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Oxidation Reactions of Some Natural Volatile Aromatic Compounds: Anethole and Eugenol*

E. M. Elgendy[a] and S. A. Khayyat[b]

[a] *Faculty of Specific Education, Mansoura University, Mansoura, Egypt*
e-mail: eman_elgendy@hotmail.com

[b] *Faculty of Educational's Girls, Ministry of Education, Jeddah, Saudi Arabia*

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Abstract—*trans*-Anethole [1-methoxy-4-(*trans*-prop-1-en-1-yl)benzene] was isolated from anise seed oil (*Pimpinella anisum*). Its photochemical oxidation with hydrogen peroxide gave the corresponding epoxy derivative together with 4-methoxybenzaldehyde. The thermal oxidation of *trans*-anethole with 3-chloroperoxybenzoic acid at room temperature resulted in the formation of dimeric epoxide, 2,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,4-dioxane, as the only product. Photochemical oxygenation of *trans*-anethole in the presence of tetraphenylporphyrin, Rose Bengal, or chlorophyll as sensitizer led to a mixture of 1-(4-methoxyphenyl)prop-2-en-1-yl hydroperoxide and 4-methoxybenzaldehyde. Eugenol was isolated from clove oil [*Eugenia caryophyllus* (Spreng.)]. It was converted into 2-methoxy-4-(prop-2-en-1-yl)phenyl hydroperoxide by oxidation with hydrogen peroxide under irradiation. Thermal oxidation of eugenol with 3-chloroperoxypenzoic acid at room temperature produced 2-methoxy-4-(oxiran-2-ylmethyl)phenol, while sensitized photochemical oxygenation (in the presence of Rose Bengal or chlorophyll) gave 4-hydroperoxy-2-methoxy-4-(prop-2-en-1-yl)cyclohexa-2,5-dien-1-one.

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Many naturally occurring alkenylbenzene derivatives, usually relatively simple allyl- or propenylbenzenes having methoxy and/or methylenedioxy substituents in the benzene ring, have been identified as components of numerous plants or their essential oils [1, 2] and used as natural flavoring and fragrance chemicals. Microbial metabolism of phenylpropenoids involves oxidation of the side chain to carboxylic acid prior to hydroxylation and cleavage of the benzene ring. For example, eugenol is oxidized to vanillic acid [3]. On the other hand, plant phenylpropenoides undergo oxidation on exposure to air. The oxidation process is enhanced by heat, irradiation [4], or in the presence of catalysts [5].

Mohan and Whalen [6] reported that oxidation of anethole (**I**) with 3-chloroperoxybenzoic acid gives epoxy derivative **Ib**. Waumans et. al. [7] found that analogous reaction with hydrogen peroxide in presence of formic or acetic acid on heating leads to 3,5-bis(4-methoxyphenyl)-2,4-dimethyltelrahydrofuran and that intermediate epoxide **Ib** could not be isolated.

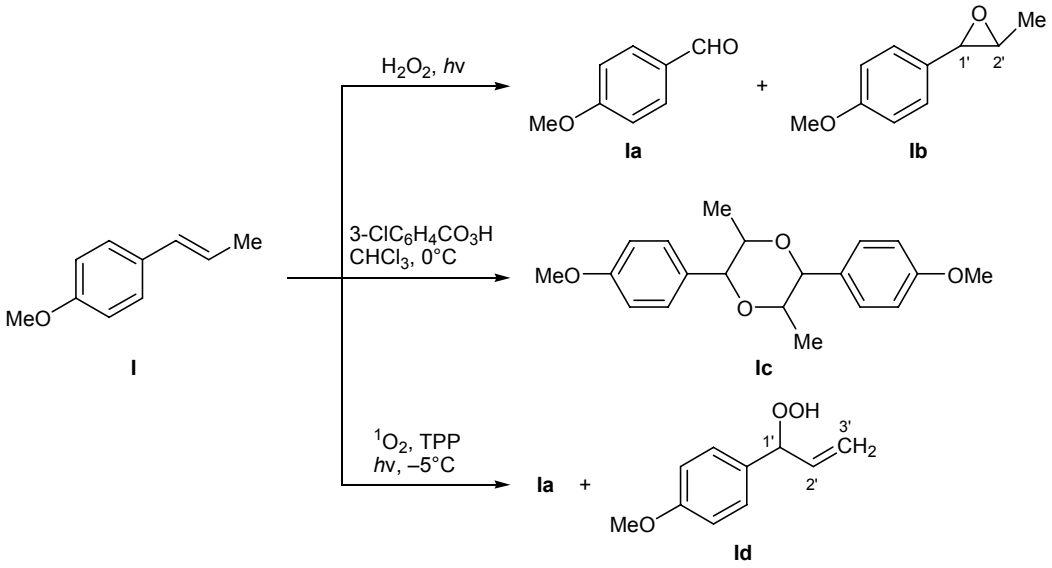
Taking into account important activities of plant phenylpropenoides and contradictory published data on epoxidation of anethole (**I**), in the present work we studied in detail oxidation reactions of *trans*-anethole (**I**) and eugenol (**II**) under different conditions (thermal and photochemical).

trans-Anethole [1-methoxy-4-(*trans*-prop-1-en-1-yl)benzene, **I**] is the major component of several essential oils, including Chinese Star Anise (*Illicium verum*), Anise seed oil (*Pimpinella anisum*), and sweet Fennel (*Foeniculum vulgare* Mill. var. dulce) [8]. The chemical structure of **I** was confirmed by spectral measurements. The ^{1}H NMR spectrum of **I** showed a doublet at δ 1.86 from protons in the methyl group, and side-chain olefinic protons on $C^{2'}$ and $C^{1'}$ resonated, respectively, as a doublet of quartets at δ 6.08 ppm and a doublet at δ 6.34 ppm. In the ^{13}C NMR spectrum of **I**, the $C^{2'}$ and $C^{1'}$ signals were located at δ_C 123.5 and 130.5 ppm, respectively.

