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# FLAVONOIDS OF *IRIS SPURIA*

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**Key word Index**—*Iris spuria*, Iridacae, flavonoids, 5,2′-dihydroxy-7,8-dimethoxyisoflavone; 5,8,2′-trihydroxy-7-methoxyflavanone

**Abstract**—Two new flavonoids were isolated from the rhizomes of *Iris spuria* and characterized as 5,2′-dihydroxy-7,8-dimethoxyisoflavone and 5,8,2′-trihydroxy-7-methoxy flavanone

## INTRODUCTION

In a previous paper, we reported the isolation and structure elucidation of three isoflavones, 5,7-dihydroxy-6,2′-dimethoxyisoflavone, iristectorigenin A and iristectorin A from the rhizomes of *Iris spuria* [1] This paper deals with the isolation and characterization of a new isoflavone (**1**) and a new flavanone (**2**) from the chloroform extract of the rhizomes of *Iris spuria*

## RESULTS AND DISCUSSION

Column chromatography of the chloroform extract, followed by preparative TLC and crystallization yielded yellow needles of compound **1**, mp 164–166°, $M^+$ at *m/z* 314 consistant with the molecular formula $C_{17}H_{14}O_6$ The IR (1660 $cm^{-1}$, C=O), UV (218, 262, 335 nm), and $^1H$ NMR ($\delta$ 8.1, 1H, C-2 proton) spectra established that compound **1** was an isoflavone. It gave a green colour with alcoholic ferric chloride solution indicating the presence of a chelated hydroxyl group Formation of a diacetate and $^1H$ NMR signals at $\delta$ 12 09 (1H, *s*) and 8.2 (1H, *s*) which disappeared on addition of $D_2O$ established the presence of two phenolic hydroxyl groups. A bathochromic shift of 13 nm in the UV spectrum on addition of $AlCl_3$ and $AlCl_3$–HCl located a hydroxyl group at C-5. Absence of a shift on addition of NaOAc indicated that C-7 was substituted by a methoxyl group. The $^1H$ NMR spectrum showed the presence of two singlets (3H) at $\delta$ 3 80 and 3.85 attributed to the methoxyls at C-7 and C-8. The singlet (1H) at $\delta$ 6 4 was assigned to C-6 because this signal shifted to $\delta$ 6.65 with $\Delta\delta$ of 0 25 ppm characteristic of an aromatic proton with a free *ortho*-hydroxyl group [2, 3]. The mass spectrum showed $[M-Me]^+$ as the base peak and this further justified location of the methoxyl group at C-8 because in 6,7-dimethoxy-5-hydroxy flavones $[M]^+$ is the predominent peak [1, 4]. RDA fragmentation ions at *m/z* 196 and 118 suggested the presence of one hydroxyl and two methoxyl groups in ring A and one hydroxyl group in ring B. More important was the $[M-17]^+$ peak which is characteristic of 2′-hydroxylated flavones [5, 6]. $^{13}C$ NMR chemical shifts for C-2 and C-3 were in agreement with the values reported for isoflavones and were in accord with the known substituent effects [7, 8]. Thus from the above data compound **1** was characterized as 5,2′-dihydroxy-7,8 dimethoxyisoflavone.

Compound **2**, mp 204–205°, $C_{16}H_{14}O_6$ [$M^+$ at *m/z* 302], gave IR (1650 $cm^{-1}$, C=O) and UV (216, 290, 330 nm) spectra indicating that it was a flavanone This was further substantiated by the $^1H$ NMR spectrum with an ABX system centred at $\delta$ 2.8, 3.05 and 5 75 for the H-2

and H-3 protons of a flavanone moiety A bathochromic shift was observed in the UV spectrum on addition of $AlCl_3$ and $AlCl_3$–HCl thus locating a hydroxyl group at C-5 Absence of a shift with NaOAc, indicated that C-7 was substituted by a methoxyl group The $^1H$ NMR spectrum showed a singlet at $\delta$ 6.00 and this signal on acetylation shifted to $\delta$ 6 20 and was assigned to C-6 [2, 3]. The chemical shifts and splitting patterns of the B-ring protons in the $^1H$ NMR spectrum and $[M-17]^+$ peak in the mass spectrum indicated that the B-ring was substituted at C-2′. The RDA fragmentation ions at *m/z* 182 and 120 further suggested the presence of two hydroxyl and one methoxyl group in ring A and one hydroxyl group in ring B. Thus compound **2** was characterized as 5,8,2′-trihydroxy-7-methoxyflavanone Supporting evidence for the structure of **2** was provided by the $^{13}C$ NMR spectral data Assignments were based on chemical shift arguments and by comparison with a closely related flavanone [9]

