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IRISPURINOL, A 12a-HYDROXYROTENOID FROM *IRIS SPURIA*

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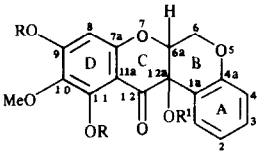
Key Word Index—*Iris spuria*; Iridaceae; 12a-hydroxyrotenoid; irispurinol.

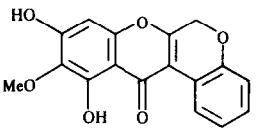
Abstract—A new 12a-hydroxyrotenoid was isolated from the rhizomes of *Iris spuria* and characterised as (−)-9,11,-12a-trihydroxy-10-methoxyrotenoid.

INTRODUCTION

Previously we reported the isolation and structure elucidation of four isoflavones, 5,7-dihydroxy-6,2′-dimethoxyisoflavone, iristectorigenin A, iristectorin A and 5,2′-dihydroxy-7,8-dimethoxyisoflavone, and a flavanone, 5,8,2′-trihydroxy-7-methoxyflavanone from the rhizomes of *Iris spuria* [1, 2]. In this paper we report the isolation of a new 12α-hydroxyrotenoid (**1**) from a methanolic extract of the rhizomes of *I. spuria*.



1 R = H
2 R = Ac



3

RESULTS AND DISCUSSION

Compound **1**, $C_{17}H_{14}O_7$ ([M]$^+$ = *m/z* 330), gave a positive Durham's test for rotenoids. A green colour with alcoholic ferric chloride solution indicated the presence of a chelated hydroxyl group. This was supported by the UV absorption bands (MeOH) at 216, 294 and 350 (sh) nm, IR bands at 3250 (*br*, OH) and 1640 (chelated C=O) cm^{-1} and ^{1}H NMR signals for an ABC system (δ 4.36, IH, *dd*, *J* = 5.5 and 11 Hz; 4.38, IH, *t*, *J* = 11 Hz; 4.79, IH, *dd*, *J* = 5.5 and 11 Hz) attributed to the sequence OCH_2–CH–O. In agreement with the latter assignment, the ^{13}C NMR spectrum of **1** showed resonances at δ 75.5(*d*), 62.2(*t*) and 65.0(*s*) for C-6a,C-6 and C-12a respectively. The position of two phenolic hydroxyl groups in ring D was indicated from the changes in the UV spectrum upon addition of diagnostic shift reagents. The ^{1}H NMR spectrum showed a singlet at δ 3.77 (3H) attributed to a methoxyl at C-10. A singlet at δ 6.0 (1H), which on acetylation shifted to δ 6.38, was assigned to C-8 [2,3]. The chemical shifts and multiplicity of signals in the ^{1}H and ^{13}C NMR spectra of **1** indicated that ring A was unsubstituted. On acetylation, **1** gave the triacetate **2** which showed in its ^{1}H NMR spectrum the signals of an aliphatic acetyl group (δ 1.88), assigned to the 12a position, and two aromatic acetyl groups (δ 2.1 and 2.3).

The above data suggested the structure of a 12a-hydroxyrotenoid for **1**. Acid catalysed dehydration of **1** gave **3** $C_{17}H_{12}O_6$([M]$^+$ = *m/z* 312). which showed a sharp singlet at δ 5.10 for two protons in its ^{1}H NMR spectrum. This suggested that the aliphatic hydroxyl group was on the B/C ring junction in **1**. In the mass spectrum of **1**, RDA fragmentation ions at *m/z* 182 and 148 further confirmed the presence of one methoxyl and two hydroxyl groups in ring D and one hydroxyl group at the 12a-position. The *trans* B/C ring junction was assigned to **1** on the basis of H-1 chemical shift [4,5]. It was impossible to correlated the Cotton effect curve to the absolute configuration on account of the absence of proper models. It is interesting to note that there is no substitution on the A-ring of **1** whereas previously only A ring-substituted 12a-hydroxyrotenoids have been isolated.