Photochemical epoxidation of *trans*-anethole (**I**) with hydrogen peroxide (H_2O_2, 30% by volume) in ethanolic medium under irradiation with sodium light (irradiation time 55 h) to give 65% of 4-methoxybenz-

* The text was submitted by the authors in English.

Scheme 1.



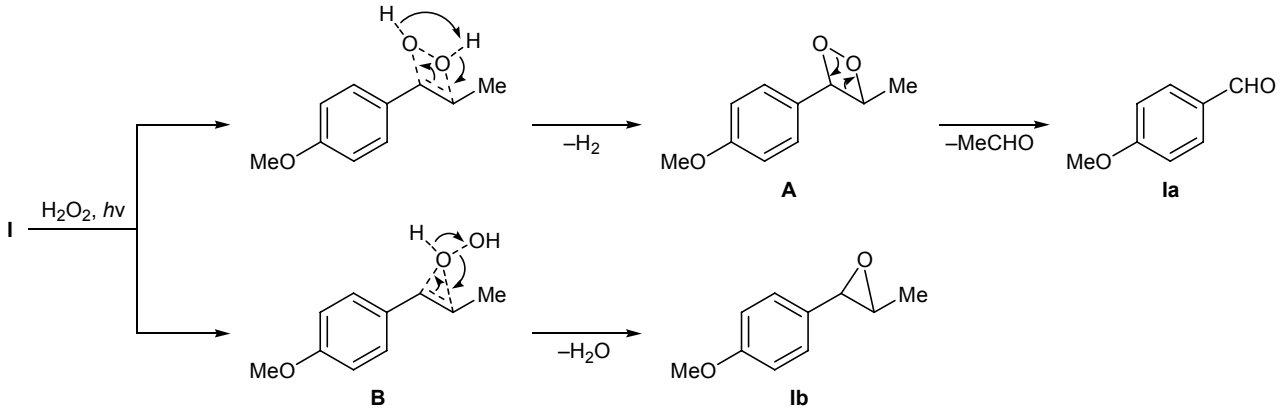
aldehyde (**Ia**) and 35% of monoepoxy derivative, 2-(4-methoxyphenyl)-3-methyloxirane (**Ib**) (Scheme 1).

The structure of epoxidation products **Ia** and **Ib** was established by spectral measurements. The IR spectrum of **Ia** contained an absorption band at 1699 cm^{-1} due to the aldehyde carbonyl group, and the CHO proton signal appeared in the ^1H NMR spectrum as a singlet at δ 9.86 ppm; no signals assignable to protons at the anethole side-chain double CH=CH bond were present. The aldehyde carbonyl carbon atom resonated in the ^{13}C NMR spectrum at δ_C 190.7 ppm, and the molecular ion peak in the mass spectrum of **Ia** had an *m*/*z* value of 136. Compound **Ib** displayed in the ^1H NMR spectrum a doublet at δ 0.96 ppm from the CH_3 group in the oxirane ring, a doublet of quartets at δ 3.36 ppm from 2′-H, and a doublet at δ 3.90 ppm from 1′-H. In the ^{13}C NMR spectrum of **Ib**, signals from the oxirane carbon atoms were present at δ_C 64.1 ($C^{2'}$) and 71.4 ppm ($C^{1'}$). The mass spectrum of **Ib** contained the molecular ion peak at *m*/*z* 164.

