

and Sugowdz (1979) as important volatile constituents of purple passion fruit juice, cannot be found in this study. According to the above two reports, the isomer may be hidden in the larger peak of hexyl hexanoate of purple passion fruit in this study or the amount of the isomer may be too small.

Ethanol, which is a major component (ca. 100 ppm) identified in the previous report (Murray et al., 1972), is found only as a trace compound in this study, probably due to the poor retention ability of ethanol on Tenax-GC. However, another study of purple passion fruit flavor by this group indicated that ethanol was the major component identified from the headspace (>50%) when the adsorbent used was charcoal instead of Tenax-GC (Kuo, 1982).

From Table I it can be clearly seen that the hybrid passion fruit has the strongest flavor intensity among the three passion fruits. The sensory evaluation data also indicates that the hybrid passion fruit is retaining not only the highest flavor intensity but also the characteristic aroma of both yellow and purple passion fruit (Kuo, 1982). This is the main reason to choose the hybrid passion fruit as the raw material for the processing of passion fruit juice.

The study of the flavor components from the skin of passion fruit indicated that compounds with "green-note" character such as hexanol, hexanal, and other similar aliphatic alcohols are richer in the skin than in the juice (Kuo, 1982). At present, the cold-press-type method is used for the production of passion fruit juice in industry; thus the flavor of the skin may contaminate the juice during processing. Since the skin of purple passion fruit has the strongest green note while the hybrid passion fruit has the lowest (Kuo, 1982), the hybrid passion fruit seems to have another reason to be chosen as the raw material for the processing of passion fruit juice.

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Received for review March 16, 1982. Accepted June 24, 1982.

Photochemical Reactions of Eugenol and Related Compounds: Synthesis of New Flavor Chemicals

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Eugenol was irradiated in a methanol solution for various periods. The main photochemical product was 4-cyclopropyl-2-methoxyphenol (12–28%). In addition to the cyclopropyl derivative, three methanol solvent addition products, 2-methoxy-4-*n*-propylphenol (4–7%), 2-methoxy-4-(2-methoxypropyl)phenol (3–7%), and 2-methoxy-4-(1-methoxypropyl)phenol, were formed. The solvent addition products were not obtained when acetonitrile was used as a solvent. The eugenol-related compounds, safrol, methyleugenol, ethyleugenol, and estragole, also produced cyclopropyl derivatives (1-cyclopropyl-3,4-(methylenedioxy)benzene, 1-cyclopropyl-3,4-dimethoxyeugenol, 1-cyclopropyl-4-ethoxy-3-methoxybenzene, and 1-cyclopropyl-4-methoxybenzene, respectively) upon photochemical irradiation. The photochemical reaction mechanisms of eugenol are postulated to be di- π -methane rearrangement, disproportionation reaction, and addition reaction. The cyclopropyl derivatives possess an interesting floral, spicy odor.

It is well-known that sunlight degrades the main constituents of essential oils. Examples are the photochemical

degradation of *n*-decanal and (+)-limonene of sweet orange, (+)-limonene, dipentene, γ -terpinene, and citral of lemon oil, and *trans*-anethole of anis oil (Garnero and Roustan, 1979).

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Eugenol, a pale yellow or almost colorless liquid, is the main constituent of clove oil. Its powerful, warm-spicy odor has been used extensively in the perfumery industry. Eugenol and its structurally related compounds have been

Table I. Products and Their Yields Obtained from the Photochemical Reaction of Eugenol

amount of eugenol	solvent	irradiation time, h	yield of products, % ^a				amount of unreacted eugenol recovered
			2 ^b	3 ^c	4 ^d	5 ^e	
10.0 g	CH ₃ OH	192	12	4	3	1	5.8 g
2.0 g	CH ₃ OH	36	24	4	4	2	0.75 g
1.5 g	CH ₃ OH	43	28	7	7	2	0.09 g
3.0 g	CH ₃ CN	72	20	trace	none	none	2.1 g
15.0 mg	CH ₃ OD	22	50	3	7	2	0.15 mg

