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Photo-Oxygenation of Trans Anethole

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Abstract: Photo-oxygenation of *trans* anethole **(1)**, the main constituent of anise essential oil, using tetraphenylporphyrine (TPP) as a singlet oxygen sensitizer in chloroform gave 4-methoxybenzaldehyde (*p*-anisaldhyde) **(2)**, 2-(4-methoxyphenyl)propan-2-ol **(3)** as well as *erythro* and *threo* 1-(4-methoxyphenyl)propane-1,2-diol **(4a, 4b)**. The structures of the photo-oxygenation products were elucidated by spectral means.

Keywords: Photo-oxygenation, anethole, tetraphenylporphyrine, 4-methoxybenzaldehyde, 2-(4-methoxyphenyl)propan-2-ol**,** 1-(4-methoxyphenyl)propan-1,2-diol.

1. INTRODUCTION

Essential oils play an important role in our life because of their therapeutic activities and various applications in food industries. Essential oils are mixtures of various components like shikimates, mono-and sesquiterpenoids. The unsaturated essential oil compounds are easily oxidized, upon exposure to light, air and enhanced by temperature [1].
Photo-oxygenation reactions were carried out by several workers on some authentic individual monoterpenes, which occur frequently as major constituents of essential oils. We found that photo-oxygenation of essential oils has improved their biological activities [2].
The biological activities of *trans* anethole, as the main constituent of aniseed oil, before and after photo-oxygenation, including free radical scavenging, antimicrobial, deoxy ribonucleic acid (DNA) and protein cleaving, in addition to their hypoglycaemic effect were studied by Dawidar et al.,2008 [2].

Anise oil is obtained from the seeds of *Pimpinella anisum* L. (Umbeliferae). Its major constituent is *trans*-anethole (more than 60%) [1].
Schantz and Juvonen, 1969, reported that *trans*-anethole is autoxidized to its β- glycol, the amount of which increased initially during storage but decreased thereafter on further autoxidation *via* anisaldhyde to polymer. Thus the quality of aniseed oil depends on the presence or absence of the degradative oxidation products [3].
Garnero and Roustan, 1979, reported that *trans*-anethole undergoes a serious photo-rections as photoisomerization, photooxidation and photodimerization. Products as anisaldhyde, anise ketone, and anisic acid, are oxygenation products of *trans* anethole [4]. Lewis and Kojima, 1988, studied the mechanism of the photoisomerization, dimerization and oxygenation of *trans*- and *cis* anethole in terms of the role of monomer and dimer cation radicals [5]. Greer et al., 2000, reported on the effects of the added acid to the reaction of singlet oxygen with *trans* anethole. They suggested a new mechanism that invokes a proton transfer from methanol and benzoic acid to the formed perepoxide and Zwitter intermediates [6].
Mang *et al*., 2007, optimized a biocatalytic single-step alkene cleavage for aryl alkene compounds. They employed *trans* anethole as a model substrate, using hydrogen peroxide as an oxidizing agent. The products were identified as anisaldhyde and acetaldehyde [7]. Elgendy and Khayyat, 2008, performed photochemical oxidation of *trans* anethole using hydrogen peroxide where the corresponding epoxy derivatives together with 4-methoxybenzaldhyde were identified. They found that thermal oxidation of *trans* anethole with 3-chloroperoxybezoic acid at room temperature resulted in formation of dimeric epoxide, 2,5-bis(4-methoxyphenyl)-3,6-dimethyl-1,4-dioxin as the only product. Photo-oxygenation of *trans* anethole in the presence of tetraphenylporphyrine, Rose Bengal, or chlorophyll as sensitizers has led to a mixture of 1-(4-methoxyphenyl)prop-2-en-1-yl hydroperoxide and 4-methoxybenzaldhyde [8].

We reported here the identified photo-oxygenation products of *trans*-anethole using molecular oxygen.

