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STRUCTURE OF BLIGHINONE

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The isolation and characterisation of a new sparingly soluble quinone, Blighinone, $C_{16}H_{10}O_8$, m.p. >360° (dec.) from Blighia sapida fruit pulp was reported earlier[1]. Of the eight oxygen atoms in blighinone two were accounted for 1,4-quinone (ν_{max} 1667 cm^{-1}), three in hydroxyl groups (ν_{max} 3448 cm^{-1}), two in a carboxyl group (ν_{max} 1739 cm^{-1}) and remaining one in a six membered ring ketone (ν_{max} 1724 cm^{-1}). The studies in the physical and chemical properties of blighinone led to a provisional structure[1] in which the ring C was shown to be hydroaromatic. Detailed studies in its mass spectra have since revealed the nature of the nucleus in which ring B should be hydroaromatic having the side methyl attached to it explaining thereby the resultant 9-methyl-phenanthrene obtained by dehydrogenation of the parent molecule. As the quinone is practically insoluble the NMR spectra of it could not be recorded.

Blighinone (I), $C_{16}H_{10}O_8$ (mol. wt. 330), shows the parent peak at m/e 302 (M^+ - 28) in its mass spectra (Fig.1). The loss of 28 mass units (CO) is apparently due to the carbonyl knocked off from the ring B to give a five membered stable ion (II) as two of the hydroxyl groups are phenolic in nature (vide infra) and they could evidently be present in the ring C only because no such substitution is possible in either ring B or ring A, which would leave ring B to have the six membered ring carbonyl giving it the cyclohexadienone structure (III), an intermediate in the fragmentation of phenols[2]. The absence of the molecular ion peak m/e 330 in the mass spectra

