

THE PHOTO-SENSITIZED OXIDATION OF MORUSIN¹⁾

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Photo-sensitized oxidation of morusin (I) in the presence of sensitizers (rose bengal, hematoporphyrin) afforded morusinhydroperoxide (II), compound A (III), and two other compounds (IV, V). IV and V were formed via "ene" reaction. Photo-sensitized oxidation of I was carried out in the presence of 2,4,6-tri-tert-butylphenol, a radical quencher, or of triethylene diamine (Dabco), a singlet oxygen quencher. In the former case, II and III were not obtained, but IV and XIII, whereas in the latter case, IV and V were not obtained, but II and III. On the basis of the above results, the possible mechanism of the formation of II from I was discussed.

The authors reported the structure determination of a series of prenylflavones including morusin (I) and compound A (III) obtained from the root bark of Morus alba L.^{2,3)} and described the photooxidative

cyclization of I and other prenylflavones.⁴⁾ The similar oxidative cyclization, formation of morusinhydroperoxide (II) from I, was carried out in the presence of one-electron transfer oxidizing agents (manganese dioxide, silver oxide) in the dark, and the possible mechanism of this oxidative cyclization in the dark was postulated as drawn in Chart 1. Furthermore, it was suggested that this oxidative cyclization is model for the biosynthesis of certain uncommon flavonoids such as chaplashin (IX) and oxyisocyclo-integrin (X), which were supposed to be derived from 3-prenyl-2'-hydroxyflavone precursor.⁵⁾ On the other hand, it has been described that a large number of natural products may be formed by the oxidative coupling of their phenol precursors⁶⁾ and such phenol precursors may be oxidized photochemically in the presence of natural pigments serving as sensitizers, particularly in plants.⁷⁾ In this connection, we attempted the photo-sensitized oxidation of I.

A solution of I (50 mg) and hematoporphyrin (6 mg) in benzene containing 25 % methanol (15 ml) was externally irradiated in a glass vessel with a 200 W tungsten lamp for 5 hr. Blank runs without any dye gave no reaction. The reaction products were purified by preparative TLC to give II, IV and V in 6 %, 30 % and 4 % yield, respectively.⁸⁾ When rose bengal (10 mg) was used as a sensitizer instead of hematoporphyrin, II, III and IV were obtained in 17 %, 2 % and 4 % yield, respectively.⁹⁾ The products (II and III) were identified with authentic specimens^{2,4)} by ir spectroscopy and mixed melting point. The structural elucidations of IV and V