2. EXPERIMENTAL

2.1 Materials:

TPP was obtained from Fluka Company. *trans* anethole was supplied by Sigma Company. Photo-oxygenation apparatus consists of sodium lamp (Phillips G/5812 SON), cylindrical jar (15w x 20l x 30h cm) filled with ethanol, sample tube which was inserted in the jar, and cooling unit with alcoholic thermometer. Dry oxygen was supplied from external cylinder. Distance between sodium lamp and sample tube was 10 cm.

2.2 General procedure for photo-oxygenation:

A solution of *trans* anethole (1 ml) in chloroform (50 ml) and a few mgs of tetraphenylporphyrine (TPP) was irradiated for 24 hrs. using the described apparatus. The solvent was evaporated at 20˚C/0.1 torr to give an oily material. The crude photooxygenation products were separated on silica gel column using petroleum ether (60-80˚C) as eluent to remove the sensitizer. The excess of *trans* anethole was eluted by petroleum ether: ethyl acetate (9:1). The photo products were eluted by petroleum ether: ethyl acetate (3:2), and separated by preparative TLC**.**

4-methoxybenzaldehyde (*p*-anisaldhyde) (2)

Colour: Pale yellow oil, UV, λ_{max} (ethanolic solution), nm: 276, 287; IR, ν, (oil film), cm^{-1}: 3020 (C–H, aromatic, str.), 2949, 2866 (CH_3 aliphatic and C-H aldehydic), 1690 (carbonyl group), 1590 (C=C aromatic), 1530 (C=C aliphatic); EIMS, m/z (rel. int.): 136 [M^+] (45) corresponding to $C_8H_8O_2$, 135 [M^+-H] (100), 107 [M^+-CHO] (30), 92 [M^+-CH_3 & CHO] (30), 77[M^+ - OCH_3 & CHO] (70); ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 3.89 (3H, s, OCH_3, H-7), 7.01 (2H, d, J = 8.7 Hz, H-2 and H-6), 7.84 (2H, d, J = 8.7 Hz, H-3 and H-5), 9.89 (1H, s, CHO, H-8).

2-(4-methoxyphenyl)propan-2-ol (3)

Colour: Light yellow oil, UV, λ_{max} (ethanolic solution), nm: 249, 315; IR, ν, (oil film), cm^{-1}: 3443 (broad band, OH group), 3052 (C–H, aromatic, str.), 2969, 2934 (CH_3 aliphatic), 1380, 1020, and 938; ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 1.25 (6H, s, $2CH_3$), 3.88 (3H, s, OCH_3), 6.70 (1H, s, OH), 6.95 (2H, d, J= 8 Hz, H-3, H-5), 8.04 (2H, d, J =8 Hz, H-2, H-6); EIMS, m/z (rel. int.): 166 [M^+] (0.5), 165 [M^+-1] (14), 149 [M^+-OH] (89), 148 [M^+-H_2O] (13), 135 [M^+-OCH_3] (49), 107 [M^+-C_3H_7O] (10), 76 [M^+-OCH_3 & C_3H_7O] (22), 71 (59), 70 (30), 69 (50), 57 (100).