^a Amount of the compound recovered/(amount of eugenol used - amount of unreacted eugenol recovered) × 100. ^b 4-Cyclopropyl-2-methoxyphenol. ^c 2-Methoxy-4-*n*-propylphenol. ^d 2-Methoxy-4-(2-methoxypropyl)phenol. ^e 2-Methoxy-4-(1-methoxypropyl)phenol.

known to be photosensitive. Gaibel and Fisbein (1970), for example, reported that safrole, which is a major constituent of the oil of sassafras and is used to large quantities of flavoring agent in confectionaries, soft drinks, and ice cream, produces 4-cyclopropyl-1,2-(methylenedioxy)-benzene upon photochemical irradiation in methanol. The present study investigates the products obtained from eugenol and related compounds upon photochemical irradiation.

EXPERIMENTAL SECTION

Materials. Commercially obtained chemicals were distilled before use in a spinning band distillation apparatus (Perkin-Elmer Model 251 Auto Annular Still) to the following purities: eugenol (99.9%), safrole (99.8%), methyleugenol (99.8%), and estragole (99.8%). Ethyleugenol was obtained at 99.9% purity and used without further treatment.

Photochemical Reaction of Samples. The solutions (300 mL) containing eugenol (1) were irradiated for various periods (Table I) under a nitrogen stream by using a 10-W low-pressure mercury lamp (2537 Å) in a quartz container at 20 °C. The reaction conditions are shown in Table I, along with the yields of the reaction products.

Photochemical reaction of eugenol (1) in methanol-*O-d* was performed in the same manner as eugenol in methanol, and the experimental conditions and results are shown in Table I.

Safrole (11), methyleugenol (13), ethyleugenol (15), and estragole (17) were treated in the same manner as eugenol, except acetonitrile was used as a solvent for these compounds. The reaction mixtures obtained were stored for analysis. The reaction conditions and the product yields are shown in Table II.

Isolation and Identification of Photochemical Reaction Products. Eugenol in Methanol. The reaction mixtures obtained from the methanol solutions of eugenol were distilled under reduced pressure (70–80 °C/0.8 mmHg). The distillate (7.8 g) was found by GC/MS analysis to consist of unreacted eugenol (1, 72%) and 2-methoxy-4-*n*-propylphenol (3, 4%). The components in the residue were isolated by using thin layer chromatography (Merck silica gel; solvent, benzene), and identified by MS, IR, ¹H NMR, and ¹³C NMR. The compounds identified are 4-cyclopropyl-2-methoxyphenol (2, 12%), 2-methoxy-4-(2-methoxypropyl)phenol (4, 3%), and 2-methoxy-4-(1-methoxypropyl)phenol (5, 1%).

Eugenol in Methanol-*O-d*. The reaction mixture was subjected to gas chromatographic analysis without distillation. The gas chromatographic peak area percent of products corresponding to compounds 1–5 is shown in Table I. The deuterium compositions of each product analyzed by GC/MS are shown in Table III.

Safrole, Methyleugenol, Ethyleugenol, and Estragole in Acetonitrile. The acetonitrile was removed from the reaction mixtures that each contained only two components: the unreacted original compound and one product. The products obtained from each compound are shown in Table II, along with the reaction conditions and odor descriptions. The unreacted material was precipitated with Kharash reagent [(2,4-dinitrophenyl)sulfonyl chloride] from each reaction mixture; the precipitates were removed by using column chromatography (silica gel, 30 cm × 1.8 cm i.d.), with 50 mL of benzene as a developing agent. After the solvent was evaporated, each product was purified by fractional distillation. The products were identified by comparing their MS, IR, ¹H NMR, and ¹³C NMR spectra to those of authentic compounds.