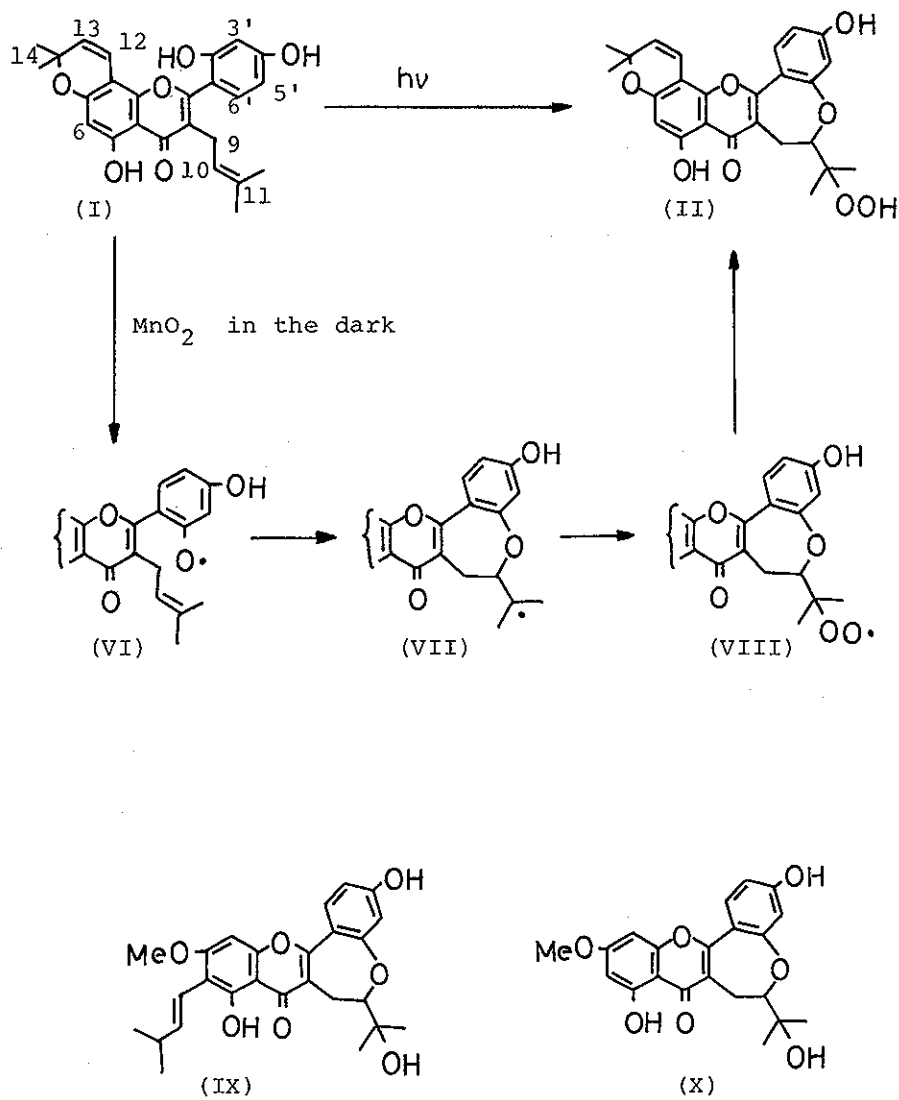


Chart 1

were accomplished on the basis of the following spectral data.

Compound (IV), $C_{25}H_{22}O_7$ (M^+ 434), mp 199-200°, yellow prisms from n-hexane - ether, positive on Gibbs test, ir [ν_{\max}^{Nujol} 3350, 1670, 1640, 1625 cm^{-1}], uv [λ_{\max}^{EtOH} nm(log ϵ): 213(4.50), 273(4.44), 305(sh 3.87), 310(sh 3.84), 350(sh 3.71); $\lambda_{\max}^{EtOH+AlCl_3}$: 213(4.45), 226(4.44), 281(4.46), 348(3.85), 405(3.59); $\lambda_{\max}^{EtOH+NaOMe}$: 277(4.38), 300(sh 4.14), 320(sh 4.05), 393(3.98)]. These uv spectra exhibited the absorption patterns similar to those of I.²⁾ nmr (δ in acetone- d_6) [1.46(6H, s, $C_{14} - CH_3 \times 2$), 1.82(3H, s, $C_{11} - CH_3$), 3.85(2H, s, C_9 and $C_{10} - H$), 5.65(1H, d, $J = 10Hz$, $C_{13} - H$), 5.80, 6.07 (each 1H, br s, $C_{11} = CH_2$), 6.17(1H, s, $C_6 - H$), 6.45(1H, dd, $J = 2$ and $9Hz$, $C_5 - H$), 6.53(1H, d, $J = 2Hz$, $C_3 - H$), 6.63 (1H, d, $J = 10Hz$, $C_{12} - H$), 7.15(1H, d, $J = 9Hz$, $C_6 - H$), 8.82, 12.95(2H, s, and 1H, s, OH, disappeared on addition of D_2O)], ms m/e: 434(M^+), 419($M^+ - CH_3$), 203(XI, formed from the ion at 419 by a reverse Diels-Alder reaction). From these data, compound (IV) is represented by the formula IV.

