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

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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-chloroperoxycbenzoic 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-chloroperoxycbenzoic 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.

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 phenylpropenoids 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-chloroperoxycbenzoic 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-dimethyltetrahydrofuran and that intermediate epoxide Ib could not be isolated.

Taking into account important activities of plant phenylpropenoids 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 1H NMR spectrum of I showed a doublet at δ 1.86 from protons in the methyl group, and side-chain olefinic protons on C2 and C3 resonated, respectively, as a doublet of quartets at δ 6.08 ppm and a doublet at δ 6.34 ppm. In the 13C NMR spectrum of I, the C2 and C3 signals were located at δC 123.5 and 130.5 ppm, respectively.

Photochemical epoxidation of trans-anethole (I) with hydrogen peroxide (H2O2, 30% by volume) in ethanolic medium under irradiation with sodium light (irradiation time 55 h) to give 65% of 4-methoxybenz-
aldehyde (Ia) and 35% of monoepoxy derivative, 2-(4-methoxyphenyl)-3-methyl oxirane (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 ¹³C NMR spectrum at δc 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 CH₃ 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 ¹³C NMR spectrum of Ib, signals from the oxirane carbon atoms were present at δc 64.1 (C²) and 71.4 ppm (C¹). The mass spectrum of Ib contained the molecular ion peak at m/z 164.

Thermal oxidation of trans-anethole (I) with m-chloroperoxybenzoic 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 δc 70.1 and 81.5 ppm in the ¹³C NMR spectrum of Ic were assigned to C³/C⁶ and C²/C⁵ 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