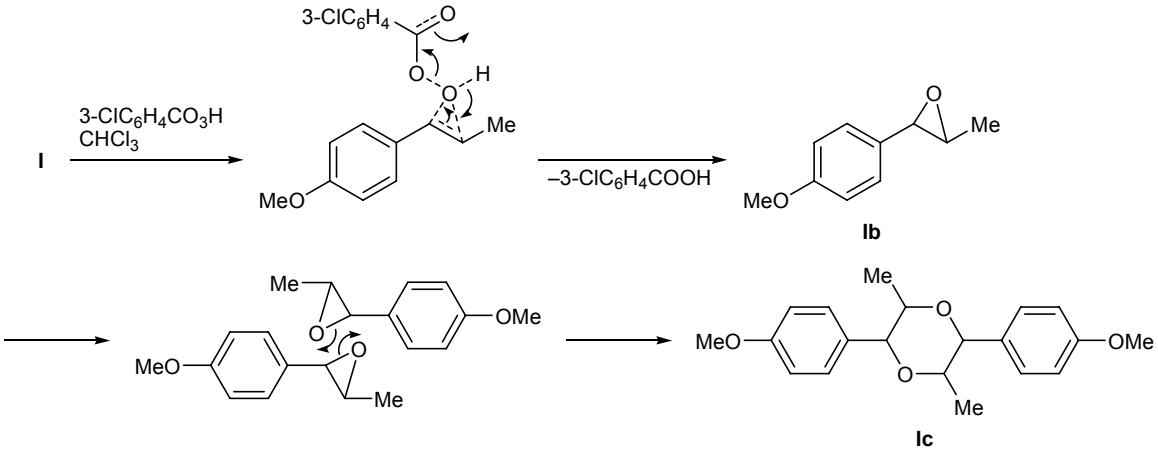
Thermal oxidation of *trans*-anethole (**I**) with *m*-choroperoxybenzoic acid in chloroform at room temperature gave 2,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,4-dioxane (**Ic**) as the only product in almost quantitative yield (Scheme 1). The ^1H NMR spectrum of **Ic** contained a six-proton doublet at δ 1.19 ppm from the methyl protons, a doublet of quartets at δ 4.27 ppm from protons in positions *3* and *6* of the dioxane ring, and a doublet at δ 5.82 ppm from protons in positions *2* and *5*. Signals at δ_C 70.1 and 81.5 ppm in the ^{13}C NMR spectrum of **Ic** were assigned to C^3/C^6 and C^2/C^5 in the 1,4-dioxane ring. The molecular ion of **Ic** had an *m*/*z* value of 328.

Interestingly, the photoinduced oxygenation of compound **I** in the presence of tetraphenylporphyrin (TPP), Rose Bengal (RB), or chlorophyll (CP) as

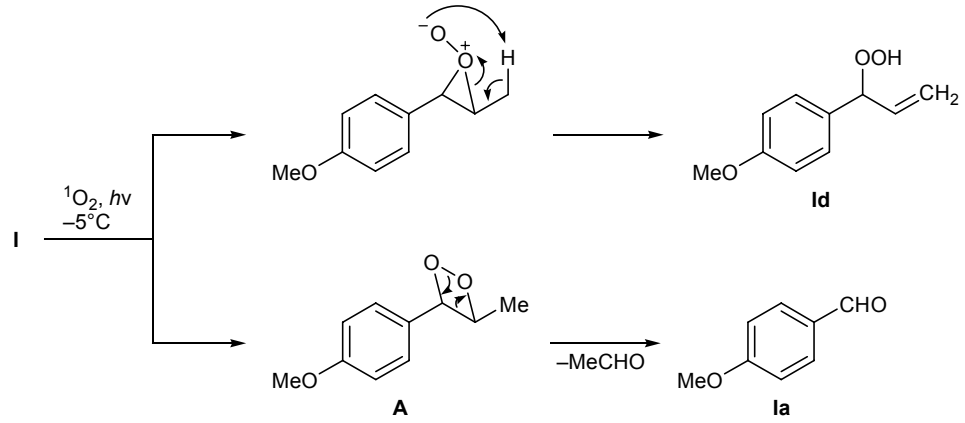
Scheme 2.



Scheme 3.



Scheme 4.

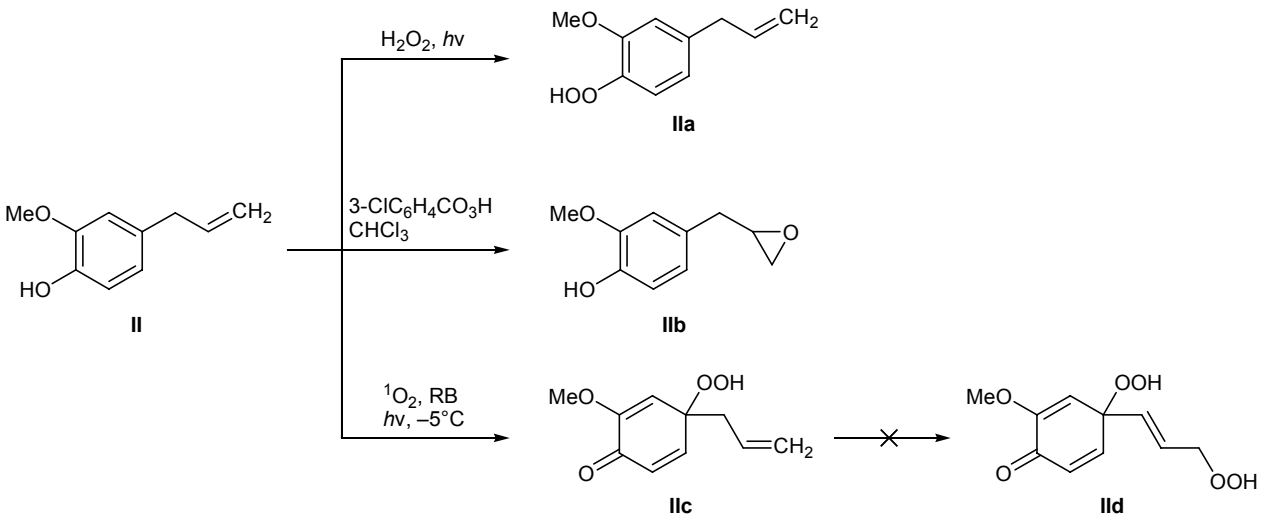


singlet oxygen sensitizer led to the formation of 1-(4-methoxyphenyl)-prop-2-en-l-yl hydroperoxide (**Id**) together with aldehyde **Ia** (Scheme 1). Compound **Id** showed in the ^{1}H NMR spectrum a doublet at δ 3.90 ppm from the side-chain allylic proton at $C^{1'}$, a two-proton doublet of doublets at δ 5.35 from the $C^{3'}H_2$ group, a complex multiplet at δ 6.05 ppm from 2′-H, and a singlet at δ 8.60 ppm due to proton in the hydroperoxide group.