Compound (V), $C_{25}H_{24}O_7$ (M^+ 436), mp 171-178°, yellow prisms from benzene, positive on Gibbs test, ir [ν_{\max}^{Nujol} 3200, 1650, 1615, 1595 cm^{-1}], uv [λ_{\max}^{MeOH} nm(log ϵ): 206(4.62), 271(4.60), 300(sh 4.09), 320(sh 3.95), 350(sh 3.88); $\lambda_{\max}^{MeOH+AlCl_3}$: 206(4.62), 227(4.49), 279(4.63), 341(3.99), 410(sh 3.86); $\lambda_{\max}^{MeOH+NaOMe}$: 273(4.59), 315(sh 4.17), 380(4.11)], nmr (δ in acetone- d_6) [1.44(6H, s, $C_{14} - CH_3 \times 2$), 1.58(3H, s, $C_{11} - CH_3$), 2.72(2H, m, $C_9 - H \times 2$), 4.25(1H, m, $C_{10} - H$), 4.66, 4.77(each 1H, br s, $C_{11} = CH_2$), 5.63(1H, d, $J = 10Hz$, $C_{13} - H$), 6.16(1H, s, $C_6 - H$), 6.48-6.70(3H, m, C_3 , C_5 , and $C_{12} - H$), 7.36

