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OXIDATION OF THE ANTHOCYANIDIN-3,5-DIGLUCOSIDES WITH H_2O_2: THE STRUCTURE OF MALVONE*

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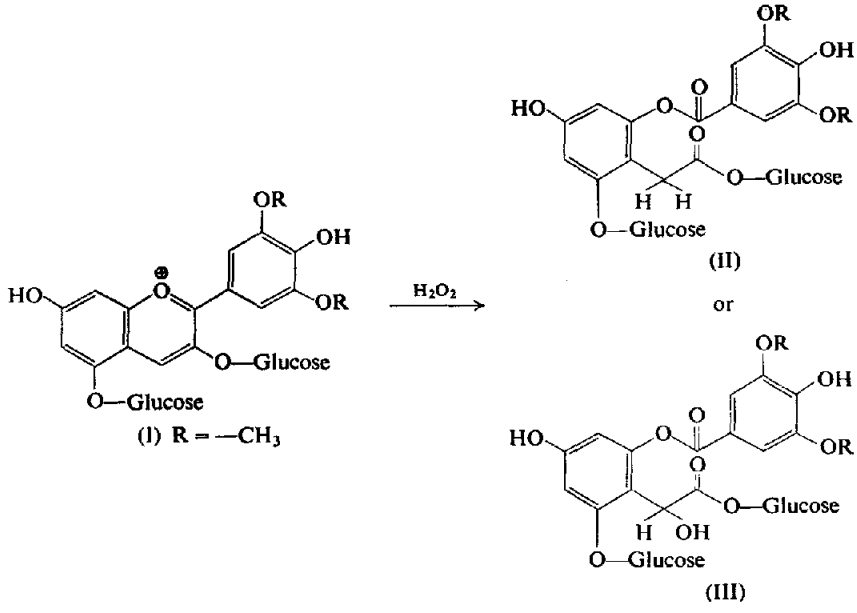
Abstract—The structure of malvone (II), obtained by oxidation of malvidin-3,5-diglucoside (I) with H_2O_2 in aqueous solution, has been established and a reaction mechanism is proposed.

INTRODUCTION

ANTHOCYANIDIN-3,5-diglucosides, which contain no *ortho*-hydroxy groups in the B-ring (I), undergo carbon–carbon cleavage between the 2- and 3-positions upon treatment with H_2O_2 in aqueous solution yielding *ortho*-benzoyloxy phenylacetic acid esters (I → II) or esters of the trihydroxy madelic acid (I → III).[1]



Because of difficulties encountered in the isolation of the phloroglucinol-containing fragment, the structure of the oxidation product, malvone, obtained from malvidin-3,5-diglucoside (I), was not determined with certainty.[1]

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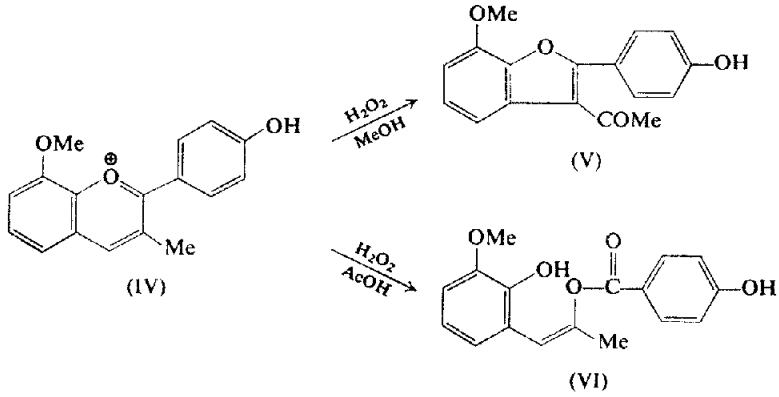
[1] P. KARRER and G. DE MEURON, *Helv. Chim. Acta* **15**, 507 (1932).

On the other hand, oxidation of 3-methylflavylium salts (IV) yielded in aq. methanolic solution-3-acetyl benzofurans (V)[2] and in acidic solutions an enol benzoate (VI),[3] demonstrating the marked effect of substituents on the flavylium nucleus and solvent used.



In this paper, further evidence for structure II for malvone is presented.