A probable mechanism for the formation of aldehyde **Ia** and epoxy derivatives **Ib** in the photochemical oxidation of *trans*-anethole (**I**) with hydrogen peroxide is shown in Scheme 2. Attack by hydrogen peroxide on the side-chain double bond in molecule **I** gives dioxetane intermediate **A** which decomposes to form acetaldehyde and 4-methoxybenzaldehyde (**Ia**). Alternatively, the reaction of **I** with H_2O_2 could involve oxirane intermediate **B**, and elimination of water molecule from the latter yields oxirane **Ib**. Numerous attempts to obtain epoxide **Ib** under thermal conditions, in particular by reaction of **I** with *m*-chloroperoxybenzoic acid at room temperature according to [6], were unsuccessful. In all cases, the only isolated product was 1,4-dioxane derivative **Ic** which could be formed via dimerization of epoxide **Ib** (Scheme 3). Scheme 4 illustrates a probable mechanism of photosensitized oxygenation of *trans*-anethole (**I**) in the presence of tetraphenylporphyrin (TPP), Rose Bengal (RB), or chlorophyll (CP), leading to the formation of hydroperoxide **Id** and aldehyde **Ia**. Presumably, the process involves peroxirane and dioxetane intermediates, respectively.

Eugenol (4-allyl-2-methoxyphenol, **II**) is the major component of the essential oil extracted from *Eugenia Caryophyllus* (*Myrtaceae*) [9]. The chemical structure of **II** was confirmed by spectral measurements. The ^{1}H NMR spectrum of **II** contains a doublet from the $C^{1'}H_2$ group at δ 3.31 ppm, a doublet of doublets at δ 5.05 ppm from two methylene protons in position 3′, and a multiplet at δ 5.94 ppm which is characteristic of the side-chain 2′-H proton. In the mass spectrum of **II** the molecular ion peak with *m*/*z* 164 was observed.

Scheme 5.



Photochemical epoxidation of eugenol (**II**) with hydrogen peroxide (H_2O_2, 30 % by volume) in ethanolic medium using sodium lamp gave 4-allyl-2-methoxyphenyl hydroperoxide (**IIa**) in ~45% yield, while no other products were detected (Scheme 5). The structure of hydroperoxide **IIa** was determined on the basis of spectral measurements. The ^1H–^1H COSY spectrum showed a doublet of doublets at δ 3.27 ppm from the allylic methylene group in position *1′*, a doublet of doublets at δ 5.04 ppm from the methylene protons in position *3*', a complex pattern at δ 5.93 ppm typical of proton in position *2′* of the allylic side chain, and a singlet at δ 8.32 ppm from the hydroperoxide proton. Hydroperoxide **IIa** showed in the mass spectrum the molecular ion peak at *m*/*z* 180.

When epoxidation of compound **II** was carried out using *m*-choroperoxybenzoic acid in chloroform at room temperature, we obtained 2-methoxy-4-oxiranylmethylphenol (**IIb**) as the only product in quantitative yield (Scheme 5). The ^1H NMR spectrum of **IIb** contained a doublet of doublets at δ 2.54 from one proton of the methylene group on $C^{3'}$, a complex multiplet at δ 2.78 ppm from the other proton on $C^{3'}$, a doublet at δ 2.80 ppm from the $C^{1'}H_2$ group, and a complex multiplet at δ 3.13 ppm from 2′-H. The molecular ion in the mass spectrum of **IIb** had an *m*/*z* 180.