The co-occurence of 5,7-dihydroxy-6,2′-dimethoxyisoflavone and irispurinol in the rhizomes of *I. spuria* is biogentically interesting and is consistant with the biogentic scheme proposed for rotenoids[6,7]. The possibility of **1** being an artefact was ruled out by the fact that TLC showed the presence of **1** in the extract from the outset.

EXPERIMENTAL

Collection of plant material and spectral methods are as described previously[I]. The air-dried rhizomes (2 kg) of *Iris spuria* after extraction with $CHCl_3$ were re-extracted with hot MeOH. The residue after evapn (30 g) was chromatographed on silica gel using a petrol–EtOAc gradient. The fractions eluted with 30 and 40% EtOAc on CC and prep. TLC (hexane–Me_2CO, 3:2) afforded **1** (50 mg)mp 255–256°(pale yellow needles, EtOAc), R_f 0.24 (CH_2Cl_2–MeOH,19:1), 0.52 (hexane–Me_2CO, 3:2), $[\alpha]_D^{22}$-75.23° (MeOH); UV λ_{max}^{MeOH} nm: 216, 294, 350 (sh); +NaOAc 298, 340; +$AlCl_3$ 304, 360; +NaOAc–H_3BO_3 296,335; IR ν_{max}^{KBR} cm^{-1}: 3250, 1640, 1480, 1450, 1280, 1210, 1200, 1160, 1132, 1100, 1060, 1000, 960, 840 etc.; ^{1}H NMR (270 MHz, DMSO-d_6): δ 3.77(3H, *s*, OMe), 4.36 (IH, *dd*, $J_{6eq\text{-}6a}$ = 5.5 and $J_{6eq\text{-}6ax}$ = 11 Hz, H-6_{eq}), 4.38 (IH, *t*, $J_{6ax\text{-}6a}$ = 11 Hz, H-6_{ax}), 4.79 (IH, *dd*, *J* = 2 and 8 Hz, H-6a), 6.05 (IH, *s*, H-8), 6.87 (IH, *dd*, *J* = 2 and 8Hz, H-4), 7.02 (IH, *ddd*, *J* = 8, 8, 2 Hz, H-2), 8.2 (IH, *dd*, *J* = 8, 2 Hz, H-1), 10.8 (IH, *s*, OH), 11.8 (IH, *s*, OH); ^{13}C NMR (67.88 MHz, DMSO-d_6):δ 194.0(C-12), 159.26 (C-7a), 156.5 (C-11), 156.02 (C-9), 154.26 (C-4a), 131.6 (C-10),

130.0 (C-1) 129.44 (C-2), 120.1 (C-3), 119.2 (C-1a), 116.49 (C-11a), 101.2 (C-4), 94.5 (C-8), 75.5 (C-6a), 65.0 (C-12a), 62.2 (C-6), 59.0 (OMe); EIMS *m/z* (rel. int.): 330 (40), 312 $[M-H_2O]^+$ (12), 298(5), 183(100), 182(90), 168(60), 167(50), 155(7), 149(10), 148(60), 147(90) etc.

Acetylation (Ac_2O-4-dimethylaminopyridine) gave a triacetate (**2**), mp 206°, R_f 0.66 (hexane–Me_2CO, 3:2), $C_{23}H_{20}O_{10}$. ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.88, 2.1 and 2.3 (9H, 3*s*, 3 × OCOMe), 3.85 (1H, *s*, OMe), 4.39 to 4.8 (3H, *m*, H-6_{ax}H-6_{eq} and H 6a), 6.38 (1H, *s*, H-8), 6.80 (1H, *dd*, $J=8$, 2 Hz, H-4), 7.0 to 7.25 (2H, *m*, H-2 and H-3), 8.35 (1H, *dd*, $J=8$, 2 Hz, H-1).