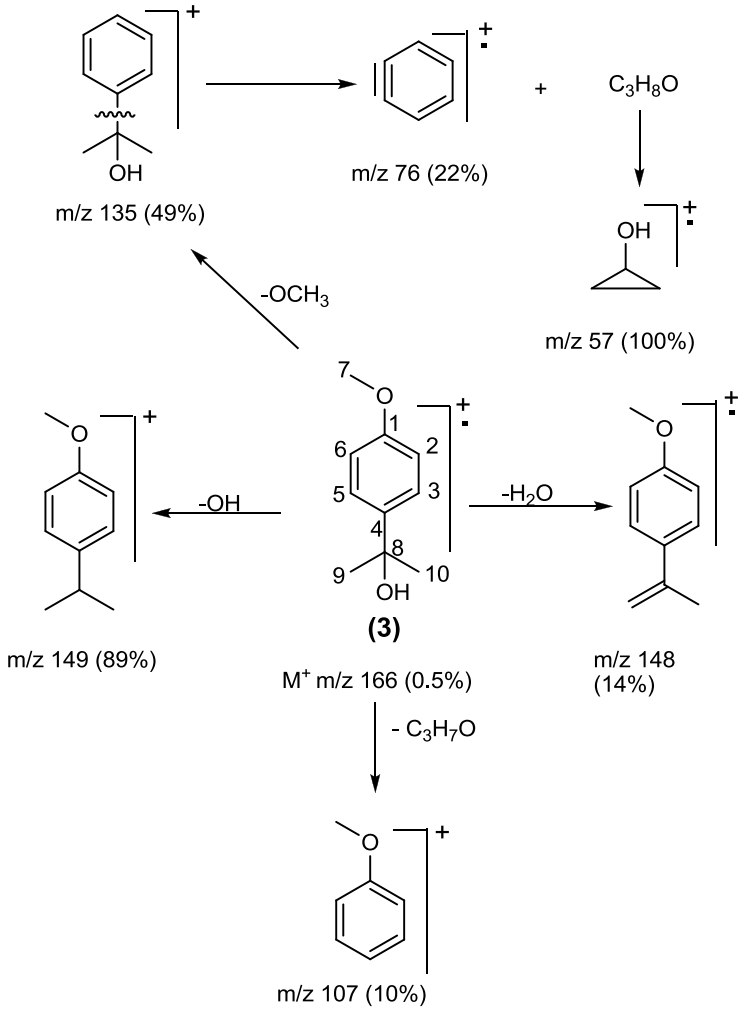
1-(4-methoxyphenyl)propane-1,2-diol (4a, 4b) (2:1 molar ratio)

Colour: Light yellow oil, UV, λ_{max} (ethanolic solution), nm: 269, 282; IR, ν, (oil film),cm^{-1}: 3450-3500 (broad band, OH group), 3062, 3027(C–H, aromatic, str.), 2954, 2925, 2856 (CH_3 aliphatic), 1600 ((C=C aromatic),1450, 1070, and 1027; ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm (4a): 1.05 (3H, d, J= 6.6 Hz, H-10a), 1.750 (1H, br.s, OH), 2.62 (1H, br.s, OH), 3.82 (3H, s, OCH_3), 3.84 (1H, m, H-9a), 4.33 (1H, d, J = 7.8 Hz, at C-8a), 6.89 (2H, d, J= 8.7 Hz, H-2a, H-6a), 7.29 (2H, d, J= 7.8 Hz, H-3a, H-5a); ^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm (4b) : 1.11 (3H, d, J= 6.6 Hz, H-10b), 1.75 (1H, br.s, OH), 2.62 (1H, br.s, OH), 3.82 (3H, s, OCH_3), 4.00 (1H, m, H-9b), 4.60 (1H, d, J = 7.8 Hz, H-8b), 6.89 (2H, d, J = 8.7 Hz, H-2b, H-6b), 7.29 (2H, d, J = 7.8 Hz, H-3b, H-5b); EIMS m/z (rel.int.): 182 [M^+] (3), 167 [M^+-CH_3] (6), 151[M^+-OCH_3] (4), 148 [M^+-2OH] (28) 164 [M^+-H_2O] (5), 137 [M^+-H_2O & C_2H_4] (82), 136 (10), 135 (22), 133 (5), 109 (28), 107 [M^+-$C_3H_7O_2$] (10), 97 (36), 85 (51), 84 (25), 83 (68), 81 (28), 71 (57), 69 (65), 57 (100), 54 (78).

