

5,7-DIHYDROXYCHROMONE FROM *ARACHIS HYPOGOEA* SHELLS*

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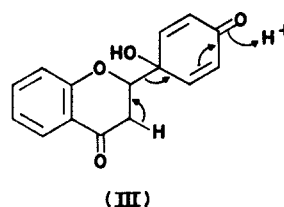
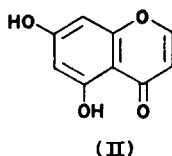
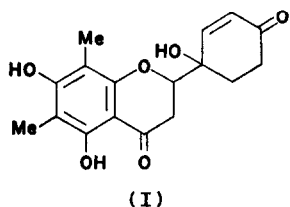
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Abstract—5,7-Dihydroxychromone (II), eriodictyol and luteolin have been isolated from peanut shells (*Arachis hypogaea*), this is only the second example of a natural chromone unsubstituted in the 2,3-positions. The co-occurrence of (II), eriodictyol and luteolin indicates the likelihood of a common origin and supports a biosynthetic scheme involving the phenol oxidation of a 4'-hydroxyflavanone and the subsequent loss of the B-ring as hydroquinone.

WITH ONE exception, all the naturally occurring chromones known so far are substituted in the 2- and/or 3-positions. flavones and flavonols, isoflavones, 2-methylchromones and 2-hydroxymethylchromones Fukushima *et al*¹ recently reported the isolation of leptorumol, the first natural chromone (5,7-dihydroxy-6,8-dimethylchromone) unsubstituted in the 2- and 3-positions. Leptorumol, a constituent of *Leptorumohra miqueliana* Ito, is accompanied in the plant by its 7-glucoside, farrerol (5,7,4'-trihydroxy-6,8-dimethylflavanone) and the flavanone derivative (I). We now report the second example of a natural chromone (II) unsubstituted in the 2,3-positions.



An acetone extract of groundnut (peanut) shells, after the removal of sitosterol, was chromatographed on silica gel. Elution with benzene-acetone gave three phenolic fractions. The fast moving phenol (0.02% of the shells) crystallized from ethanol in pale yellow prisms, m.p. 272–273°, identified as 5,7-dihydroxychromone, $C_9H_6O_4$ (M^+ 178). The NMR spectrum in acetone showed four hydrogens in the aromatic region. Two signals at 1.97 and 3.83 (chemical shifts on the τ scale) with vicinal coupling (J 7 Hz) can be assigned to 2- and 3-H of a chromone. Two *meta*-coupled doublets (J 2 Hz) centered at 3.63 and 3.77 are characteristic of the 6,8-protons in 5,7-dihydroxychromone (II). 5,7-Dihydroxychromone (m.p. 272°) was synthesized in 1902 by Kostanecki *et al.*²

The two other phenolic compounds subsequently eluted from the column were identified as eriodictyol (m.p. 267°) and luteolin (m.p. 330°). Harborne³ has suggested that naringenin

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¹ FUKUSHIMA, S., NORO, T., SAIKI, Y., UENO, A. and AKAHORI, Y. (1968) *J. Pharm. Soc. (Japan)* **88**, 1135

² VON KOSTANECKI and DE R. DE WILDT, J. C. (1902) *Chem. Ber.* **35**, 861

³ HARBORNE, J. B. (1967) *Comparative Biochemistry of the Flavonoids*, p. 87, Academic Press, New York

and eriodictyol, the flavanone analogues of apigenin and luteolin, probably occur fairly widely in plants, although the recorded instances are relatively few. Eriodictyol has been recently isolated from the seeds of *Garcinia livingstonei*.⁴ Luteolin, as glycosides and the aglycone, occurs in numerous plants.⁵

The isolation of 5,7-dihydroxychromone is of considerable biogenetic interest. 2-Methylchromones are assumed to be derived from five acetate units, but in contrast with flavones and isoflavones, we have no experimental data on their biosynthesis. Since 2-hydroxymethylchromones are known, 5,7-dihydroxychromone may be formed from the corresponding 2-methylchromone by oxidation to the carboxylic acid via the carbinol and aldehyde, followed by decarboxylation. However, the co-occurrence of eriodictyol and luteolin supports Birch and Thompson's suggestion, based on the co-occurrence of leptorumol, farrerol and I, that chromones may be formed by a phenol oxidation of 4'-hydroxyflavanones to (III) and its derivatives, which then undergo fission to chromones and hydroquinone.⁶ Birch and Thompson achieved the chemical conversion of 4'-hydroxyflavanone, by the action of thallium trifluoroacetate in trifluoroacetic acid,⁷ to chromone and hydroquinone.

EXPERIMENTAL

Powdered peanut shells (500 g) were extracted in a Soxhlet with acetone for 8 hr. The solvent was removed and the residue (4 g), dissolved in C₆H₆, was submitted to column chromatography on silica gel. The first few fractions eluted with C₆H₆ gave waxy and terpenoid material. Elution with C₆H₆ containing 10% acetone gave a compound which crystallized from EtOH in pale yellow prisms (0.12 g), m.p. 272–273°, identified as 5,7-dihydroxychromone. Further elution with benzene containing 20% acetone led successively to eriodictyol (0.09 g), m.p. 267°, and luteolin (0.4 g), m.p. 330°.

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⁴ SRIVASTAVA, S. N. and SHARMA, V. N. (1966) *Current Sci.* **35**, 290.

⁵ Ref. 3, p. 39.

⁶ BIRCH, A. J. and THOMPSON, D. J. (1972) *Australian J. Chem.* **25**, 2731.

⁷ MCKILLOP, A., SWANN, B. P. and TAYLOR, F. C. (1970) *Tetrahedron* **26**, 4031.