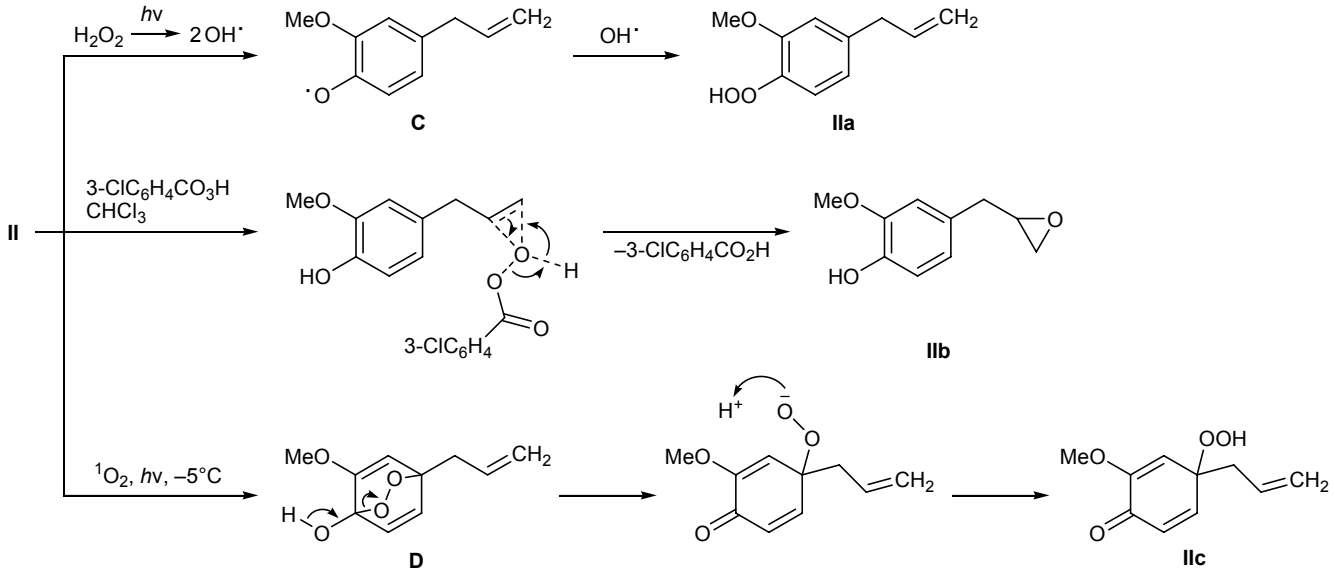
On the other hand, photochemical oxygenation of compound **IIa** in presence of Rose Bengal (RB) or chlorophyll (CP) as singlet oxygen sensitizer gave 4-hydroperoxy-2-methoxy-4-(prop-2-en-1-yl)cyclohexa-2,5-dien-1-one (**IIc**), while no other photooxidation products were detected even when the irradiation time was prolonged (Scheme 5). The yields are given in table. The IR spectrum of **IIc** contained an absorption band at 1690 cm^{-1} due to stretching vibrations of the carbonyl group. In the ^1H NMR spectrum of **IIc**, we observed a complex pattern at δ 2.53 ppm from the methylene protons on $C^{1'}$, a doublet of doublets at δ 5.13 ppm from the terminal side-chain methylene group ($C^{3'}H_2$), a multiplet at δ 5.67 ppm from 2′-H, and a singlet at δ 8.73 ppm from the hydroperoxide group. Compound **IIc** displayed the molecular ion peak at *m*/*z* 196 in the mass spectrum.

Youssef [10] found that photosensitized oxygenation of eugenol (**II**) in the presence of tetraphenylporphyrin gave 4-hydroperoxy-2-methoxy-4-(prop-2-en-1-yl)cyclo-hexa-2,5-dien-1-one (**IIc**) which was converted into 4-hydroperoxy-4-(3-hydroperoxyprop-1-en-1-yl)-2-methoxycyclohexa-2,5-dienone (**IId**) upon prolonged irradiation. In our experiments on oxygenation of eugenol (**II**) using Rose Bengal (RB) or chlorophyll (CP) as singlet oxygen sensitizer instead of TPP hydroperoxide **IIc** was the only product: neither com-

Photosensitized oxygenation of *trans*-anethole (**I**) and eugenol (**II**) in the presence of tetraphenylporphyrin (TPP), Rose Bengal (RB), and chlorophyll (CP)

Initial comp. no.	Solvent	Sensitizer	Reaction time, h	Yield, %	Product (ratio)
I	$CHCl_3$	TPP	5	60	**Ia**, **Id** (38 : 62)
	EtOH	RB	8	33	**Ia**, **Id** (39 : 61)
	$CHCl_3$	CP	12	40	**Ia**, **Id** (35 : 65)
II	EtOH	RB	11	35	**IIc**
	$CHCl_3$	CP	16	42	**IIc**

Scheme 6.



pound **IIa** nor **IId** was detected even after prolonged irradiation. The mechanisms of formation of products **IIa**, **IIb**, and **IIc** may be illustrated by Scheme 6, according to which photochemical decomposition of hydrogen peroxide generates two hydroxyl radicals. One OH· radical abstracts hydrogen atom from the phenolic hydroxy group in molecule **II** to give H_2O and phenoxy radical **C**. Combination of the latter with the second OH· radical produces hydroperoxide **IIa**. The other hydroperoxide derivative, compound **IIc** is most likely to be formed through endoperoxide intermediate **D**. Presumably, the oxidation of **II** with *m*-chloroperoxybenzoic acid involves intermediate oxirane like **B** (Scheme 2), and elimination of *m*-chlorobenzoic acid leads to oxirane **IIb**.

It is known that some hydroperoxides induce photochemical DNA damage [11, 12]. A sample of DNA was mixed with a solution of compound **Id** or **IIc**, and the resulting mixture was irradiated using a sodium lamp. The results (see Experimental) clearly indicated that compounds **Id** and **IIc** induce a moderate to high degree of DNA degradation when the irradiation time is longer than 8 h.

