5 Hough, L and Powell, D B (1960) *J Chem Soc* 16
6 Hillis, W E and Urbach, G (1958) *Nature* **182**, 656
7 Gage, T B, Deuglass, C D and Wander, S H (1951) *Analyt Chem* **23**, 1582
8 Harborne, J B (1958) *J Chromatogr* **1**, 473
9 Feigl, F (1960) *Spot Tests in Organic Chemistry*, p 467 Elsevier, Amsterdam
10 Venkatraman, K (1962) *The Chemistry of Flavonoid Compounds* (Geissman, T A, ed) p 70 Pergamon Press, Oxford

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ISOFLAVONES OF *IRIS SPURIA*

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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

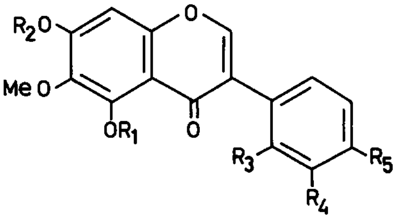
Compound **2**, mp 237°, was identified as iristectorigenin A [5] from its physical data and direct comparison with an authentic sample The ^{13}C NMR of **2** has been measured and is reported here for the first time Comparison of the set of five signals corresponding to carbon atoms 5–9 of **1** with **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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test [9], $C_{17}H_{14}O_6$ UV λ_{max}^{MeOH} nm 262, 330 sh, +NaOMe 270, 320, +$AlCl_3$ 272, 320; +$AlCl_3$–HCl 272, 320; +NaOAc 270, 340; +NaOAc–H_3BO_3 270, 340 IR ν_{max}^{KBr} cm^{-1} 3400, 1670, 1640, 1620, 1520, 1470, 1450, 1390, 1320, 1240, 1190, 1080, 1000, 950, 920 etc ^{1}H NMR (270 MHz, DMSO-d_6) δ3 731 (3H, *s*, OMe), 3 748 (3H, *s*, OMe), 6 530 (1H, *s*, H-8), 6 996 (1H, *ddd*, *J* = 8, 7, 1 Hz, H-5′), 7 089 (1H, *dd*, *J* = 8, 1 Hz, H-3′), 7 237 (1H, *dd*, *J* = 7, 2 Hz, H-6′), 7 398 (1H, *ddd*, *J* = 8, 8, 2 Hz, H-4′), 8 220 (1H, *s*, H-2), 12 937 (1H, *s*, OH—exchangeable with D_2O) ^{13}C NMR (67 88 MHz, DMSO-d_6) δ55 49 (*q*, OMe), 59 84 (*q*, OMe), 93 92 (*d*, C-8), 104 69 (*s*, C-10), 111 30 (*d*, C-3′), 119 75 (*s*, C-1′), 119 92 (*d*, C-5′), 120 04 (*s*, C-3), 129 80 (*d*, C-4′), 131 48 (*s*, *d*, C-6, C-6′), 152 70 (*s*, C-5), 153 03 (*s*, *s*, C-7, 2′), 155 12 (*d*, C-2), 157 41 (*s*, C-9), 180 03 (*s*, C-4) EIMS (probe) 70 eV, *m/z* (rel int) 314 $[M]^+$ (100), 300 (10), 299 $[M-15]^+$ (50 8), 296 $[M-18]^+$ (29), 283 (20), 182 (10), 132 (15) etc (Found C, 64 72, H, 4 51 $C_{17}H_{14}O_6$ requires C, 64 96, H, 4 46%) Acetylation (Ac_2O–pyridine) gave a diacetate, mp 176–178°, R_f 0 8 (CH_2Cl_2–MeOH, 49 1), $C_{21}H_{18}O_8$ ^{1}H NMR (60 MHz, $CDCl_3$) δ2 40 (3H, *s*, ArOAc), 2 43 (3H, *s*, ArOAc), 3 8 (3H, *s*, OMe), 3 86 (3H, *s*, OMe), 7 1 (1H, *s*, H-8), 7 33 (4H, *m*, H-3, H-4′, H-5′, H-6′), 7 96 (1H, *s*, H-2) Methylation (Me_2SO_4–K_2CO_3–Me_2O) gave a diMe ether, mp 170° (EtOAc), $C_{19}H_{18}O_6$

Compound **2** (850 mg), isolated from petrol–EtOAc (3 2) fractions, mp 237° (cream coloured needles, MeOH, lit [5] 234–235°), $C_{17}H_{14}O_7$ ^{13}C NMR (67 88 MHz, DMSO-d_6) δ55 75 (*q*, OMe), 59 95 (*q*, OMe), 93 89 (*d*, C-8), 104 85 (*s*, C-10), 113 33 (*d*, C-5′), 115 31 (*d*, C-2′), 121 75 (*s*, *d*, C-3, C-6′), 121 87 (*s*, C-1′), 131 43 (*s*, C-6), 146 73 (*s*, C-3′), 147 30 (*s*, C-4′), 152 71 (*s*, C-5), 153 31 (*s*, C-7), 154 21 (*d*, C-2), 157 50 (*s*, C-9), 180 54 (*s*, C-4) EIMS *m/z* (rel int) 331 $[M+1]^+$ (20), 330 $[M]^+$ (100), 315 $[M-15]^+$ (50), 312 (40), 287 (60), 272 (5), 183 (3), 150 (2), 149 (15), 69 (30) etc

Compound **3** (600 mg), isolated from EtOAc-insoluble MeOH extract by CC over silica gel ($CHCl_3$–MeOH, 6 1), mp 213–214° (lit [5] 212–214°), $C_{23}H_{24}O_{12}$, acid hydrolysis to **2** and glucose (co-PC), mmp and co-TLC with authentic sample of iristectorin A

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REFERENCES

1 Markham, K R and Ternai, B (1976) *Tetrahedron* **32**, 2607
2 Wagner, H, Chari, V M and Sonnenbichler, J (1976) *Tetrahedron Letters* **21**, 1799
3 Pelter, A, Ward, R S and Bass, R J (1978) *J Chem Soc Perkin Trans* 1, 666
4 Jha, H C, Zilliken, F and Breitmaier, E (1980) *Can J Chem* **58**, 1211
5 Morita, N, Shimokoriyama, M, Shimizu, M and Arisawa, M (1972) *Chem Pharm. Bull* **20**, 730
6 Chang, C J (1978) *Lloydia* **41**, 17
7 Van den Broucke, C O, Dommisse, R A, Esmans, E L and Lemli, J A (1982) *Phytochemistry* **21**, 2581
8 Levy, G C, Lichter, R L and Nelson, G L (1980) *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, p 111 John Wiley, New York
9 King, F E, King, T J and Manning, L C (1957) *J Chem Soc* 563