RESULTS

The crystalline oxidation product, malvone, was obtained as fine needles by oxidation of malvidin-3,5-diglucoside (I) according to Karrer.[1] Thin-layer chromatography on cellulose using BuOH:AcOH:H_2O (4:1:5) showed no impurities present. Addition of sodium ethylate to the solution of malvone in EtOH (λ_{max} 284 nm logϵ 5·59) resulted in a bathochromic shift (λ_{max} 334 nm, logϵ 5·69) of the u.v. spectrum, demonstrating that the 4′-hydroxy group was unaffected by the oxidation. Upon addition of $FeCl_3$ to the aqueous solution of malvone, no significant colour change was observed, indicating that no —OH groups in *meta* position were present in the molecule.* The i.r. spectrum in KBr pellet showed an ester band at 1736 cm^{-1}. The mass spectroscopic molecular weight determination could not be done because of the low volatility of the compound. However, when malvone was heated to 450° in the solid insertion chamber of the mass spectrometer, the mass spectrogram showed major fragments, which were interpreted as follows: *m/e* 346 (parent peak for the aglucone VII), 197 (syringic acid, VIII), 181 (syringic acid radical, IX). A metastable peak was present at *m/e* 129·3, resulting from the breakdown of the syringic acid radical (IX) to 2,6-dimethoxy phenol radical (X).

The 100 MHz NMR spectrum of malvone (in DMSO-d_6, Fig. 1) showed the presence to two aromatic hydroxy groups (singlet, δ 9·74 and multiplet δ 9·45). For the two aromatic protons of the syringic acid substituent a singlet at δ7·32 and two doublets for the aromatic protons of the phenylacetic acid derivative (δ 6·52, $J = 1$ c/s, δ 6·34, $J = 1$ c/s). The two anomeric protons of the glucose substituents were detected as two doublets (δ 5·41, $J = 7$ c/s and δ 4·73, $J = 7$ c/s). The six protons of the two methoxy groups of syringic acid gave rise to a singlet at δ 3·85. The sugar hydroxy groups gave a broad signal (multiplet, δ 3·90–5·40). The multiplet at δ 2·70–3·80 contains the sugar protons and signals from DMSO-d_6 as well as the triplet at δ 1·04 and the signal at δ 2·50.

* 3,5-Dihydroxy benzoic acid gives a gray-brownish colour on addition of $FeCl_3$.

[2] L. JURD, *J. Org. Chem.* **29**, 2602 (1964).
[3] L. JURD, *Tetrahedron* **22**, 2913 (1966).

