

TWO ISOFLAVONOIDS FROM THE FRESH BULBS OF *IRIS TINGITANA*

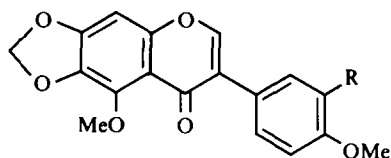
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(Revised received 21 December 1979)

Key Word Index—*Iris tingitana*; Iridaceae; 5,4'-dimethoxy-6,7-methylenedioxyisoflavone; 5,4'-dimethoxy-3'-hydroxy-6,7-methylenedioxyisoflavone.

Iris tingitana Boiss. & Reut. is widely grown in the Mediterranean region as an ornamental plant. Although many contributions concerning the chemistry of *Iris* plants have appeared [1-5], the title plant has not been investigated phytochemically. The present paper deals with the structure elucidation of two new isoflavones (1 and 2) isolated from the ether-soluble fraction. The isolation of five known compounds is also reported: acetovanillone, irisfloreantin, irisolidone, irigenin and 5,3',4'-trimethoxy-6,7-methylene dioxyisoflavone.



The first unknown, **1**, mp 180-183°, $C_{18}H_{14}O_6$, exhibits UV absorption at 270 and 330 nm characteristic of an isoflavonoid, IR absorption bands at 1660 (C=O), 1610 (C=C) and 940 cm^{-1} (methylenedioxy: supported by the sharp singlet of two protons at δ 6.08 and by the Labat test [6] (green colour)), two singlets at δ 8.00 (2-H), and 6.78 (8-H) in the ^1H NMR spectrum and the fragment ions m/e 132 (from B-ring) and 194 (from A-ring), produced by the retro-Diels-Alder cleavage, in the mass spectrum. Also, oxidation of **1** with KMnO_4 resulted in the production of anisic acid supporting the presence of a 4'-methoxy group and treatment of **1** with anhydrous AlCl_3 in ether gave a monodemethylated derivative. From these data, the structure of **1** was determined as 5,4'-dimethoxy-6,7-methylenedioxyisoflavone, which has been obtained previously from irisolone by methylation [7, 8]. This is the first report of irisolone methyl ether as a natural compound.

The second unknown, **2**, mp 203-205°, $C_{18}H_{14}O_7$, exhibits IR absorption bands at 3250 (OH), 1660, 1610 and 940 cm^{-1} and the fragment ions m/e 148 (from B-ring) and 194, indicating an additional hydroxy group in the B-ring. ^1H NMR signals for three aromatic protons on the B-ring show the ABX-type coupling [δ 7.02 (d, J = 8 Hz, 5'-H), 7.25 (dd, J = 8 and 2 Hz, 6'-H), and 7.70 (d,

J = 2 Hz, 2'-H)]. When **2** was treated with diazomethane, it gave 5,3',4'-trimethoxy-6,7-methylenedioxyisoflavone. The positions of hydroxy and methoxy substituents were still ambiguous, so that a NOE experiment was performed. Irradiation of a deuteriopyridine solution of **2** at a frequency (3.76 ppm) corresponding to the absorbance of one of the methoxy groups caused an increase in the integrated intensity of the 5'-H aromatic proton signal (23% NOE). Thus, the structure of **2** must be 5,4'-dimethoxy-3'-hydroxy-6,7-methylenedioxyisoflavone.

EXPERIMENTAL

All mps are uncorr. The IR spectra were examined as KBr pellets, UV spectra were measured in MeOH, ^1H NMR spectra were measured using TMS as int. standard. MS were measured at 70 eV using a direct insertion probe. Si gel refers to Si gel 'Merck' for column chromatography and Si gel GF₂₅₄ 'Merck' for TLC and preparative TLC. The plant material was obtained through Dr. A. F. Halim from the Faculty of Agriculture, University of El-Mansoura, Egypt.

Extraction and isolation. Fresh bulbs (2.5 kg) of *Iris tingitana* were cut and refluxed in MeOH at 100° for 1 hr. The alcoholic extract was distilled under red. pres. and the aq. syrup was extracted several times with Et_2O . The combined ethereal extract was evapd to give 14 g ether-soluble fraction, which was mixed with 30 g Si and chromatographed on a column packed with 600 g Si, and eluted with C_6H_6 - CHCl_3 (1:1); CHCl_3 ; CHCl_3 -MeOH (100:1), (100:3) and (100:10) respectively.

