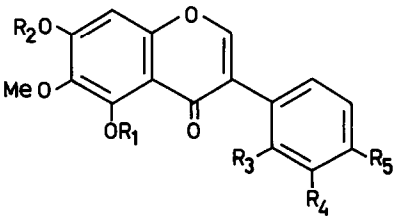
Compound **2**, mp 237°, was identified as iristectorigenin A [5] from its physical data and direct comparison with an authentic sample The ^{13}C NMR of **2** has been measured and is reported here for the first time Comparison of the set of five signals corresponding to carbon atoms 5–9 of **1** with **2** (see Experimental), shows an identical A-ring substitution in both compounds Correlation with reported data [6, 7] and consideration of known substituent effects [8] also allow the placement of a methoxyl group at C-6 and not at C-8 in **1** because the latter position would have shifted the C-9 signal upfield [7]

Compound **3**, mp 213–214°, was identified as iristectorin A [5], a 7-*O*-β-D-glucoside of **2**, by acid hydrolysis and mmp with an authentic sample

EXPERIMENTAL

Mps are uncorr For ^{1}H and ^{13}C NMR TMS was used as int standard The air dried defatted rhizomes (1 7 kg) of *I spuria* L, collected in October (voucher 8624, deposited at the Herbarium of Botany Department, Kashmir University), were extracted with MeOH The dried extract was re-extracted with hot EtOAc The resulting extract was separated by CC over silica gel

Compound **1** (65 mg) was obtained from petrol–EtOAc (4 1) fractions, mp 194° (pale yellow needles, MeOH), R_f 0 62 (hexane–EtOAc, 1 1), 0 56 (hexane–Me_2CO, 3 2), positive Gibbs



1 R_1, R_2, R_4, R_5 = H, R_3 = OMe
2 R_1, R_2, R_3 = H; R_4 = OH; R_5 = OMe
3 R_1, R_3 = H, R_2 = Glc, R_4 = OH, R_5 = OMe

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