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CRYSTAL AND MOLECULAR STRUCTURE OF THE ISOFLAVONES IRILIN B AND BETAVULGARIN

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The molecular structures of the isoflavones irilin B and betavulgarin, which were isolated for the first time from the aerial part of Iris tenuiflora, *were solved by x-ray structure analyses.*

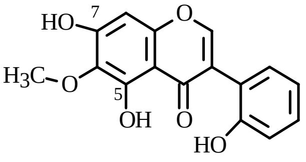
Key words: *Iris tenuiflora*, isoflavones, irilin B, betavulgarin, XSA.

The family Iridaceae includes the genus *Iris*, which numbers 300 species, of which 16 have been described in Pakistan.

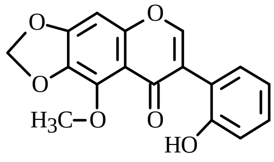
I. tenuiflora grows in Mongolia and Iran and in the province of Belujistan in Pakistan. Ground roots of this plant mixed with curds are used in folk medicine to treat diarrhea. Flavonoids were isolated previously from the aerial part of this plant [1, 2].

A phytochemical investigation of various *Iris* species led to the isolation of flavanones, isoflavanones, benzoquinones, and aromatic compounds [3, 4].

Herein we report the isolation and x-ray structure analyses (XSA) of irilin B (**1**) and betavulgarin (**2**), which were isolated previously from other species [5, 6] and are found for the first time in *I. tenuiflora.*



1



2

Figure 1 shows the molecular structures of **1** and **2** from the XSA. The condensed part (atoms O1 and C2-C10) in **1** and **2** is practically planar (atoms are coplanar within ±0.025 and ±0.022 Å, respectively). The aromatic ring bound to it is also planar (±0.025 Å). The five-membered heterocycle in **2** adopts the flattened envelope conformation (atoms C6, C7, O2, and O3 are coplanar within ±0.002 Å) around C12 (deviation 0.145 Å).

The aromatic ring in the molecules is slightly rotated relative to the plane of the bicyclic system: by 39.3° in **1**; 45.4° in **2**. Nevertheless, the aromatic hydroxyl (C6′-OH) in both molecules is positioned *syn* relative to the ketone (C4=O5) and forms an intramolecular H-bond O5...H–O6 (Fig. 1). The parameters of this intramolecular H-bond in **1** and **2** are 2.60 and 2.59 (O5...O6), 1.58 and 1.72 Å (O5...H), and 164.2 and 161.2° (O5...H–O6 angle), respectively. This H-bond may stabilize such an orientation since an aromatic ring with a methoxyl in a related isoflavone is positioned approximately perpendicular to the bicyclic system due to its absence [7]. Furthermore, The H of the other hydroxyl in **1** (C5–O4H) is also directed toward C5. Therefore, it forms another intramolecular H-bond with the following parameters: O4...O5, 2.59 Å; H...O5, 1.76 Å; O4–H...O5, 151.2°.

Atoms of the aromatic ring and the oxygen-containing groups in the flavone part deviate from the plane in both molecules (especially **1**). This may be due to steric repulsion of functional groups placed successively on C4, C5, C6, and C7.

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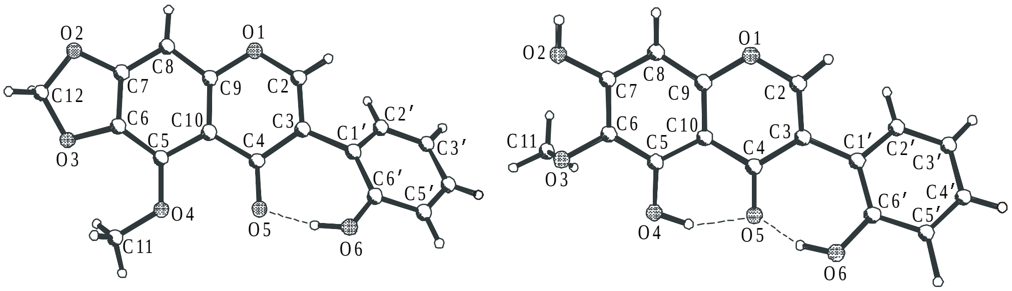
TABLE 1. Bond Lengths (Å) and Angles (deg) in **1** and **2**