## EXPERIMENTAL

Collection of plant material and instrumental methods are as described previously [1] The air-dried rhizomes (1 5 kg) of *Iris spuria* after prior defatting were extracted with $CHCl_3$ The resulting extract on CC (silica gel) gave a fraction from petrol–EtOAc (9 1) mixture which on repeated CC and prep TLC (hexane–EtOAc–MeOH, 15 9 1) afforded **1** (40 mg), mp 164–166°, yellow needles (MeOH), $R_f$ 0 65 (hexane–EtOAc, 1 1), $C_{17}H_{14}O_6$ UV $\lambda_{max}^{MeOH}$ nm 218, 262, 335 sh, +NaOAc 262, 335, +$AlCl_3$ 275, 335, +$AlCl_3$–HCl 275, 335, IR $\nu_{max}^{KBr}$ $cm^{-1}$ 3450, 1660 (C=O), 1600, 1500, 1440, 1380, 1320, 1280, 1220, 1100, 1050 etc. $^1H$ NMR (400 MHz, $CDCl_3$). $\delta$ 3.80 (3H, s, OMe), 3.85 (3H, s, OMe), 6 4 (1H, s, H-6), 7 09 (1H, *dd*, *J* = 8, 2 Hz, H-3′), 6 99 (1H, *ddd*, *J* = 8 5, 8, 1 Hz, H-5′), 7 17 (1H, *dd*, *J* = 8, 2 Hz, H-6′), 7 35 (1H, *ddd*, *J* = 8 5, 8, 2 Hz, H-4′), 8 0 (1H, s, OH), 8 1 (1H, s, H-2), 12 9 (1H, s, OH) $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 56 37 (OMe), 61 60 (OMe), 155 89 (C-2), 122 88 (C-3), 182 07 (C-4), 157 91 (C-5), 96 60 (C-6), 130. 59 (C-8), 159 31 (C-7), 104 88 (C-10), 155.83 (C-2′), 121 03 (C-1′), 119 29 (C-3′), 129 91 (C-4′), 119 52 (C-5′), 128 87 (C-6′). EIMS *m/z* (rel. int.). 314 (5), 300 (40), 299 (100), 297 (12), 296 (10), 284 (80), 281 (40), 196 (33 8), 181 (70), 153 (26 9), 145 (10), 118 (8) etc Acetylation ($Ac_2O$–pyridine) gave a diacetate, mp 125°, $R_f$ 0 72 (hexane–EtOAc, 1 1), $C_{21}H_{18}O_8$ $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 2 20 (3H, s, Ac) 2 3 (3H, s, Ac), 3 85 (6H, s, 2x OMe), 6 65 (1H, s, H-8), 7 2 to 7 36 (4H, m, H-3′, 4′, 5′, 6′), 7 8 (1H, s, H-2)

Compound **2** (50 mg), isolated from petrol–EtOAc (7 3) fractions, mp 204° (cream coloured needles, EtOAc), $R_f$ 0 39 (hexane–EtOAc, 1 1) $C_{16}H_{14}O_6$ UV $\lambda_{max}^{MeOH}$ nm 218, 290, 335 sh, +$AlCl_3$ 316, 340, +$AlCl_3$–HCl 316, 340, +NaOAc 290, 335 +NaOAc–$H_3BO_3$ 290, 335 IR $\nu_{max}^{KBr}$ $cm^{-1}$ 3200 (OH), 1650 (C=O), 1600, 1580, 1460, 1355, 1300, 1270, 1240, 1110, 1090, 1070, 990, 950, 910, 820 $^1H$ NMR (90 MHz, $Me_2CO$-$d_6$) $\delta$ 2 80 (1H, *dd*, *J* = 16, 4 Hz, H-3), 3 05 (1H, *dd*, *J* = 16 0, 10 Hz, H-3) 3 70 (3H, s, OMe), 5.75 (1H, *dd*, *J* = 10, 4 Hz, H-2), 6 0 (1H, s, H-6), 6 88–7 0 (1H, m, H-5′), 7 05 (1H, *dd*, *J* = 8, 2 Hz, H-3′), 7 3–7 45 (1H, m, H-4′), 7.56 (1H, *dd*, *J* = 8, 2 Hz, H-6′), $^{13}C$ NMR (22.5 MHz, $Me_2CO$-$d_6$) $\delta$ 60 0 (OMe) 74 5 (C-2), 42 0 (C-3), 194 5 (C-4), 94 7 (C-6), 158 0 (C-5), 162 3 (C-7), 129 2 (C-8), 154 0 (C-9), 101 0 (C-10) 125 5 (C-1′), 152 0 (C-2′), 115 2 (C-3′), 128 7 (C-4′), 120 0 (C-5′), 127 0 (C-6′) EIMS *m/z* (rel int) 302 (80), 285 (10), 284 (30), 269 (100), 241 (20), 182 (60), 167 (90), 120 (10) Acetylation ($Ac_2O$–pyridine) gave a triacetate $C_{22}H_{20}O_9$, $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 2 25 (6H, s, 2xAc) 2.30 (3H, s, Ac), 3 80 (3H, s, OMe) 6 20 (1H, s, H-6), 7 0–7 56 (4H, m, H-3′, 4′, 5′, 6′) Methylation ($Me_2SO_4$–$K_2CO_3$–$Me_2CO$) gave a triMe ether, mp 170° (petrol–EtOAc), lit [9] 174°

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