Instruments. Infrared spectra (IR) were measured on liquid films on NaCl plates with a Hitachi Model EPI-G3 grating infrared spectrometer. Proton magnetic resonance spectra (¹H NMR) were recorded on a Hitachi Model R-20A magnetic resonance spectrometer (60 MHz) in deuteriochloroform with tetramethylsilane as an internal standard. Carbon-13 magnetic resonance (¹³C NMR) spectra were determined at 100 MHz with a JEOL 100 NMR spectrometer and tetramethylsilane as an internal standard. A Hewlett-Packard Model 5710-A gas chromatograph equipped with a flame ionization detector and a fused silica capillary column (50 m × 0.23 mm i.d.) coated with Carbowax 20M was used for routine analysis. A Hitachi Model M-80 combination mass spectrometer/gas chromatograph (Hewlett-Packard Model 5710A) equipped with Hitachi Model M-6010 and M-003 data system was used for GC/MS analysis.

Table II. Products Obtained from the Eugenol-Related Compounds by Irradiation with a Mercury Lamp

eugenol-related compd ^a	amount of reactant, g	irradiation time, day	products ^a	yield of product, % ^b	odor descriptions of product	amount of unreacted reactant recovered
safrole (11)	2	4	1-cyclopropyl-3,4-(methylenedioxy)benzene (12)	31	floral, safrole-like	0.82 g
methyleugenol (13)	2	3	1-cyclopropyl-3,4-dimethoxyeugenol (14)	38	spicy, floral, smoky	0.46 g
ethyleugenol (15)	1.2	2	1-cyclopropyl-4-ethoxy-3-methoxybenzene (16)	33	spicy, floral, smoky	0.26 g
estragole (17)	2	5	1-cyclopropyl-4-methoxybenzene (18)	23	oily, fatty, floral	0.82 mg

^a See Figure 4 for the structures. ^b Amount of the compound recovered/(amount of reactant used - amount of unreacted reactant recovered) × 100.

Table III. Results of Deuterium Analysis on the Products Obtained from Irradiated Eugenol in Methanol-*O-d* (Percent)

no. of deuterium incorporated	compd 1	compd 2	compd 3	compd 4	compd 5
d_0	87	83	3	1	1
d_1	12	16	81	88	84
d_2	1	1	16	11	15

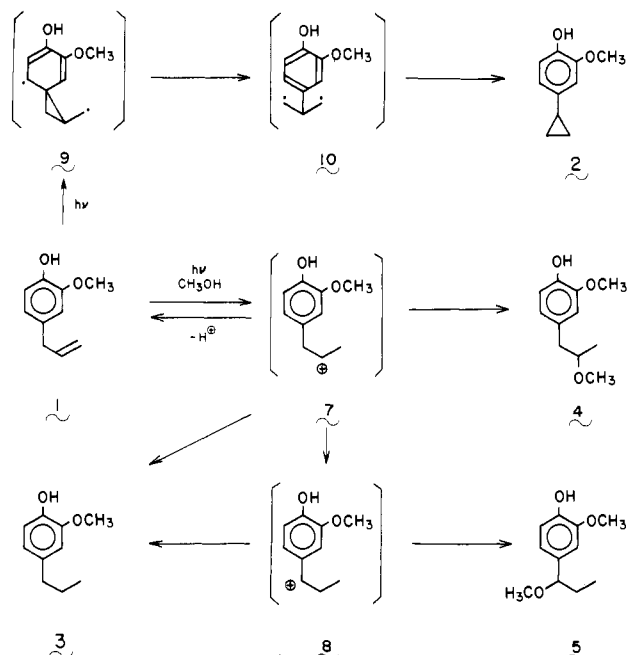


Figure 1. Postulated formation mechanisms of the products obtained from irradiated eugenol.

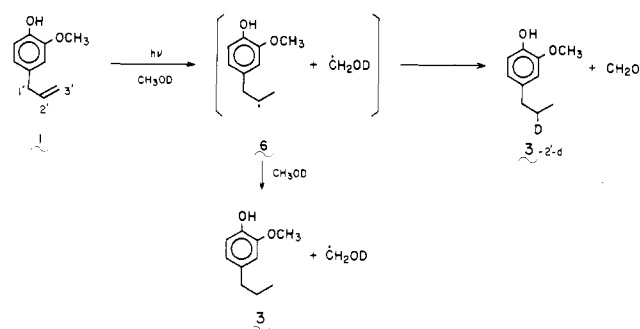


Figure 2. Postulated radical process of compound 3 formation.