Bond	**1**	**2**	Angle	**1**	**2**
O(1)-C(2)	1.344 (2)	1.350 (3)	C(2)-O(1)-C(9)	119.67 (14)	118.95 (18)
O(1)-C(9)	1.371 (2)	1.370 (3)	C(6)-O(3)-C(11)	113.57 (15)	105.70 (19)
O(2)-C(7)	1.348 (2)	1.364 (3)	O(1)-C(2)-C(3)	125.42 (16)	125.3 (2)
O(3)-C(6)	1.382 (2)	1.385 (3)	C(2)-C(3)-C(4)	117.55 (16)	118.9 (2)
O(3)-C(11)	1.467 (3)	1.414 (3)	C(2)-C(3)-C(1′)	118.23 (16)	118.3 (2)
O(4)-C(5)	1.348 (2)	1.340 (3)	C(4)-C(3)-C(1′)	124.21 (16)	122.7 (2)
O(5)-C(4)	1.265 (2)	1.232 (3)	O(5)-C(4)-C(10)	120.53 (16)	123.2 (2)
O(6)-C(6′)	1.375 (3)	1.359 (3)	O(5)-C(4)-C(3)	122.31 (16)	120.8 (2)
C(2)-C(3)	1.353 (3)	1.336 (3)	C(10)-C(4)-C(3)	117.15 (15)	115.99 (19)
C(3)-C(4)	1.451 (2)	1.464 (3)	O(4)-C(5)-C(6)	118.74 (15)	126.4 (2)
C(3)-C(1′)	1.496 (3)	1.493 (3)	O(4)-C(5)-C(10)	121.18 (16)	117.08 (19)
C(4)-C(10)	1.437 (2)	1.464 (3)	C(6)-C(5)-C(10)	120.05 (16)	116.5 (2)
C(5)-C(6)	1.383 (3)	1.377 (3)	O(3)-C(6)-C(5)	119.88 (16)	128.9 (2)
C(5)-C(10)	1.420 (2)	1.438 (3)	O(3)-C(6)-C(7)	119.52 (16)	109.0 (2)
C(6)-C(7)	1.406 (3)	1.381 (3)	C(5)-C(6)-C(7)	120.32 (16)	122.1 (2)
C(7)-C(8)	1.393 (3)	1.361 (3)	O(2)-C(7)-C(8)	122.77 (17)	126.1 (2)
C(8)-C(9)	1.377 (3)	1.387 (3)	O(2)-C(7)-C(6)	116.59 (16)	110.1 (2)
C(9)-C(10)	1.400 (2)	1.400 (3)	C(8)-C(7)-C(6)	120.63 (16)	123.8 (2)
C(1′)-C(6′)	1.405 (3)	1.393 (3)	C(9)-C(8)-C(7)	118.10 (16)	114.9 (2)
C(1′)-C(2′)	1.408 (3)	1.398 (3)	O(1)-C(9)-C(8)	116.73 (15)	113.9 (2)
C(2′)-C(3′)	1.387 (3)	1.388 (4)	O(1)-C(9)-C(10)	119.83 (15)	121.6 (2)
C(3′)-C(4′)	1.382 (4)	1.366 (5)	C(8)-C(9)-C(10)	123.41 (16)	124.5 (2)
C(4′)-C(5′)	1.374 (4)	1.372 (4)	C(9)-C(10)-C(5)	117.42 (16)	118.23 (19)
C(5′)-C(6′)	1.392 (3)	1.392 (3)	C(9)-C(10)-C(4)	120.33 (15)	118.93 (19)
O(2)-C(12)		1.423 (3)	C(5)-C(10)-C(4)	122.13 (15)	122.84 (19)
O(4)-C(11)		1.418 (3)	C(6′)-C(1′)-C(2′)	117.25 (18)	117.9 (2)
			C(6′)-C(1′)-C(3)	123.93 (17)	118.3 (2)
			C(2′)-C(1′)-C(3)	118.70 (18)	123.7 (2)
			C(3′)-C(2′)-C(1′)	121.6 (2)	121.3 (3)
			C(4′)-C(3′)-C(2′)	119.8 (2)	119.8 (3)
			C(5′)-C(4′)-C(3′)	119.9 (2)	120.4 (3)
			C(4′)-C(5′)-C(6′)	120.9 (2)	120.5 (3)
			O(6)-C(6′)-C(5′)	117.2 (2)	117.0 (2)
			O(6)-C(6′)-C(1′)	122.26 (17)	122.9 (2)
			C(5′)-C(6′)-C(1′)	120.5 (2)	120.1 (2)
			C(7)-O(2)-C(12)		105.76 (19)
			C(5)-O(4)-C(11)		120.61 (19)
			O(3)-C(12)-O(2)		108.4 (2)



1 **2**

Fig. 1. Molecular structures and atomic numberings of **1** and **2**.

Table 1 gives bond lengths and angles in **1** and **2**. Equivalent bonds and angles show no significant differences. However, the bond lengths of the ketones (C4=O5) in **1** and **2** [1.265(2) and 1.232(3) Å, respectively] are substantially lengthened compared with the normal value [8, 9] and differ from each other.