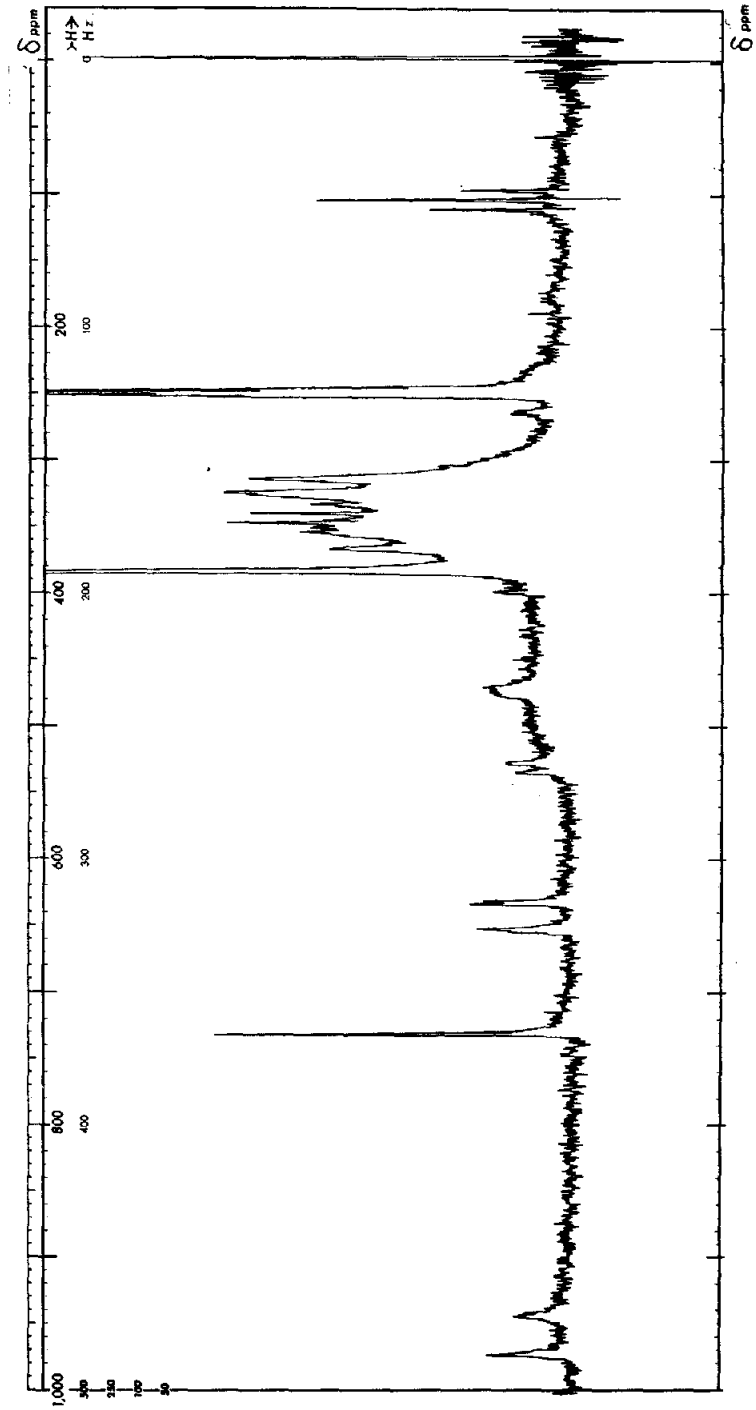


FIG. 1. 100 MHz NMR SPECTRUM OF MALVONE IN DMSO-d_6; TMS AS INTERNAL REFERENCE.

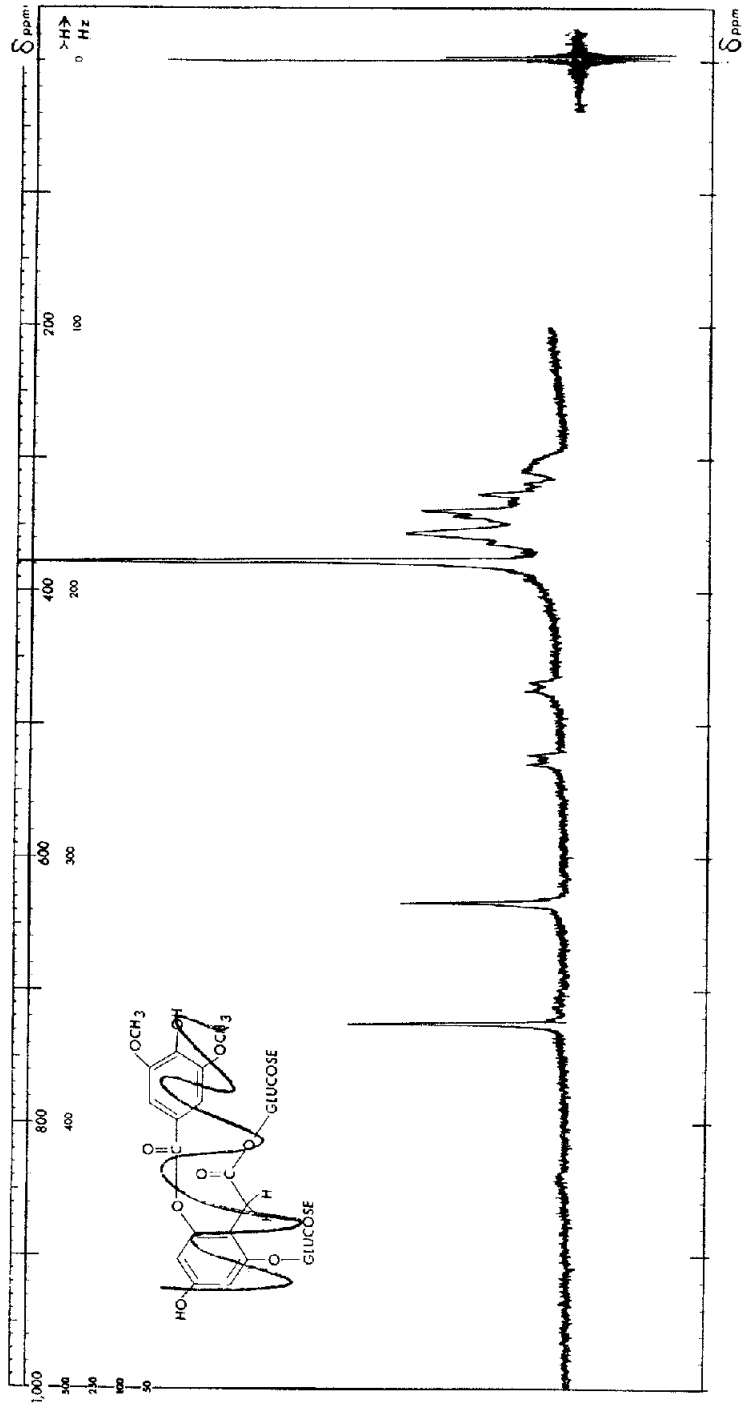
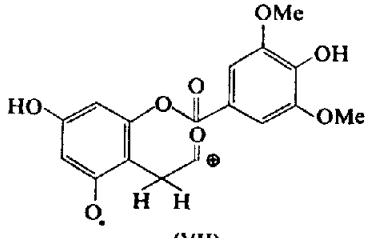
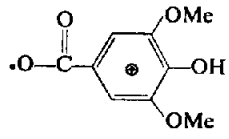


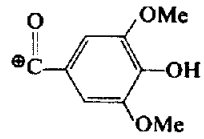
FIG. 2. 100 MHz NMR SPECTRUM OF TRIMETHYLSILYLATED MALVONE IN CCl_4. TMS AS INTERNAL REFERENCE.