Isolation of known compounds. Acetovanillone: Eluted with CHCl_3 - C_6H_6 (1:1) on the SiO_2 column and recrystallized from C_6H_6 as colourless prisms, mp 114-115°. Irisfloreantin: Eluted with CHCl_3 -MeOH (100:1) and recrystallized from MeOH as colourless needles, mp 175°. 5,3',4'-Trimethoxy-6,7-methylenedioxyisoflavone: Eluted with CHCl_3 -MeOH (100:1) and recrystallized from MeOH as colourless needles, mp 178-180°. Irisolidone: Eluted with CHCl_3 -MeOH (10:1) and recrystallized from MeOH as fine prisms, mp 188-189°. Irigenin: Eluted with CHCl_3 -MeOH (10:1) and recrystallized from MeOH as pale yellow needles, mp 183°.

1 was eluted with CHCl_3 - C_6H_6 (1:1) on the SiO_2 column, and recrystallized from MeOH as colourless needles, mp 180-183°, no colour with FeCl_3 , green colour to the Labat test for methylenedioxy group. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 270 (4.26), 330 (3.50).

IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1660 (C=O); 1610 (C=C); 940 ($\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$). Calc. for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32. Found: C, 66.10; H, 4.25. MS m/e : 326 (M^+). ^1H NMR (10% solution in Py-d_5): δ 3.72 and

4.15 (3 H each, s, OMe), 6.08 (2 H, s, $\text{CH}_2\text{<O}$), 6.78 (1 H, s), 8.00 (1 H, s), 7.05 and 7.72 (2 H, each on the B-ring, *d*, *J* = 8.5 Hz).

Partial demethylation of 1. **1** (18 mg) was refluxed with dry AlCl_3 (200 mg) in 4 ml of absolute Et_2O . After 10 hr, the reaction mixture was poured in ice-water, and the yellow deposit separated, boiled with HOAc (2 ml) and HCl (1 ml) for 5 min, diluted with H_2O and extracted with EtOAc. Evapn of the solvent gave pale yellow crystals (14 mg), mp 214–215°, green colour with FeCl_3 . ^1H NMR (in CDCl_3): δ 3.84 (3 H, s, OMe), 6.07 (2 H, s, $\text{CH}_2\text{<O}$), 6.48 (1 H, s, C-8), 7.87 (1 H, s, C-2), 6.96 and 7.44 (2 H, each on the B-ring, *d*, *J* = 8 Hz). The product is an isomer of irisolone, i.e. 5-hydroxy-4'-methoxy-6,7-methylenedioxyisoflavone.

Oxidation of 1 with KMnO_4 . **1** (100 mg) was warmed with 15 ml Me_2CO and KMnO_4 added gradually till a pink colour persisted. The solid was filtered off, washed with Me_2CO , extracted with hot H_2O and filtered. The clear filtrate was acidified and the deposit was separated and recrystallized from hot H_2O to give colourless needles of anisic acid (16 mg), mp and mmp with authentic sample 186–187°.

2 was eluted with CHCl_3 –MeOH (100:3) and recrystallized from MeOH as colourless minute prisms, mp 203–205°, green colour to FeCl_3 , green colour to the Labat test, positive to the Gibbs reagent [7]. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3250 (OH); 1660 (C=O); 1610 (C=C); 940, 930 ($\text{CH}_2\text{<O}$). Calc. for $\text{C}_{18}\text{H}_{14}\text{O}_7$: C, 63.16; H, 4.12. Found: C, 63.00; H, 4.20. MS *m/e*: 342 (M^+). ^1H NMR

(10% solution in $\text{Py}-d_5$): δ 3.76 and 4.12 (3 H each, s, OMe), 6.08 (2 H, s, $\text{CH}_2\text{<O}$), 6.76 (1 H, s), 8.02 (1 H, s), 7.70 (1 H, *d*, *J* = 2 Hz), 7.02 (1 H, *d*, *J* = 8 Hz) and 7.25 (1 H, *dd*, *J* = 8 and 2 Hz). **2** was treated as usual with CH_2N_2 to give a monomethyl ether, which was identical in all respects to 5,3',4'-trimethoxy-6,7-methylenedioxyisoflavone.

Acknowledgements—We are indebted to Dr. A. F. Halim, Faculty of Pharmacy, El. Mansoura University, for providing the plant materials. We are also thankful to Mr. T. Kumagai for measuring the NMR spectra.

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