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WANZLICK OXIDATION WITH 3-HYDROXYCOUMARINS

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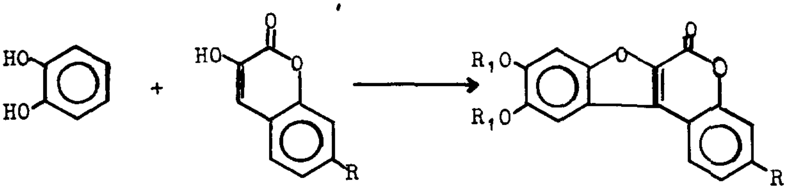
Wanzlick and co-workers[1] have shown that catechol may be oxidatively coupled with suitable 1,3-dicarbonyl compounds in the presence of potassium ferricyanide to give benzofuran derivatives. Thus dimedon, dihydroresorcinol and 4-hydroxycoumarins[1,2,3] were used in oxidative couplings with success. A synthesis of wedelolactone was made possible from catechol and 4,5-dihydroxy-7-methoxycoumarin[1]. Similarly other coumestans have been prepared in connection with the total syntheses of pterocarpin[2,4] and erosnin[3].

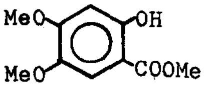
Mentzer et al.[5] have used 6-methyl-4-hydroxy-α-pyrone to give 5,6-dihydroxy-2,3-(6'-methyl-3',4'-α-pyrono)benzofuran and 6-phenyl-4-hydroxy-α-pyrone to yield the analogous 6-phenyl derivative.

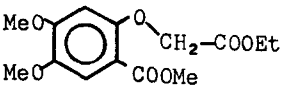
We find that Wanzlick oxidation proceeds smoothly with 3-hydroxycoumarins as well. Thus 3-hydroxycoumarin and catechol gave 5,6-dihydroxycoumarino (3',4'-2,3)coumarone(I) which was subsequently methylated to (II), m.p. 291-2° (lactone carbonyl absorption at 1730 cm^{-1})[6]. 3-Hydroxy-7'-methoxycoumarin and catechol gave 5,6-dihydroxy-7'-methoxycoumarino(3',4'-2,3)coumarone (III) in excellent yield. This was converted to its trimethyl ether (IV), m.p. 268-70° (lactone carbonyl absorption at 1710 cm^{-1}) which has been synthesized unambiguously as follows:

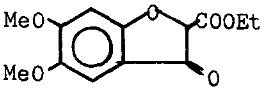
Methyl 2-hydroxy-4,5-dimethoxybenzoate[7] was condensed with ethyl bromoacetate to give the di-ester (V), m.p. 87° which on Dieckmann cyclisation afforded ethyl 5,6-dimethoxycoumaran-3-one-2-carboxylate (VI), m.p. 144-5° (carbonyl absorption at 1675 cm^{-1}). This on Pechmann condensation with resorcinol monomethylether gave 5,6,7'-trimethoxycoumarino(3',4'-2,3)coumarone, m.p. 268-9°, identical in all respects with Wanzlick oxidation product (IV) (mixed m.p., superimposable i.r. spectra). The condensation of (VI) was also done with resorcinol to give 5,6-dimethoxy-7'-hydroxycoumarino(3',4'-2,3)coumarone (VII), m.p. 310° (lactone carbonyl absorption at 1730 cm^{-1}). The latter was methylated to (IV) and acetylated to (VIII), m.p. 295° (lactone carbonyl absorption at 1725 and acetyl absorption at 1760 and 1240 cm^{-1}).



(I) $R = R_1 = H$
(II) $R = H,\ R_1 = CH_3$
(III) $R = OMe,\ R_1 = H$
(IV) $R = OMe,\ R_1 = CH_3$
(VII) $R = OH,\ R_1 = CH_3$
(VIII) $R = OCOCH_3, R_1 = CH_3$







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