We can conclude that the oxidation of *trans*-anethole and eugenol can be effected under photochemical conditions using hydrogen peroxide to obtain either epoxy or hydroperoxy derivatives. Novel hydroperoxides can also be obtained by photosensitized oxygenation. Probably, such hydroperoxides are generated *in situ* upon irradiation of anethole or eugenol in the presence of DNA, and they can be responsible for some adverse effects in living cells. Therefore, it seems to be relevant to elucidate biological consequences of hydroperoxides **Id**, **IIa**, and **IIc** with DNA and other cell components. The genotoxicity of such DNA intercalators possessing an additional oxidative potential was not studied previously.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 16 FPC FT-IR spectrophotometer from samples prepared as thin films. The ^1H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Bruker Avance DPX 400 spectrometer. The mass spectra were obtained on a Joel JMS 600H instrument coupled with a Hewlett–Packard HP 6890 Series gas chromatograph (HP-5 column, 30 m×0.32 mm×0.25 μm; cross-linked 5% dimethylpolysiloxane). A Philips G/5812 SON sodium lamp was used as irradiation source for photochemical reactions. Analytical and preparative thin-layer chromatography was performed on Polygram SIL G/W 254 silica gel (Mecherey-Nagel). Solvents were removed from the reaction mixtures and extracts using a rotary evaporator (20°C, 15 mm). *trans*-Anethole (**I**) was extracted from oil of *Pimpinalla anisum* (*Apiaceae*) plant, and eugenol (**II**) was extracted from *Eugenia Caryophyllus* (*Myrtaceae*) plant.

1-Methoxy-4-(*trans*-prop-1-en-1-yl)benzene (I, *trans*-anethole). Colorless solid, mp. 20°C, $C_{10}H_{12}O$ (*M* 148.206). IR spectrum, ν, cm^{-1}: 3019, 2965, 2836, 1607, 1510, 1235, 1171, 1030. ^1H NMR spectrum, δ, ppm: 1.86 d (3H, CH_3, J =7 Hz), 3.78 s (3H, OCH_3),

6.08 d.q (1H, 2′-H, J = 7, 16 Hz), 6.34 d (1H, 1′-H, J = 16 Hz), 6.82 d (2H, 2-H, 6-H, J = 8 Hz), 7.25 d (2H, 3-H, 5-H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19 (CH_3), 55 (OCH_3), 114 (C^2, C^6), 123.5 ($C^{2'}$), 127 (C^3, C^5), 130.5 ($C^{1'}$), 131 (C^4), 159 (C^1).

2-Methoxy-4-(prop-2-en-1-yl)phenol (II, eugenol). Colorless oil, $C_{10}H_{12}O_2$ (M 164.238). IR spectrum, ν, cm^{-1}: 3518, 3073, 2976, 1838, 1639, 1614, 1500, 1363, 1153, 1030. ^{1}H NMR spectrum, δ, ppm: 3.31 d (2H, 1′-H, J = 8 Hz), 3.85 s (3H, OCH_3), 5.05 d.d (2H, 3′-H, J = 12, 8 Hz), 5.57 s (1H, OH), 5.94 m (1H, 2′-H), 6.68 m (2H, 3-H, 6-H), 6.84 d (1H, 5-H, J = 8 Hz,). ^{13}C NMR spectrum, δ_C, ppm: 40 ($C^{1'}$), 55.9 (OCH_3), 111.3 ($C^{3'}$), 114.6 (C^6), 115.6 (C^3), 121.5 (C^5), 132 (C^4), 138 ($C^{2'}$), 144 (C^2), 146.9 (C^1).

Photochemical oxidation of *trans*-anethole (I) and eugenol (II) with hydrogen peroxide (*general procedure*). A solution of 30% hydrogen peroxide, 2.5 ml, was carefully added in a dropwise manner over a period of 5 min to a solution of 5 mmol compound **I** or **II** in 25 ml of ethanol under stirring at 0°C. The mixture was irradiated for 55 h using a sodium lamp in a nitrogen atmosphere. The mixture was then evaporated under reduced pressure at room temperature to give a resinous material. The residue was treated with 25 ml of chloroform, the extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel using petroleum ether (bp 60–80°C)–diethyl ether (9:2) to isolate compounds **Ia** and **Ib** (from **I**) or **IIa** (from **II**).

4-Methoxybenzaldehyde (Ia). Yield 0.34 g (65%), colorless oil, $C_8H_8O_2$ (M 136.152). IR spectrum, ν, cm^{-1}: 3014, 2933, 2836, 1699, 1607, 1500, 1451, 1117. ^{1}H NMR spectrum, δ, ppm: 3.87 s (3H, OCH_3), 7.0 d (2H, 3-H, 5-H, J = 7 Hz), 7.83 d (2H, 2-H, 6-H, J = 7 Hz), 9.86 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 55.4 (CH_3O), 114.2 (C^3, C^5), 129.8 (C^1), 131.8 (C^2, C^6), 164.5 (C^4), 190.7 (CHO). GC–MS data: retention time 16.163 min; m/z (I_{rel}, %): 136 (80), $[M]^+$, 135 (100) $[M - H]^+$, 107 (15) $[M - CHO]^+$, 92 (20) $[C_6H_4O]^+$, 77 (25) $[C_6H_5]^+$, 65 (5) $[C_5H_5]^+$.

