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Revised structures for iselin and iliensin and the identity of the former with archangelin

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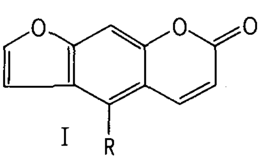
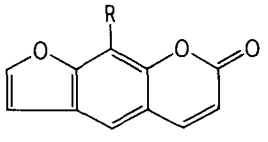
Summary. Structures of iselin and iliensin have been revised. The structure (**Ib**) is secured for iselin by a direct comparison (m.p., UV, IR, PMR) with archangelin. The synthesis of iliensin (**IIb**) has been effected through the condensation of xanthotoxol (**II**, R = OH) and β-cyclolavandulyl bromide (**III**). The synthetic product has been shown to be identical with natural iliensin.

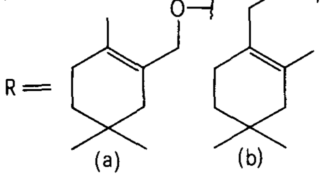
Plants belonging to the family Umbelliferae constitute a rich source of structurally diverse prenylated coumarins, and hence have been the subject of extensive investigation for many years. Very recently, 2 new furocoumarins, iselin and iliensin, have been isolated from the roots of *Seseli iliense* (Regl et Schmalh) Lipsky, and represented by (**Ia**) and (**IIa**), respectively[2]. The physical constants and the spectral data of iselin were almost identical with those of archangelin (**Ib**) recently synthesized by us[3]. Their close resemblance prompted us to re-examine the structures of iselin and iliensin. This communication presents evidence for the correct structures of iselin and iliensin as (**Ib**) and (**IIb**), respectively.

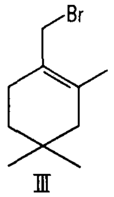


I



II





III

The spectral properties of iselin on comparison with those of the 4 isomeric types of monoalkoxy-furocoumarins[3,4] confirm iselin to be of the bergaptyl (**I**) type. Of the 2 part structures (**a**) and (**b**) considered[2] for the terpenoid residue, (**b**) is favoured over (a) on biogenetic grounds as has been pointed out earlier[3]. Moreover, β-cyclolavandulal[5] and the corresponding acid[6] have been isolated from a related species, *Seseli indicum* (Wight and Arnold). The new structure (**Ib**) assigned to iselin corresponds to that of archangelin, a furocoumarin from *Angelica archangelica* L. A direct comparison (m.p., UV, IR, PMR) conclusively established their identity. Iselin is, therefore, not a new natural product. Iliensin does indeed belong to the xanthotoxyl (**II**) type as suggested by the Russian workers. However, part structure (**b**) for the terpenoid moiety looked certain for the reasons mentioned in the case of iselin. In order to confirm this, we have synthesized compound (**IIb**) by condensing xanthotoxol (**II**, R = OH) with β-cyclolavandulyl bromide. The identity of this compound with iliensin is obvious from its m.p. and spectral data. A mixture of β-cyclolavandulyl bromide (**III**, 0.3 g)[7], xanthotoxol (**III**, 0.2 g), anhydrous K_2CO_3 (3 g) and acetone (50 ml) was stirred and refluxed for 36 h, after which the acetone solution was filtered and the residue washed with dry acetone. The filtrate and washings were then mixed together and the solvent was removed. The residual oil was chromatographed over Al_2O_3 and eluted with petroleum-ether + benzene (9:1). The 1st fraction on concentration and cooling gave a solid (~ 10%). Repeated crystallization of this solid gave iliensin, m.p. 71–72 °C, whose spectroscopic properties were identical in all respects with those recorded on natural iliensin. We therefore conclude that iliensin is (**IIb**).

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[3] R.B. Bates, D.J. Eckert, S.K. Paknikar and V.P. Thalacker, Tetrahedron Lett. *1972*, 3811 and references cited therein.

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[7] Prepared from lavandulol via cyclolavandulic acid.