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THE SYNTHESIS AND ISOLATION OF CAFFEOQUINONE AND CAFFEOQUINONE METHYL ESTER

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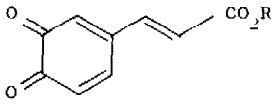
This communication describes the synthesis and isolation of the biologically important intermediate[1-8] caffeoquinone (1), and of its methyl ester (2). (2) serves as a useful model for studies of the chemistry of another important biological intermediate[1-8] chlorogenoquinone (3). Although stable products derived by the trapping of (1), (2) and (3) in situ with suitable reagents have been described[2,3,9,10] this is believed to be the first reported isolation of (1) and (2) in crystalline form.

(1) was prepared in 71% yield by the oxidation of caffeic acid (1 mol.) with o-chloranil[11] (1.1 mol.) in tetrahydrofuran/diethyl ether (1/4, v/v). The mixture was stirred for 2h. at between -60 and -70°, and the red product crystallised out on standing at -40° overnight. (2) was similarly prepared in 75% yield from methyl caffeate, the solvent being tetrahydrofuran/diethyl ether (1/1, v/v). Both (1) and (2) are unstable at temperatures as low as -20°. The crystalline products were separated from the reaction mixtures by rapid vacuum filtration at between -20 and -30°. Both products are stable when stored at -80°.

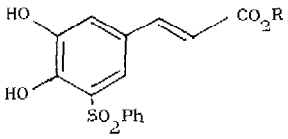
The UV spectrum of (2) (CH_3CN) changes markedly over a period of 1h. from one showing maxima at 246, 253, 305 and 396 mμ to one with maxima at 223, 288 and 319 mμ. Isosbestic points occur at 224, 267 and 354 mμ. The UV spectrum of (2) (EtOH) changes rapidly over 40 min. from one showing maxima at 248, 302 and 375 mμ to one with maxima at 216, 297 and 327 mμ, isosbestic points occurring at 225, 273 and 369 mμ.

(1) and (2) reacted with benzenesulphinic acid in THF to form (4) and (5) respectively[12]. (4) exists as colourless crystals, m.p. 228-230°, M^+ 320, ν_{max} (KBr) 3320, 1685, 1435, 1294, 1203, 1147, 853, 740 and 683 $cm.^{-1}$, τ ($\mathrm{C_6^2H_6}$-acetone) 1.86-2.47 (7H, m), 2.56 (1H,d, J=2Hz.) 3.60 (1H,d, J=15.7Hz.), λ_{max} (EtOH) 240 (ε 21,000), 295 (13,750) 332 (12,000) and 372 mμ (5,100).

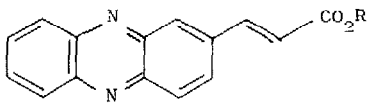
(5) exists as colourless crystals, m.p. 219-220°, M^+ 334, ν_{max} (KBr) 3376, 1707, 1644, 1486, 1285, 1264, 1179, 1144 and 720 $cm.^{-1}$, τ ($\mathrm{C_6^2H_6}$-acetone) 1.88-2.50 (7H,m) , 2.59



(1) R = H
(2) R = Me
(3) R = $C_6H_7(OH)_3COOH$



(4) R = H
(5) R = Me



(6) R = H
(7) R = Me

(1H,d, J 2Hz.), 3.62 (1H,d, J=16Hz) and 6.27 (3H,s), λ_{max} (EtOH) 242 (ε 21,000), 301 (8,800) 347 (14,500) and 370 mμ (14,000).

The position of substitution of the phenylsulphonyl group in the phenolic ring of (4) and (5) is established by the doublet nature (J=2Hz) of the absorptions, integrating for 1 proton at τ 2.56 and 2.59 respectively.

(1) and (2) reacted with o-phenylenediamine in THF to give (6) and (7) respectively (6) gave yellow-brown crystals, m.p. 252-253°, from pyridine/ethanol (1/4, v/v). (7) gave yellow-brown crystals, m.p. 149-150°, from pyridine/ethanol (1/9, v/v). Spectral details of (6) and (7) agree with those published.[13]

Studies of the chemistry of (1) and (2) are in progress with a view to forming a better understanding of the coupling reactions between o-quinonoid species and plant proteins. Details will be published elsewhere.

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