2-(4-Methoxyphenyl)-3-methyloxirane (Ib). Yield 0.18 g (35%), colorless oil, $C_{10}H_{12}O_2$ (M 164.206). IR spectrum, ν, cm^{-1}: 3003, 2949, 2830, 1613, 1500, 1467, 1171, 1041. ^{1}H NMR spectrum, δ, ppm: 0.96 d (3H, CH_3, J = 7 Hz), 3.36 d.q (1H, 2′-H, J =8, 16 Hz), 3.82 s (3H, OCH_3), 3.90 d (1H, 1′-H, J = 16 Hz), 6.89 d (2H, 3-H, 5-H, J = 8 Hz), 7.22 d (2H, 2-H, 6-H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 17.9 ($C^{3'}$), 55.3 (OCH_3), 64.1 ($C^{2'}$), 71.4 ($C^{1'}$), 113.8 (C^3, C^5), 128.7 (C^2, C^6), 132 (C^1), 163 (C^4). GC–MS data: retention time 12.075 min; m/z (I_{rel}, %): 164 (100) $[M]^+$, 149 (30) $[M - CH_3]^+$, 133 (20) $[M - OCH_3]^+$, 119 (3) $[M - C_2H_5O]^+$, 103 (30) $[C_8H_7]^+$, 93 (5) $[C_6H_5O]^+$, 92 (3) $[C_6H_4O]^+$, 77 (30) $[C_6H_5]^+$, 65 (15) $[C_5H_5]^+$.

2-Methoxy-4-(prop-2-en-1-yl)phenyl hydroperoxide (IIa). Yield 0.41 g (100%), colorless oil, $C_{10}H_{12}O_3$ (M 180.238). IR spectrum, ν, cm^{-1}: 3520, 3057, 2922, 2831, 1602, 1521, 1365, 1144. ^{1}H NMR spectrum (^{1}H–^{1}H COSY; DMSO-d_6), δ, ppm: 3.27 d.d (2H, 1′-H, J = 16, 8 Hz), 3.73 s (3H, OCH_3), 5.01 d (1H, 3′-H, J = 8 Hz), 5.09 d (1H, 3′-H, J = 20 Hz), 5.93 m (1H, 2′-H), 6.54 d (1H, 6-H, J = 8 Hz), 6.68 d (1H, 5-H, J = 8 Hz), 6.73 s (1H, 3-H), 8.32 s (1H, OOH). GC–MS data: retention time 16.767 min; m/z (I_{rel}, %): 180 (60) $[M]^+$, 163 (3) $[M - OH]^+$, 153 (20) $[M - C_2H_3]^+$, 137 (100) $[M - C_2H_3O]^+$, 124 (40) $[M - C_4H_8]^+$, 105 (15) $[M - C_3H_7O_2]^+$, 91 (65) $[C_6H_3O]^+$, 65 (20) $[C_5H_5]^+$.

Oxidation of *trans*-anethole (I) and eugenol (II) with *m*-chloroperoxybenzoic acid (*general procedure*). A solution of 10 mmol of 80% *m*-chloroperoxybenzoic acid was added dropwise over a period of 15 min to a solution of 5 mmol of compound **I** or **II** in 25 ml of chloroform under stirring at 0°C. The mixture was then stirred at room temperature under nitrogen, the progress of the reaction being monitored by TLC and peroxide test (using a 10% solution of KI). The mixture was carefully washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 ml) and distilled water (3 × 10 ml). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure at room temperature. The residue was purified by column chromatography on silica gel using petroleum ether (bp 60–80°C)–diethyl ether (9:2) to isolate compound **Ic** (from **I**) or **IIb** (from **II**) as viscous oily substances.

2,5-Bis(4-methoxyphenyl)-3,6-dimethyl-1,4-dioxane (Ic). Yield 0.78 g (95%), colorless oil, $C_{20}H_{24}O_4$ (M 328.412). IR spectrum, ν, cm^{-1}: 3461, 3068, 2981, 2825, 1726, 1607, 1505, 1424, 1176. ^{1}H NMR spectrum (^{1}H–^{1}H COSY), δ, ppm: 1.19 d (6H, CH_3, J = 7 Hz), 3.84 s (6H, OCH_3), 4.27 d.q (2H, 3-H, 6-H, J = 7 Hz), 5.82 d (2H, 2-H, 5-H, J = 7 Hz), 6.95 d (4H, 3′-H, 5′-H, J = 8 Hz), 7.41 d (4H, 2′-H, 6′-H, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 19 (CH_3), 55.2 (OCH_3), 70.1 (C^3, C^6), 81.5 (C^2, C^5), 114.1 ($C^{3'}$, $C^{5'}$), 127.9 ($C^{3''}$), 128.6 ($C^{2'}$, $C^{6'}$), 129.5 ($C^{5''}$), 129.7 ($C^{2''}$), 129.8 ($C^{6''}$), 133.1 ($C^{1'}$), 134.5 ($C^{1''}$), 159.7 ($C^{4'}$), 164.8 ($C^{4''}$). Mass spectrum, m/z (I_{rel}, %): 328 (6) $[M]^+$, 314

(3) $[M - CH_2]^+$, 301 (5) $[M - C_2H_3]^+$, 297 (3) $[M - CH_3O]^+$, 283 (5) $[M - C_2H_5O]^+$, 253 (1) $[M - C_3H_7O_2]^+$, 238 (3) $[M - C_4H_{10}O_2]^+$, 164 (4) $[M/2]^+$, 161 (1) $[C_{10}H_9O]^+$, 106 (3) $[C_7H_6O]^+$, 92 (15) $[C_6H_4O]^+$, 59 (100) $[C_2H_3O_2]^+$.