1 on acid catalysed dehydration with methanolic-HCl for 8 hr at 100° and work-up in usual manner gave **3** (crystals from MeOH), mp 206°, R_f 0.64 (hexane–Me_2CO, 3:2), $C_{17}H_{12}O_6$. UV λ_{max}^{MeOH} nm: 216, 280, 340; +$AlCl_3$ 216, 288, 330; IR ν_{max}^{KBr} cm^{-1}: 3200, 1640, 1520, 1480, 1460, 1400, 1310, 1280, 1220, 1200, 1150, 1000 etc.; ^{1}H NMR (Me_2CO-d_6): δ 3.90 (3H, *s*, OMe), 5.10 (2H, *s*, C-6), 6.50 (1H, *s*, H-8), 7.00 (1H, *dd*, $J=8$, 2 Hz, H-4), 7.25 to 7.50 (2H, *m*, H-2 and H-3), 8.65 (1H, *dd*, $J=8$, 2 Hz, H-1); EIMS *m/z* (rel. int.): 312 (100), 297(60), 284(7), 269(40), 183(8), 182(10), 168(15), 149(70), 130(10), 129(11) etc.

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A BIFLAVONOID FROM *GARCINIA NERVOSA*

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Key Word Index—*Garcinia nervosa*; Guttiferae; new biflavonoid; flavanonylflavone; I-5, II-5, I-7, II-7, I-3′, I-4′, II-4′-heptahydroxy-[I-3, II-8]-flavanonylflavone; structural elucidation.

Abstract—A new biflavonoid has been isolated from the leaves of *Garcinia nervosa*. Its structure I-5, II-5, I-7, II-7, I-3′, I-4′, II-4′-heptahydroxy-[I-3, II-8]-flavanonylflavone was elucidated with the help of chemical and spectral methods.

INTRODUCTION

The genus *Garcinia* consisting of 180 species has been the subject of considerable phytochemical investigations due to the interesting biological properties of many of its species [1, 2]. The genus has been a major source of prenylated xanthones [3], benzophenones [4] and biflavonoids mainly with a 3/8-linkage [5]. Work on the stem bark of *G. nervosa* has recently been performed and a new xanthone named nervosaxanthone has been isolated [6]; however, no biflavonoid could be isolated. We have now investigated the ether soluble part of the alcoholic extract of leaves of *G. nervosa* and report on the isolation of a new biflavonoid characterised with the help of chemical and spectroscopic methods as I-5, II-5, I-7, II-7, I-3′, I-4′, II-4′-heptahydroxy-[I-3, II-8]-flavanonylflavone (**1**).

RESULTS AND DISCUSSION

The diethyl ether soluble portion of the alcoholic extract was subjected to CC over silica gel. Elution with benzene–ethyl acetate (2:3) afforded crude **1** which was purified by preparative TLC and crystallized from benzene–methanol as yellow crystals, mp 232–234°.

Compound **1** analysing for $C_{30}H_{20}O_{11}$ gave a positive ferric chloride test and a pink colour with Zn–HCl and Mg–HCl suggesting that it was a hydroxylated flavonoid derivative. Treatment of **1** with dimethyl sulphate and potassium carbonate in acetone furnished a heptamethyl ether, mp 123–125°. The IR spectrum of **1** exhibited absorptions at 3300 (OH), 1690 (5-hydroxyflavanone) and 1610 cm^{-1} (5-hydroxyflavone). The IR spectrum of the methyl ether of **1** possessed bands at 1645 and 1675 cm^{-1}. Such spectral changes on methylation are reminiscent of the behaviour of flavanone and flavone systems [7] bearing hydroxyl groups at C-5. The UV spectrum of **1** showed absorption maxima at 255 sh, 265 and 320 nm. The shifts of the maxima in the presence of NaOMe, $AlCl_3$, $AlCl_3$–HCl, NaOAc and NaOAc–H_3BO_3 were also studied but did not prove to be very informative due to the superimposition of bands from the two flavonoid units. The structure was further elucidated with the help of ^{1}H, ^{13}C NMR and mass spectrometry.