

A NOVEL RING OPENING IN 2'-METHOXYISOFLAVANONE

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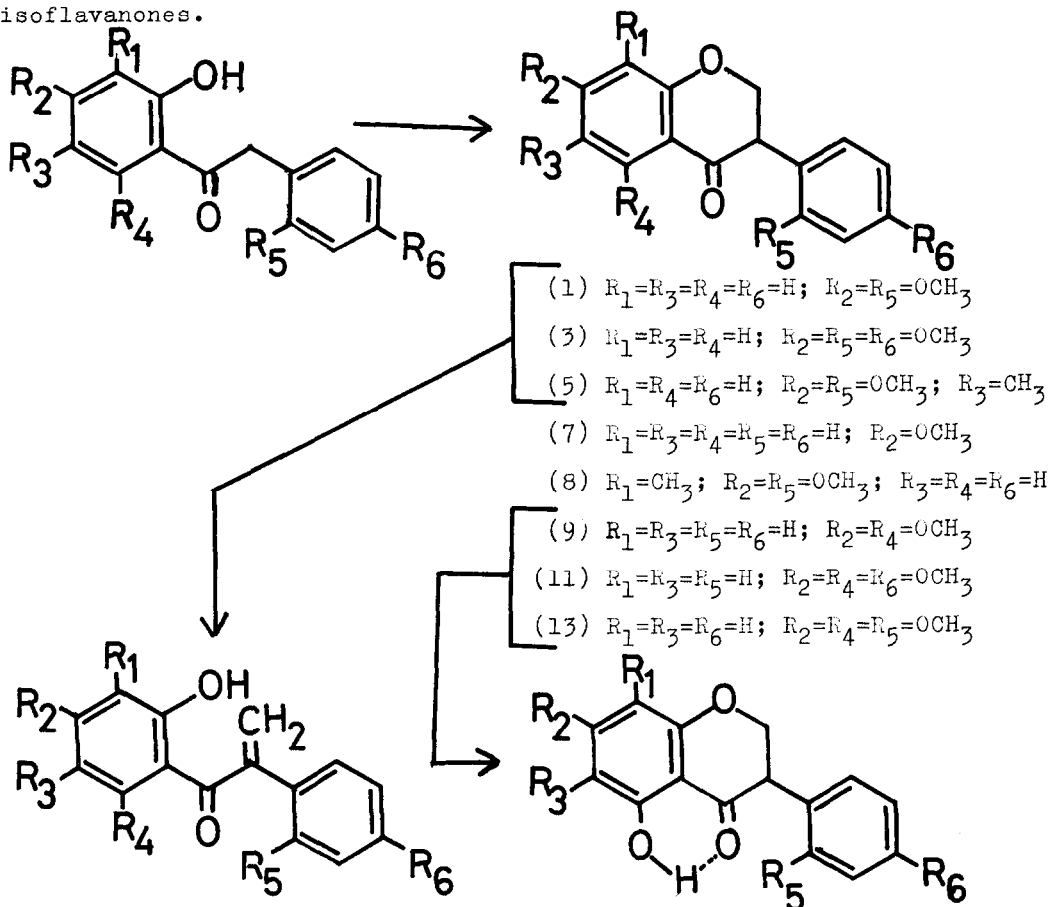
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In an attempted new synthesis of dehydropterocarpan and coumestans to provide a laboratory example for the proposed scheme of biogenesis¹, 2'-methoxyisoflavanones were considered to be suitable precursors for 2'-hydroxyisoflavanones. However, 7,2'-dimethoxyisoflavanone (1) when treated with aluminium chloride-acetonitrile, a reagent successfully used for selective demethylation of 2'-methoxyisoflavones², did not undergo any change. When refluxed with aluminium chloride-dioxan for 3 hr, 7,2'-dimethoxyisoflavanone (1), m.p. 88-89° (negative ferric reaction), yielded an isomeric compound, C₁₇H₁₆O₄, m.p. 110-12°, which gave a positive ferric reaction. In its IR spectrum, this compound showed $\nu_{\text{C=O}}$ at 1620 cm⁻¹ and in UV spectrum, λ_{max} at 235 and 285 nm clearly indicating that the isoflavanone skeleton had been affected. Its NMR spectrum exhibited two singlets of three protons each at δ 3.58 & 3.84 showing the presence of two methoxyls. Doublets at δ 5.62 & 5.91 (one proton each), J = 2Hz, were indicative of a typical absorption for a vinyl group. A singlet at δ 13.0 showed the presence of a chelated hydroxyl group while absorptions for seven aromatic protons were observed between δ 6.2 & 7.8.

These results indicated that the expected selective demethylation at position 2' had not occurred but instead the hetero ring in isoflavanone had opened to give 2-hydroxy-4-methoxyphenyl 2-methoxy- α -vinyl-benzyl ketone (2). This structure has been further supported by mass spectral data where it showed M⁺ at m/e 284 (68%), M-31⁺ peak at m/e 253 (10%) and M-133⁺ peak, due to the loss of ring B fragment, at m/e 151 (100%).

The scope of this novel ring opening has been studied by taking differently substituted isoflavanones and a necessary condition for observing this type of ring opening has been found to be the presence of a 2'-methoxy group in the absence of substitution at C5 and C8. Thus 7,2',4'-trimethoxy-(3) and 7,2'-dimethoxy-6-methyl-(5) isoflavanones on similar treatment with aluminium chloride-dioxan gave respectively 2-hydroxy-4-methoxyphenyl 2,4-dimethoxy- α -vinyl-benzyl-(4) and 2-hydroxy-4-methoxy-5-methylphenyl 2-methoxy- α -vinyl-benzyl-(6) ketones. 7-Methoxy-(7) and 7,2'-dimethoxy-8-

methyl-(8) isoflavanones remained unaffected while 5,7-dimethoxy-(9), 5,7,4'-trimethoxy-(11) and 5,7,2'-trimethoxy-(13) isoflavanones underwent selective demethylation at position-5 to afford respectively 5-hydroxy-7-methoxy-(10), 5-hydroxy-7,4'-dimethoxy-(12) and 5-hydroxy-7,2'-dimethoxy-(14) isoflavanones.



- (2) $R_1=R_3=R_4=R_6=H$; $R_2=R_5=OCH_3$
 (4) $R_1=R_3=R_4=H$; $R_2=R_5=R_6=OCH_3$
 (6) $R_1=R_4=R_6=H$; $R_2=R_5=OCH_3$; $R_3=CH_3$

- (10) $R_1=R_3=R_5=R_6=H$; $R_2=OCH_3$
 (12) $R_1=R_3=R_5=H$; $R_2=R_6=OCH_3$
 (14) $R_1=R_3=R_6=H$; $R_2=R_5=OCH_3$

References

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