Anal. Calcd. for $C_{19}H_{22}IN$: C, 58.32; H, 5.67; N, 3.58. Found: C, 58.40; H, 5.67; N, 3.64.

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The Chemical Examination of *Iris nepalensis*. III. Isolation and Structure of Irisolidone

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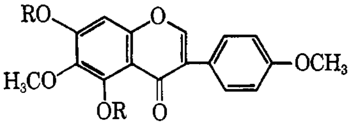
Isolation of irisolone[1] and irigenin[2] from the rhizomes of *Iris nepalensis* D. Don (*Iridaceae*) has been reported earlier. Petroleum ether extracts of plants do not usually contain flavonoids[3] but here an examination of this extract indicated the presence of a new isoflavone in 0.01% yield. This has been characterized as 5,7-dihydroxy-6,4′-dimethoxyisoflavone (I, R = H) and named irisolidone.

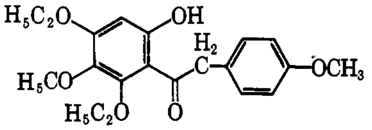


I

Irisolidone gave the characteristic color reactions of isoflavones. Its infrared spectrum showed strong absorption in the 6–6.6-μ region usually associated with flavonoid systems,[4] and the ultraviolet absorption spectrum was similar to that of irisolone and tri-O-methyltectorigenin.

Irisolidone showed correct analysis for $C_{17}H_{14}O_6$ and two methoxyl groups. Color with ferric chloride and formation of diacetate, dimethyl ether, and a diethyl ether (I, R = Ac, CH_3, and C_2H_5, respectively) showed the presence of two free hydroxyl groups in the molecule. Specific color reactions further indicated that one of these must be located in the 5-position and that vicinal hydroxyl groups were not present. A bathochromic shift of 10 mμ in the ultraviolet spectrum characteristic of 5-hydroxyl was observed on addition of aqueous aluminum chloride[5,6] and a similar shift of 5 mμ on addition of fused sodium acetate suggested a 7-hydroxyl. Though a shift of 10 mμ[7] is usually associated with the presence of 7-hydroxyl, Gottlieb and Magalhaes have recently reported a shift of only 8 mμ for caviunin.[4]

Irisolidone dimethyl ether was identical with tri-O-methyltectorigenin. This along with the formation of antiarol and anisic acid on alkali fusion of the dimethyl ether established the substitution pattern for irisolidone which was confirmed by the alkaline degradation of diethyl ether first to the deoxybenzoin (II) and then to 3,5-diethoxy-4-methoxyphenol and anisic acid.



II

Comparison of authentic 5,7-dihydroxy-6,4′-dimethoxyisoflavone[8] (mixture melting point and infrared spectrum) with irisolidone showed the two to be identical.

A number of species belonging to *Iridaceae* have been examined for isoflavonoids and as a result of this it is possible to make some observations regarding their biogenesis and chemical taxonomy which may be of significance.

Thus it is interesting that all the isoflavonoids so far reported from this family have tectorigenin substitution pattern in ring A, as indicated in Table I.

Table I

Plant	Isoflavonoid	Substitution in ring A	Substitution in ring B
I. florentina *I. kumaonensis* *I. germanica*	Irigenin	5-OH 6-OCH$_3$ 7-OH	3′-OH 4′-OCH$_3$ 5′-OCH$_3$
I. tectorum	Tectorigenin	5-OH 6-OCH$_3$ 7-OH	4′-OH
I. nepalensis	Irisolone	5-OCH$_3$ $\left.\begin{matrix}\text{6-O}\\\text{7-O}\end{matrix}\right>\text{CH}_2$	4′-OH
	Irisolidone	5-OH 6-OCH$_3$ 7-OH	4′-OCH$_3$
	Irigenin	5-OH 6-OCH$_3$ 7-OH	3′-OH 4′-OCH$_3$ 5′-OCH$_3$

With respect to the substitution pattern of ring B the above members of *Iridaceae*, with the exception of *I. tectorum*, elaborate isoflavones with oxygen functions at the 3′-, 4′-, and 5′-positions. *I. tectorum*, on the other hand, produces tectorigenin which carries only a 4′-hydroxyl. *I. nepalensis* contains both types of isoflavonoids and thus appears genetically related to the two. Further, all isoflavonoids from *Iridaceae* have a 6-methoxyl, with the exception of irisolone which has a 6,7-methylenedioxy group. Formation of this may involve an oxidative cyclization of the methoxyl as suggested by Barton[9] in connection with the biogenetic origin of the methylenedioxy group in alkaloids, etc.

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Experimental Section

All ultraviolet spectra were measured with a Beckman Model DC instrument in 95% alcohol. Infrared spectra were measured in a Perkin-Elmer Infracord either in chloroform or Nujol mulls.

Isolation of Irisolidone (I, R = H).—Air-dried powdered rhizomes (50 kg.) of *Iris nepalensis* were extracted four times with hot petroleum ether (b.p. 60–80°) and then with chloroform. The chloroform extract yielded irisolone[1] and irigenin,[2] whereas the petroleum ether extract, on concentration to about 2 l. and standing in refrigerator for a few days, deposited a solid. This was dissolved in methanol and the solution on concentration yielded a yellow compound which on further crystallization gave irisolidone (5 g.), m.p. 195–196°, lit.[8] m.p. 191–192°. Irisolidone gave a blue color with ferric chloride, positive tests with boric acid,[10] boric acid in acetic anhydride (Dimroth reagent), and Gibb reagent,[11] and negative tests with chloropentaminocobaltic chloride[12] and sodium amalgam.[13] Infrared bands (in chloroform) occurred, *inter alia*, at 2.85, 6.05, 6.15, 6.25, 6.35, 6.65, 6.90, 9.40, 9.65, 10.10, and 11.98 μ. The ultraviolet spectrum in 95% ethanol showed a single maximum at 270 mμ (log ϵ 4.65). On the addition of 3 drops of 10% aqueous aluminum chloride the maximum shifted to 280 mμ (log ϵ 4.72). Addition of saturated alcoholic fused sodium acetate solution also shifted the maximum to 275 mμ (log ϵ 4.65).