3. RESULTS AND DISCUSSIONS

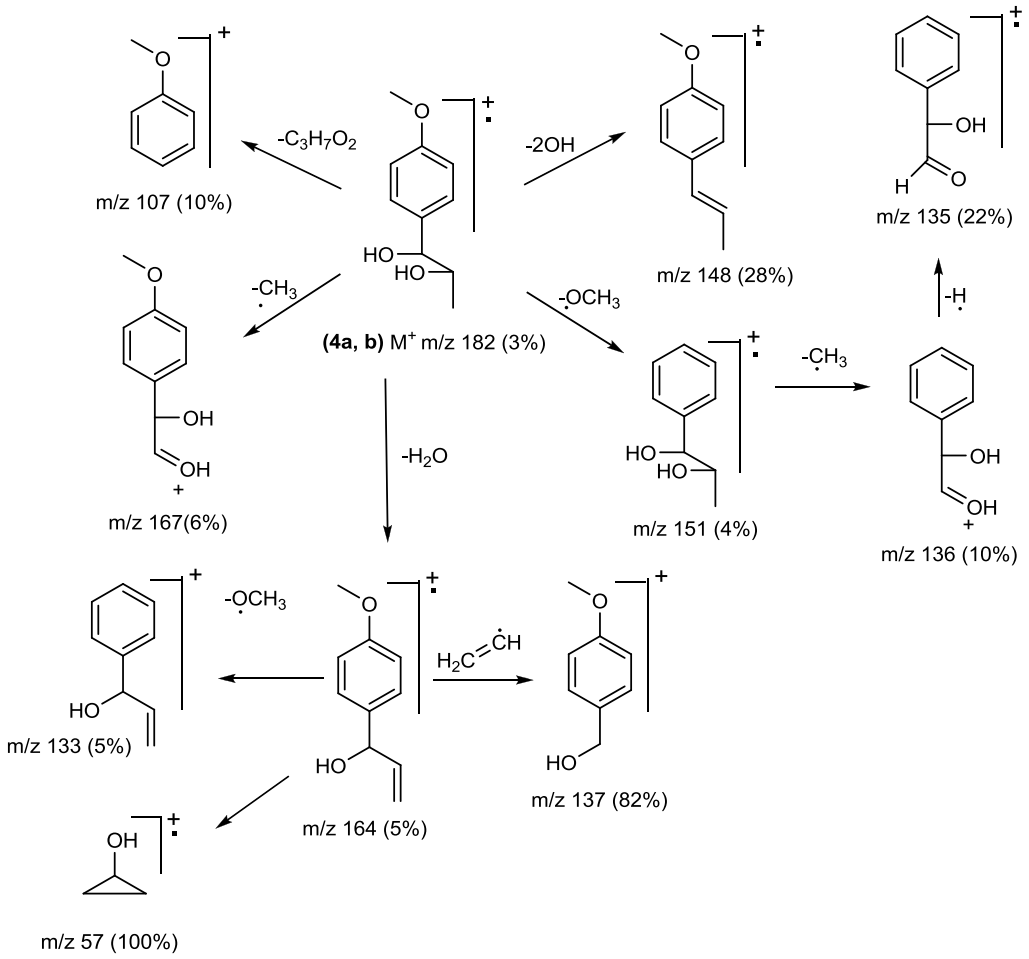
The reaction was carried out in $CHCl_3$, in the presence of tetraphenylporphyrine (TPP) as a singlet oxygen sensitizer at -20˚C for 24 hrs. The resulting mixture was separated to three products identified as 4-methoxybenzaldehyde (*p*-anisaldhyde) **(2)**, 2-(4-methoxyphenyl)propan-2-ol **(3)** and *erythro* and *threo* 1-(4-methoxyphenyl)propane-1,2-diol **(4a, 4b)**.

The IR spectrum of **(2)** showed the carbonyl absorption band at 1690 cm^{-1}. Its ^{1}H-NMR spectrum revealed the presence of a singlet at δ 9.89 ppm, characteristic for the aldehydic proton and signals of *p*–disubstitued benzene (AA'BB' spin system at δ 7.84 ppm with coupling constant 8.7 Hz). Additionally, the spectrum showed the methoxyl protons at δ 3.89 ppm as a singlet. The mass spectrum of (**2**) indicated a M^+ at m/z 136 (45%) corresponding to the molecular formula $C_8H_8O_2$, and a base peak at m/z 135 (100%) due to [M^+-H].
The ^{1}H-NMR spectrum of **(3)** showed a *p*–disubstitued benzene (AA'BB' spin system at δ 8.04 and 6.95 ppm with coupling constant 8 Hz), two methoxyl and hydroxyl protons singlets at δ 3.88 and 6.70 ppm, respectively. This is in addition to a singlet of six protons at δ 1.25 ppm which was assigned to a dimethyl carbinol group. The mass spectrum of (**3**) showed ion peaks due to [M-OH], [M-H_2O], [M-OCH_3], [M-C_3H_7O] at m/z 149, 148, 135, and 107 respectively.