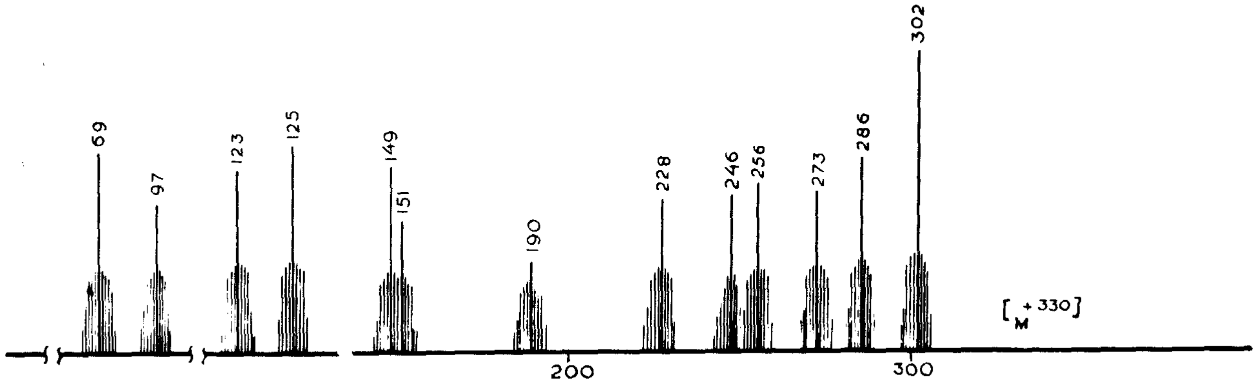


FIG. 1 Mass Spectra of BLIGHINONE

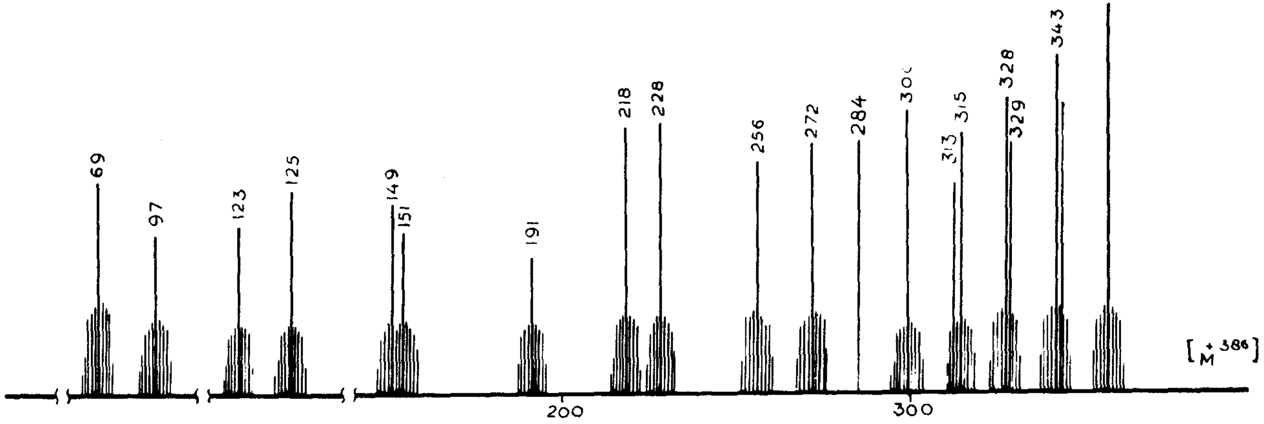
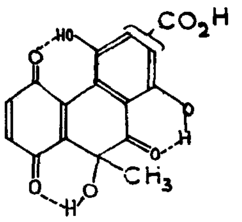
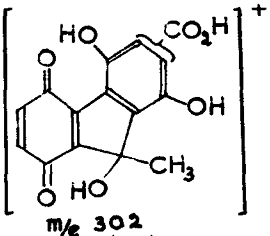


FIG. 2 Mass Spectra of Me – BLIGHINONE

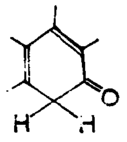
of blighinone is in agreement with the easy loss of CO. It is, however, noted that the molecular ion (m/e 330) with the loss of carbon dioxide (44 mass units) from the carboxyl attached to ring C, results in the peak m/e 286 in the mass spectra which could otherwise not be obtained from m/e 302. This inter alia confirms the molecular formula $C_{16}H_{10}O_8$.



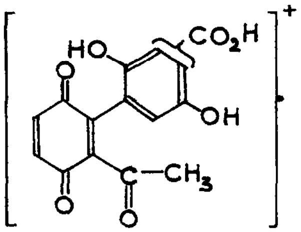
(I)



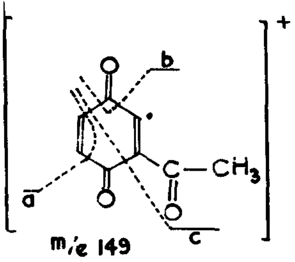
(II)



(III)



(IV)



(V)

Va m/e 125
Vb m/e 123
Vc m/e 97

The mass spectra (Fig.2) of the tri-methoxy-methyl ester obtained from blighinone by methylation with diazomethane in presence of methyl alcohol has *also been studied. In this case also the parent peak m/e 358* (M^+ - CO) *yielded successive peaks m/e 315, m/e 272 with the loss of 43 mass units* (CH_3CO) in each step - a characteristic fragmentation in the case of aryl-methyl ethers[3] - establishing at least two phenolic hydroxyl groups in blighinone. The presumption that these two hydroxyl groups are situated at para position to each other is supported by the absence of a relevent peak in the mass spectra signifying the loss of H_2O (18 mass units) from blighinone. The alternative route suggested by Djerassi et al[4] in the fragmentation pattern of aryl-methyl-ethers with the loss of 15 (CH_3) and 31 (OCH_3) mass units is also manifest from the mass spectra of methylated blighinone showing peaks at m/e 343 (358 - 15), 328 (343 - 15) and m/e 313 (344 - 31) and m/e 284 (315 - 31). In consideration of the spectral data discussed above it is assumed that ring C is a substituted aromatic ring with hydroxyl groups at positions 5 and 8. The abundant peak m/e 149 in the mass spectra of both blighinone and its methylated product can be assumed to have arisen by the opening of the ring B[5] and simultaneous elimination of the ring C as shown in structure (IV) and (V). This evidently places the third hydroxyl group at C-10 with which the side methyl is also attached. The placement of the carbonyl group at C-10 and the hydroxyl and the methyl groups at C-9, would preclude the possible chelation[1] as shown in structure (I). Further fragments with peaks at m/e 125 (82 + 43), m/e 123 (80 + 43) and m/e 97 (54 + 43) in the mass spectra of both the compounds are analogous to those expected of a substituted benzoquinone[6], as shown in (Va, Vb, Vc).

In view of the spectral data studied along with the properties of the compound and its derivatives blighinone is assigned the structure (I).

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