2-Methoxy-4-(oxiran-2-ylmethyl)phenol (IIb). Yield 0.86 g (96%), colorless oil, $C_{10}H_{12}O_3$ (*M* 180.238). IR spectrum, ν, cm^{-1}: 3515, 3073, 2933, 2836, 1639, 1613, 1505, 1354, 1111. ^1H NMR spectrum, δ, ppm: 2.54 d.d (1H, 3′-H, *J* = 5, 3 Hz), 2.78 m (1H, 3′-H), 2.80 d (2H, 1′-H, *J* = 5 Hz), 3.13 m (1H, 2′-H), 3.87 s (3H, OCH_3), 5.60 br.s (1H, OH), 6.73 d (1H, 6-H, *J* = 8 Hz), 6.76 s (1H, 3-H), 6.85 d (1H, 5-H, *J* = 8 Hz). GC–MS data: retention time 14.500 min; *m*/*z* (I_{rel}, %): 180 (65) $[M]^+$, 165 (5) $[M - CH_3]^+$, 151 (15) $[M - CHO]^+$, 137 (100) $[M - C_2H_3O]^+$, 122 (15) $[M - C_3H_6O]^+$, 91 (15) $[C_6H_3O]^+$, 65 (10) $[C_5H_5]^+$.

Photosensitized oxygenation of *trans*-anethole (I) and eugenol (II). A solution of 10 mmol of compound **I** or **II** in appropriate solvent according to the type of sensitizer used was irradiated with a sodium lamp at –5°C, a stream of oxygen being continuously passed through the solution at a low rate to avoid evaporation of the solvent. When the reaction was complete, the solvent was evaporated under reduced pressure (15 mm) at 20°C, and the residue was subjected to column chromatography on silica gel using petroleum ether (bp 60–80°C)–diethyl ether (9:2). The reaction conditions and the yields of products **Ia** and **Id** (from **I**) and **IIc** (from **II**) are given in table.

1-(4-Methoxyphenyl)prop-2-en-1-yl hydroperoxide (Id). Colorless oil, $C_{10}H_{12}O_3$ (*M* 180.206). IR spectrum, ν, cm^{-1}: 3429 br, 2830, 1629, 1505, 1381, 1241, 1106. ^1H NMR spectrum, δ, ppm: 3.80 s (3H, OCH_3), 3.90 d (1H, 1′-H, *J* =20 Hz), 5.35 d.d (2H, 3′-H, *J* = 20, 8 Hz), 6.05 m (1H, 2′-H), 6.90 d (2H, 3-H, 5-H, *J* =8 Hz), 7.28 d (2H, 2-H, 6-H, *J* = 8 Hz), 8.60 br.s (1H, OOH). ^{13}C NMR spectrum, δ_C, ppm: 55.3 (OCH_3), 74.7 ($C^{1'}$), 113.9 (C^3, C^5), 114.6 ($C^{3'}$), 127.7 (C^2, C^6), 131.9 (C^1), 140.6 ($C^{2'}$), 159.1 (C^4). GC–MS data: retention time 20.605 min; *m*/*z* (I_{rel}, %): 180 (50) $[M]^+$, 165 (60) $[M - CH_3]^+$, 163 (8) $[M - OH]^+$, 147 (1) $[M - HO_2]^+$, 137 (100) $[M - C_3H_7]^+$, 122 (20) $[M - C_3H_6O]^+$, 92 (2) $[C_6H_4O]^+$, 65 (15) $[C_5H_5]^+$.

4-Hydroperoxy-2-methoxy-4-(prop-2-en-1-yl)-cyclohexa-2,5-dien-1-one (IIc). Colorless oil, $C_{10}H_{12}O_4$ (*M* 196.238). IR spectrum, ν, cm^{-1}: 3391, 2992, 1690, 1510, 1219, 1052. ^1H NMR spectrum, δ, ppm: 2.53 m (2H, 1′-H), 3.69 s (3H, OCH_3), 5.13 d.d (2H, 3′-H, *J* = 10 Hz), 5.67 m (1H, 2′-H), 5.71 d (1H, 3-H, *J* = 4 Hz), 6.32 d (1H, 6-H, *J* = 8 Hz), 6.90 d.d (1H, 5-H, *J* = 8, 4 Hz), 8.73 s (1H, OOH). GC–MS data: retention time 20.913 min; *m*/*z* (I_{rel}, %): 196 (1) $[M]^+$, 178 (5) $[M - H_2O]^+$, 164 (70) $[M - O_2]^+$, 149 (40) $[M - CH_3O_2]^+$, 133 (20) $[M - CH_3O_3]^+$, 123 (55) $[C_7H_7O_2]^+$, 107 (70) $[C_7H_7O]^+$, 91 (50) $[C_6H_3O]^+$, 79 (100) $[C_5H_3O]^+$, 65 (15) $[C_5H_5]^+$.

Study on photochemical DNA damage by hydroperoxides Id and IIc. A solution of DNA in saline, 1 ml, was added to a solution of 1 mg of compound **Id** or **IIc** in 5 ml of ethanol, and the mixture was irradiated using a sodium lamp for 16 h at 0°C. Samples were withdrawn at different times to determine the damaging effect by the gel electrophoresis technique [13]. The photographs of the gel were taken under UV light (λ 365 nm). The results showed moderate degree of DNA damage in the presence of hydroperoxides **Id** and **IIc** after irradiation for 8 and 12 h, respectively, and high degree of DNA damage after irradiation for 12 and 16 h, respectively.

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