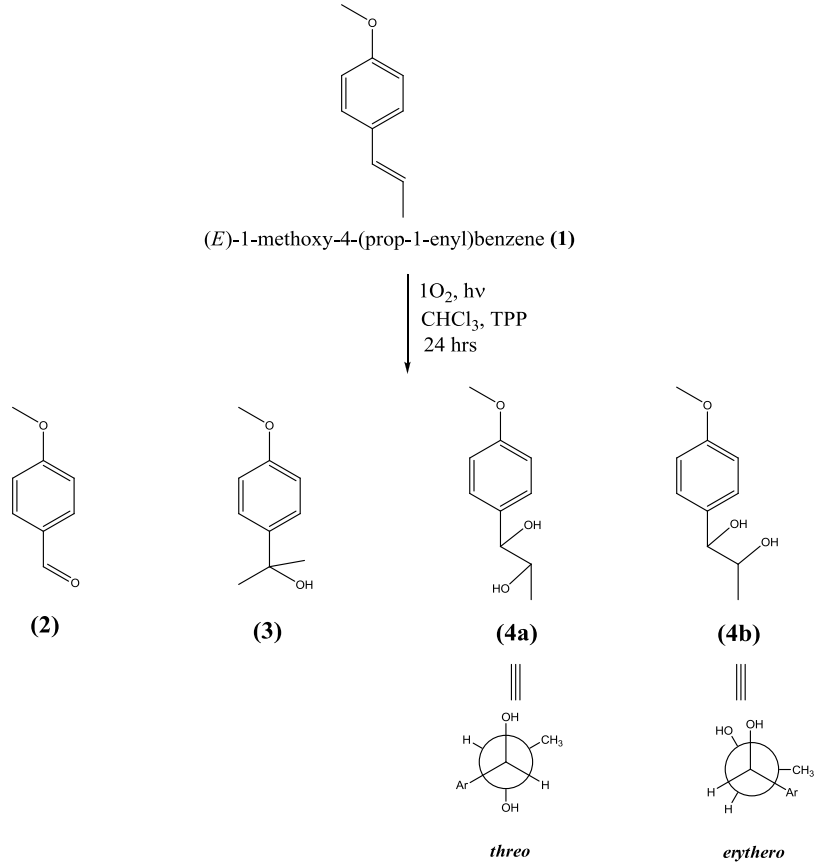
A proposed fragmentation pattern of 3

Products **(4a, b)** as a mixture were identified as *erythro* and *threo* 1-(4-methoxyphenyl)propan-1,2-diol. The IR spectrum revealed the presence of hydroxyl groups, due to the absorption broad band at 3450 -3500 cm^{-1}. ^{1}H-NMR spectrum showed *p*–disubstitued benzene (AA'BB' spin system at δ 7.29 and δ 6.89 ppm with coupling constant 8.7). The spectrum also showed a singlet at δ 3.82 ppm for the methoxyl groups. Protons of methyl groups in positions C-10a and C-10b gave the characteristic doublets at δ 1.05 and 1.11 ppm with coupling constant 6.6 Hz, whereas protons at 8a and 8b showed two doublets at δ 4.33 and 4.60 ppm with coupling constant 7.8 Hz for both. Protons at C-9a and C-9b appeared as multiplets at δ 3.84 and 4.00 ppm, respectively. Protons of hydroxyl groups were viewed at δ 1.75 and 2.62 ppm. The mass spectrum showed a molecular ion peak M^+ at m/z 182 (3%) corresponding to the molecular formula $C_{10}H_{14}O_3$.



A proposed fragmentation pattern of 4a and 4b

A probable formation of *p*-anisaldhyde (**2**) and the glycols 4a, 4b may be through the dioxetane intermediate. Whereas, the photo product **(3)** may be obtained through 1, 2 carbon shift followed by singlet oxygen attack in the protic solvents.



Scheme 1: Photo-oxygenation of *trans* anethole (1)

4. REFERENCES

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