A New Heterocyclic Ring System: 6*H*-Benzothieno[3,2-*c*] [1]benzopyran-6-one (Sulphur Analogue of Coumestan)

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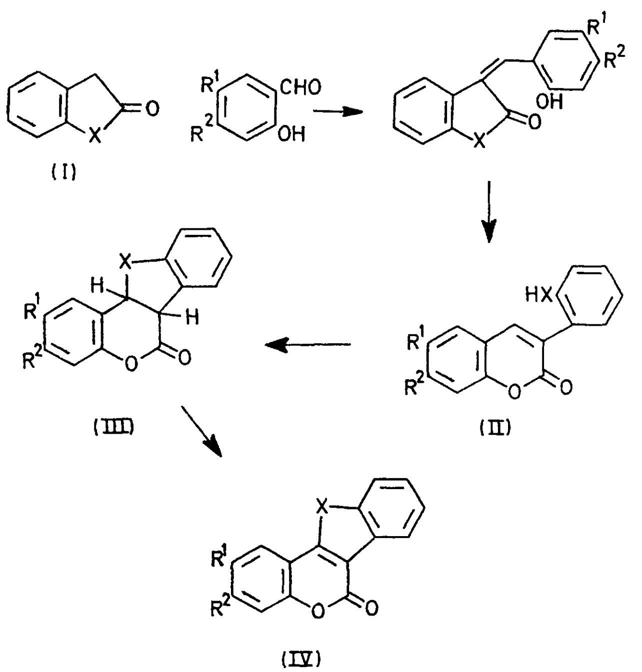
Summary The 6*H*-benzothieno[3,2-*c*][1]benzopyran-6-one ring system has been prepared.

A NUMBER of 6*H*-benzofuro[3,2-*c*][1]benzopyran-6-ones (coumestans) have been isolated from ladino clover, several have been observed to possess estrogenic activity, and the system (IV, X = O) has been generated synthetically through several multi-step syntheses.[1] We now report a simple, direct route to the previously unknown 11-thia analogues (thiacoumestans) (IV, X = S) which is different from the methods utilized in the coumestan series.

Since it is known that benzofuran-2-one (I, X = O) reacts with salicylaldehyde to produce stable 3-(2-hydroxyphenyl)-coumarins (II, X = O, $R^1 = R^2 = H$) as rearrangement products[2] and since Mustafa has shown that coumarins are very labile to thiolate addition at C-4,[3] it seemed plausible to expect that thianaphthen-2-one[4] (I, X = S) might condense with salicylaldehyde to yield 3-(mercaptophenyl)-coumarins (II, X = S) as transient intermediates on the route to the dihydro-11-thiacoumestans (III, X = S) (Scheme). Dehydrogenation would yield the desired 11-thiacoumestans (IV, X = S).



The reaction of equimolar amounts (0·66 mmol) of thianaphthen-2-one (I, X = S) and salicylaldehyde in 3 ml of ethanol containing several drops of triethylamine at 5—10° gave the desired dihydro product† (III, X = S, $R^1 = R^2 = H$), [m.p. = 143·5—145·0°, yield 79%]. Subsequent reactions of thianaphthen-2-one with 5-methoxysalicylaldehyde and 4-methoxysalicylaldehyde gave respectively (III, X = S, R^1 = OMe, R^2 = H) [m.p. = 153·5—155·0°, yield 80%] and (III, X = S, R^1 = H, R^2 = OMe) [m.p. = 142·0—143·0°, yield 82%]. The dihydro products were readily identified by their characteristic ^1H n.m.r. spectra, in particular the methinyl protons appearing as two characteristic AB doublets with J 7 Hz.

Dehydrogenations of (III, X = S) were carried out by refluxing with an equimolar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene for 11 h to give (IV, X = S, $R^1 = R^2 = H$) m.p. = 217·0—217·5°; yield 75%; (IV, X = S, R^1 = OMe, R^2 = H) m.p. = 187·0—188·0°, yield 66%, and (IV, X = S, R^1 = H, R^2 = OMe) m.p. = 190·0—191·5°, yield 66%.

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† All compounds gave satisfactory elemental analyses and i.r. and n.m.r. spectral data, in accordance with the assigned structures.

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