Anal. Calcd. for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49; 2-OMe, 19.17. Found: C, 64.76; H, 4.56; OMe, 19.14.

Irisolidone Diacetate (I, R = Ac).—The acetate was prepared from irisolidone (0.1 g.), acetic anhydride (1 ml.), and pyridine (2 drops) by allowing to stand at room temperature for 24 hr.; it crystallized from methanol in colorless needles, m.p. 162–163°.

Anal. Calcd. for $C_{21}H_{18}O_8$: C, 63.31; H, 4.55. Found: C, 63.45; H, 4.60.

Irisolidone Methyl Ether (I, R = CH_3).—A mixture of irisolidone (1.5 g.), freshly distilled dimethyl sulfate (6.4 ml.), anhydrous potassium carbonate (8.4 g.), and dry acetone (120 ml.) was refluxed for 36 hr. On working up in the usual manner, colorless plates of irisolidone methyl ether (1.35 g.), m.p. 181°, were obtained, identical with tri-O-methyltectorigenin (mixture melting point and infrared spectrum).

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.52; H, 5.26.

Irisolidone Ethyl Ether (I, R = C_2H_5).—Irisolidone (2 g.), potassium carbonate (4 g.), ethyl iodide (20 ml.), and acetone (200 ml.) were refluxed together for 40 hr. Work-up in the usual manner gave irisolidone ethyl ether, m.p. 113–114°; infrared bands (in chloroform) occurred, *inter alia*, at 6.05, 6.25, 6.35, 6.75, 6.90, 9.30, 9.45, 9.70, 10.00, and 12.00 μ.

Anal. Calcd. for $C_{21}H_{22}O_6$: C, 68.09; H, 5.99. Found: C, 68.00; H, 6.30.

4′-Methoxybenzyl 2-Hydroxy-4,6-diethoxy-5-methoxyphenyl Ketone (II).—Irisolidone ethyl ether (450 mg.) was suspended in water (30 ml.) and a slow current of nitrogen free from oxygen was passed through the suspension. After 5 min. aqueous sodium hydroxide (15 ml., 10%) was added, and the mixture was refluxed for 2 hr., cooled to room temperature, and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated, and the residue was crystallized from methanol: m.p. 102–103°. It gave a brown color with alcoholic ferric chloride.

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.42, H, 6.82.

Oxidation of Irisolidone Ethyl Ether.—The ethyl ether (0.5 g.) in acetone (50 ml.) was heated on a water bath and treated with powdered potassium permanganate in small lots until the pink color persisted. The solution was filtered and the solid was washed with acetone and then extracted with hot water. Acidification of the acqueous solution gave a solid, m.p. 186–187° (from hot water), lit.[14] m.p. 184°. It gave no depression with an authentic sample of anisic acid.

Alkali Fusion of Irisolidone Ethyl Ether.—Irisolidone ethyl ether (1 g.), sodium hydroxide (2.5 g.), and water (2 ml.) were heated in a copper tube at 220° for 45 min. Work-up in the usual manner yielded 3,5-diethoxy-4-methoxyphenol, m.p. 72°, lit.[15] m.p. 74°, and anisic acid. No depression in mixture melting points was obtained with authentic samples.

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Abnormal Products during Isolation of Isonicotinic Acid Hydrazide

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In the course of isolation of isonicotinic acid hydrazide (I) from the reaction mixture of ethyl isonicotinate and hydrazine hydrate (free from ammonia) three basic by-products, namely, symmetrical diisonicotinyl hydrazine (II), hydrazodicarbonamide (III), and 3,5-bis(4-pyridyl)-1,2,4-triazole-1-carboxhydrazide (IV), have been isolated in small quantities as artifacts arising from the large-scale operation. Their separation is to be specially considered when isonicotinic acid hydrazide is required in high purity. The solubility of II and III in dilute alkali and the solubility of II in ethanol have rendered separation possible, and the products could be finally purified by crystallization from water.

The product IV affords benzylidene and cinnamylidene derivatives. Oxidation under diverse conditions such as moderately dilute nitric acid, acid potassium permanganate, or sodium hypobromite IV gives rise to the formation of 3:5-bis(4-pyridyl)-1,2,4-triazole (V), carbon dioxide, and nitrogen. The identity of V has been confirmed by synthesis from I and isonicotinamide.[1]

Compound IV in solution of 10% sulfuric acid or in glacial acetic acid, when treated with bromine, gives a perbromide which by the action of alkali changes to V.

A solution of I in hydrazine hydrate saturated with carbon dioxide or a mixture of I, isonicotinamide, and carbohydrazide in aqueous medium when heated to reflux for some time leads to the formation of IV. Similarly, a solution of hydrazine hydrate saturated with carbon dioxide admixed with ammonia affords III.

In the formation of the by-products III and IV, the mechanism of reaction involves the participation of atmospheric carbon dioxide, hydrazine, and ammonia (decomposition product of hydrazine[2]). Hydrazine and carbon dioxide form carbazic acid[3] which with ammonia and hydrazine lead to the formation of semi-

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