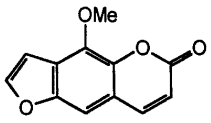
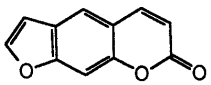
ABSTRACT

Regiospecific syntheses of furobenzopyranone (I), a new psoralen isoster, psoralen (II) and coriandrin (III) have been accomplished. Furan synthon **IV**, prepared from methyl 3-furoate **V** by various functional group manipulations, was annulated with dicyclopentadienone **VI** in the presence of ^{t}BuOLi to give the annulated product **VIIa** (70%). Flash vacuum pyrolysis of **VII** furnished oxaindacenones **VIII** (>90%). Baeyer-Villiger oxidation of sulfide **IX** derived from **VIIIb** provided furobenzopyranone (**I**).



I



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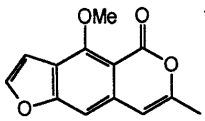
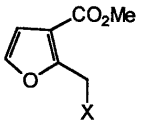
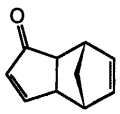


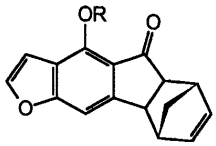
III



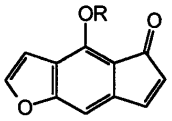
V X = H
IV X = SOPh



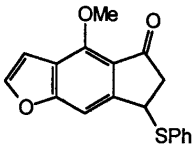
VI



VIIa R = H
VIIb R = Me

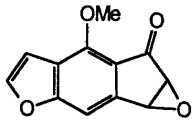


VIIIa R = H
VIIIb R = Me

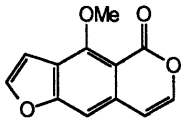


IX

The same oxaindacenone **VIIIb** has been elaborated to 7-demethylcoriandrin **X** in two steps. The epoxide **XI**, prepared from **VIIIb** has been shown to undergo facile [π^4a + π^2a] rearrangement to give **X** in an excellent yield. This simple and new protocol of



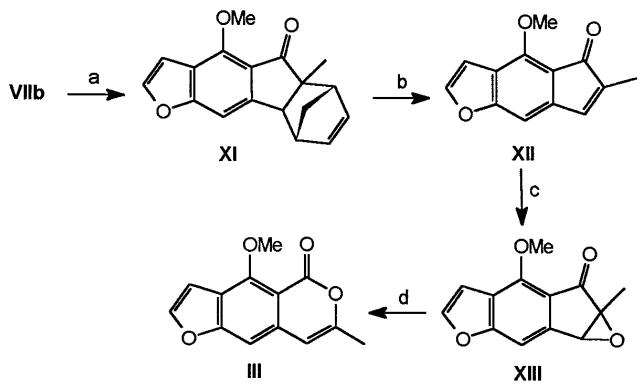
XI



X

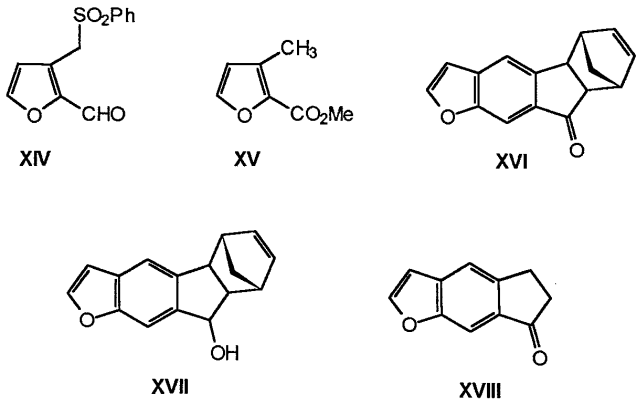
furoisocoumarin synthesis has been applied to the total synthesis of coriandrin (**III**), according to the sequence depicted in Scheme 1.

Scheme 1

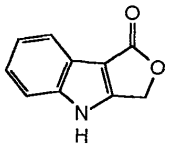


Reagents and conditions: a) LDA, MeI, THF; b) FVP 450 -475°C / 0.1 mm; c) Et_3N, H_2O_2, acetone; d) FVP 450 -475°C / 0.1 mm.

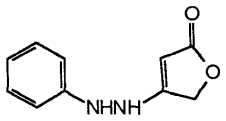
The sequence involving furan annulation, retro Diels-Alder reaction and indenol-indanone rearrangement has been adopted for the synthesis of psoralen (**II**). Sulfone aldehyde **XIV**, prepared from 3-methyl furoate **XV**, has been annulated with **VI** in the presence of NaOMe to give **XVI**. Thermolysis of **XVII**, obtainable from **XVI** by $NaBH_4$ reduction, produced oxaindacenone **XVIII**, a late-stage intermediate of psoralen (**II**) synthesis. In addition, few more oxaindacenones have been prepared following the strategy developed for **XVIII**.



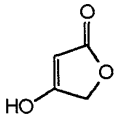
For a regiospecific entry to a wide variety of carbazole alkaloids, the synthon **XIX** has been prepared by Fischer indolisation of phenylhydrazine derivative **XX**, which, in turn, has been obtainable from tetronic acid **XXI** and phenylhydrazine.



XIX



XX



XXI