TABLE 2. Crystallographic Data, Experimental Conditions, and Refinement Parameters for the Structures of **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{16}H_{12}O_6 \cdot H_2O$	$C_{17}H_{12}O_6$
Molecular weight	318.27	312.27
Temperature, K	293	293
Space group	$P2_1/c$, Z = 4	$P2_1/c$, Z = 4
a, Å	11.779 (2)	14.302 (3)
b, Å	7.7410 (15)	7.1000 (14)
c, Å	16.566 (3)	14.965 (3)
β°	92.00 (3)	113.49 (3)
V, $Å^3$	1509.6 (5)	1393.7 (5)
ρ, g/cm^3	1.400	1.488
Absorption coefficient, μ, mm^{-1}	0.111	0.114
Crystal dimensions, mm	0.70×0.50×0.40	0.98×0.53×0.20
Range of θ, deg	2.90 to 25.98	2.75 to 26.00
Total number of reflections	2879	2742
Number of reflections [$I > 2\sigma(I)$]	2388	2025
R-factor [$I > 2\sigma(I)$]	R1 = 0.0470, wR2 = 0.1218	R1 = 0.0555, wR2 = 0.1226
R-factor (whole data set)	R1 = 0.0587, wR2 = 0.1334	R1 = 0.0808, wR2 = 0.1346
GOOF	1.093	1.066
Difference peak ED	0.526 and -0.162 $eÅ^{-3}$	0.203 and -0.203 $eÅ^{-3}$

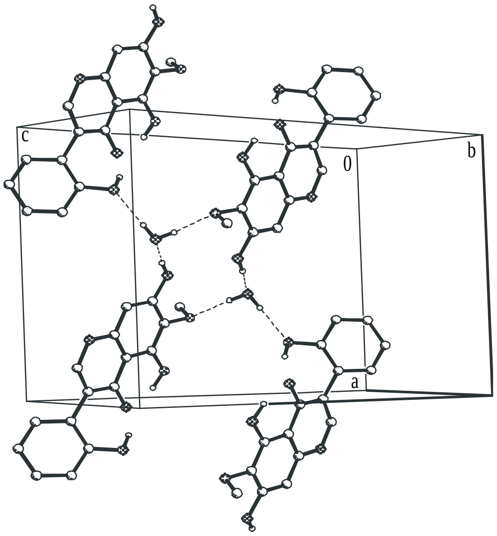


Fig. 2. Molecular packing in the crystal hydrate of irilin B.

The general tendency to lengthen the C=O bond is due to conjugation of the ketone π-electrons with those of the C2=C3 double bond and the aromatic ring through the C3–C4 and C4–C10 single bonds, respectively. The latter (significantly different from each other) is probably due to the different nature of the intramolecular H-bond.

The crystal of **1** is a hydrate. The unit cell contains a water of solvation that participates in the formation of intermolecular H-bonds. Figure 2 shows the packing, which illustrates the nature of these H-bonds. The water H atoms are directed toward the unshared pairs of O6 (Ow...O6, 2.81; H...O6, 2.00 Å; Ow–H...O6, 176.3°), the asymmetric unit, and O3 (2.92, 2.02 Å, 175.5°) of the molecule transformed by 2_1 symmetry along the *c* axis. The H atom of the hydroxyl on the molecule translated along the *a* axis is directed toward the unshared pairs of Ow from the other side (O2–H...Ow: 2.64, 1.73 Å, 174.7°). These intermoleclar H-bonds form a two-dimensional network in the crystal (in the x0z plane).

The active H of the hydroxyl (C6′–OH) in the crystal of **2** is blocked by the intramolecular H-bond. For this reason, the molecules are packed at Van-der-Waals distances.

EXPERIMENTAL

Isolation of Irilin B and Betavulgarin. Ground and air-dried plant (30 kg) was extracted with aqueous ethanol (90%). Solvent was removed to afford a resinous extract (1.8 kg).

The extract was separated using vacuum liquid chromatography on silica gel with elution by petroleum ether, a mixture of petroleum ether and dichloromethane, dichloromethane and methanol, and finally methanol. The fraction obtained by elution with CH_2Cl_2:CH_3OH (95:5) was rechromatographed over a silica-gel column to afford irilin B (0.015 g) and betavulgarin (0.030 g).

X-ray Structure Analysis. Single crystals grown from a solution of the isoflavones in $CHCl_3$ by slow evaporation at room temperature were elongated transparent prisms. The unit-cell constants and intensities of reflections were measured on a STOE Stadi-4 four-circle diffractometer ($\theta/2\theta$-scanning) using Mo $K\alpha$-radiation (graphite monochromator). Absorption corrections were not applied. Table 2 lists the principal crystallographic data and experimental conditions.

The structures were solved by direct methods using the SHELXS-97 program set. The structures were refined by full-matrix isotropic-anisotropic least-squares (LS) methods using the SHELXL-97 program. The positions of H atoms were found geometrically and refined with fixed isotropic thermal parameters $U_{iso} = nU_{eq}$, where n = 1.5 for methyls and 1.2 for others and U_{eq} is the equivalent isotropic thermal parameter of the corresponding C atoms. H atoms of hydroxyls and the water of solvation in **1** were found from a difference electron-density synthesis and refined isotropically.

Data for the XSA were deposited as a CIF file in the Cambridge Crystallographic Database (Nos. CCDC 266493 and 266494).

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