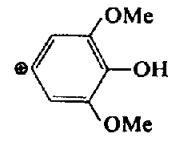
(VII)



(VIII)



(IX)



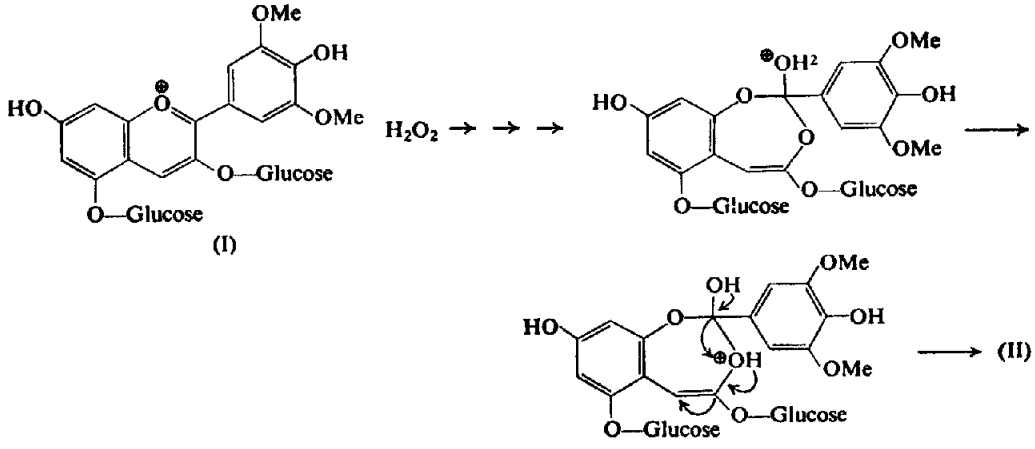
(X)

The aromatic protons of trimethyl silylated malvone (in CCl_4, Fig. 2) appeared as two singlets (δ 7·25 for the protons 2 and 6 of the syringic acid substituent and δ 6·34 for the 3 and 5 protons of the phenylacetic acid derivative).

The anomeric protons of the glucose substituted on the 2-position of the phenylacetic acid derivatives by a glycosidic bond gave a doublet at δ 5·26 ($J = 7$ c/s) and the anomeric proton of the glucose linked by ester bond at δ 4·72 (doublet, $J = 7$ c/s). The six protons of the two-methoxy group appeared at δ 3·78 (singlet). The integral of the multiplet at δ 2·90–3·68 indicated the presence of fourteen protons (twelve glucose protons plus two aliphatic protons of the phenylacetic acid derivative), showing that the data are in accordance with structure II.

DISCUSSION

The reaction mechanism of the oxidation of I in aqueous solution is a Bayer–Villiger oxidation, which follows a similar pathway as proposed by Jurd[3] for the oxidation of 3-alkylflavylium salts. However, after the nucleophilic attack of the water on the carbonium ion, the hydrogen atom migrates to the oxygen in the 3-position of the seven-membered heterocyclic ring and affects the formation of II.



The migration of H to the oxygen in the 3-position possibly is affected by the glucose substituent in the 5-position of I.

EXPERIMENTAL

Malvidin-3,5-diglucoside (I) was isolated from Seibel 9549 grapes using column chromatography on PVP.*

150 mg I was dissolved in 5 ml H_2O and 3 ml H_2O_2 were added. The reaction mixture was allowed to remain at room temperature for 8 hr. Thereafter, it was held overnight in the refrigerator, whereupon malvone crystallized in colorless needles (yield 86 mg), m.p. 162–165°. (Found: C, 49·25; H, 5·45; $-OCH_3$, 8·61. Calc. for $C_{29}H_{36}O_{19}.H_2O$: C, 49·27; H, 5·42; $-OCH_3$, 8·78.)

The mass spectrum was determined with a Hitachi–Perkin–Elmer RMU-6E spectrometer, equipped with solid insertion chamber.

Malvone was silylated according to the method of Mabry *et al.*[4] and the NMR spectrum recorded with a Varian HA-100 D spectrometer.

Acknowledgement—This paper has been approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 1681.

* Manuscript in print.

[4] T. J. MABRY, J. KAGAN and H. ROESLER, The University of Texas Publication No. 6418 (1964).