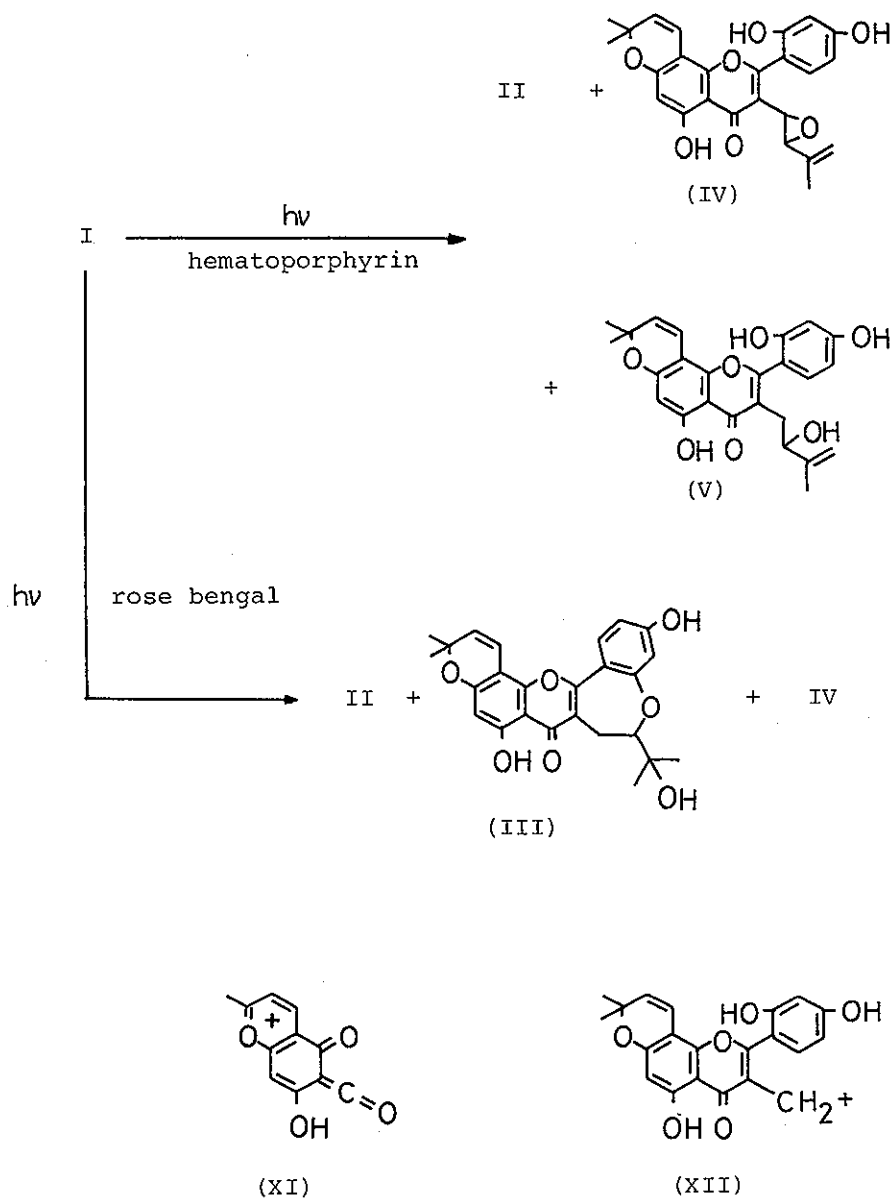


Chart 2

(1H, d, J = 9Hz, C₆, - H), 8.84, 13.04 (each 1H, br s and s, OH, disappeared on addition of D₂O)], ms m/e: 436(M⁺), 421(M⁺ - CH₃), 403(M⁺ - CH₃ - H₂O), 365(M⁺ - C₄H₇O, XII, base peak)¹⁰⁾, 351, 203(XI). From these data, compound (V) is represented by the formula V.

To elucidate the mechanism of this photo-sensitized oxidation, we tried the reactions in the presence of a radical quencher, such as 2,4,6-tri-tert-butylphenol, or a singlet oxygen quencher, such as triethylene diamine (Dabco)¹¹⁾ as follows. A solution of I (50 mg), 2,4,6-tri-tert-butylphenol (60 mg), and rose bengal (10 mg) in benzene containing 25 % methanol (15 ml) was irradiated as described above for 3 hr. The products were purified by preparative TLC to give IV and XIII in 7 % and 3 % yield, respectively. 2,4,6-Tri-tert-butylphenol was recovered in 68 % yield. II and III were not obtained in this reaction.⁹⁾ The product (XIII) was identified with authentic specimen⁵⁾ by mixed melting point. On the other hand, a solution of I (50 mg), Dabco (60 mg), and rose bengal (10 mg) in benzene containing 25 % methanol (15 ml) was irradiated as described above for 3 hr. After the purification by preparative TLC, two crystalline substances, II (15 %) and III (3 %) were obtained, but IV and V were not obtained.

It is probable that IV and V are formed via "ene" reaction.¹²⁾ A suggested mechanism involving the abstraction of the phenolic hydrogen by an excited dye triplet to produce morusinhydroperoxide (II) is drawn in Chart 4.^{7,12)} Furthermore, the formation of II from I by dye-sensitized photooxidation suggests that the formation

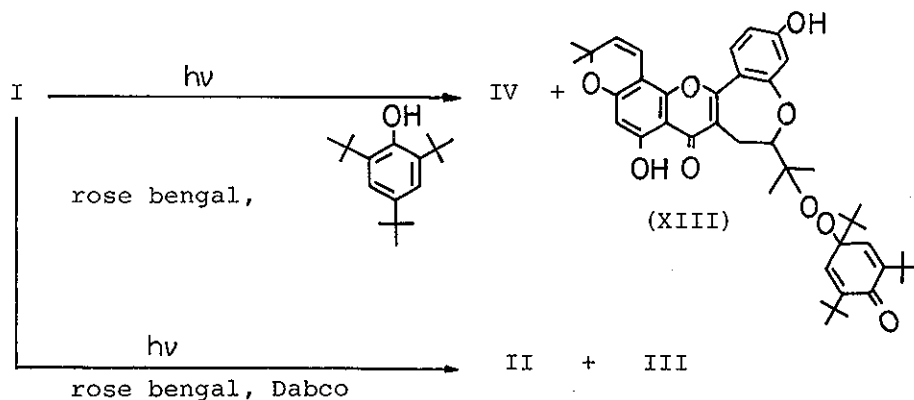


Chart 3

of uncommon flavones, such as chaplashin (IX) and oxyisocyclointegrin (X), could be initiated by a light-dye- O_2 system in the plant.^{7c)}



Chart 4

REFERENCES AND FOOTNOTES

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