The spectral data of the newly identified compounds (2-4, 14, 16, and 18) are shown in Table IV. Compounds 5, and 12 are previously reported in Leary (1977) and Gaibel and Fishbein (1970), respectively.

RESULTS AND DISCUSSION

Eugenol in Methanol Solution. The products obtained from the photochemical reaction of eugenol (1) and their postulated reaction mechanisms are shown in Figure 1. This system produced four products. The formation of a cyclopropane derivative, 2, which gives an interesting floral eugenol-like odor, has been characterized as an aromatic di- π -methane rearrangement (Koch-Pomeranz and Schmid, 1977; Hixson et al., 1973). This reaction occurs with 1,2-aryl migration. The other two minor

Table IV. Spectral Data of Newly Identified Compounds

compd	IR (neat), cm^{-1}	MS, m/z (%)	$^1\text{H NMR}$ (CDCl_3), δ	$^{13}\text{C NMR}$ (CDCl_3), δ
2	3535, 3465, 1520, 1476, 1273, 1240, 1210, 1205, 1033	164 (M^+ , 100), 149 (39), 137 (14), 133 (34), 131 (26), 121 (23), 104 (21), 103 (35), 91 (27), 78 (12), 77 (43), 65 (19), 55 (30), 51 (20), 39 (39)	0.5-1.0 (4 H, m, CH_2CH_2), 1.5-2.0 (1 H, m, CH), 3.88 (3 H, s, OCH_3), 5.43 (1 H, s, OH), 6.5-7.3 (3 H, m, aromatic H's)	8.5 (CH_2CH_2), 15.2 (PhCH), 55.9 (OCH_3), 109.1 (C_1), 114.3 (C_2), 118.4 (C_3), 135.7 (C_4), 143.5 (C_1), 146.4 (C_2)
3	3535, 3475, 2975, 2945, 1522, 1472, 1278, 1242, 1156, 1128, 1083, 800	166 (M^+ , 21), 138 (9), 137 (100), 122 (9), 94 (9), 77 (5), 65 (3), 51 (4), 39 (6)	0.92 (3 H, t, CCH_3 , $J = 7.0$ Hz), 1.2-1.9 (2 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.53 (2 H, t, PhCH $_2$, $J = 7.4$ Hz), 3.84 (3 H, s, OCH_3), 6.6-7.0 (3 H, m, aromatic H's)	13.8 (C_1), 24.9 (C_2), 37.8 (C_1), 55.8 (OCH_3), 111.0 (C_3), 114.1 (C_2), 120.9 (C_3), 134.6 (C_4), 143.5 (C_1), 146.2 (C_2)
4	3415, 2945, 1526, 1282, 1246, 1160, 1130, 803	196 (M^+ , 9), 138 (6), 137 (15), 122 (1), 59 (100), 39 (3)	1.12 (3 H, d, $J = 6.0$, CCH_3), 3.33 (3 H, s, COCH_3), 3.86 (3 H, s, Ph OCH_3), 2.7 (2 H, m, PhCH $_2$), 3.2-3.8 (1 H, m, CHOCH_3), 5.7 (1 H, br s, OH), 6.7-6.9 (3 H, m, aromatic H's)	18.9 (C_1), 42.4 (C_1), 55.8 (Ph OCH_3), 78.4 (C_2), 112.1 (C_3), 114.2 (C_2), 122.0 (C_2), 131.8 (C_4), 143.9 (C_1), 146.3 (C_2)
14	3020, 2955, 1527, 1268, 1246, 1146, 1034	178 (M^+ , 100), 163 (39), 147 (56), 135 (14), 115 (11), 107 (38), 105 (11), 103 (31), 91 (44), 79 (16), 77 (20), 65 (15)	0.5-1.0 (4 H, m, CH_2), 1.6-2.0 (1 H, m, CH), 3.83 (3 H, s, OCH_3), 3.86 (3 H, s, OCH_3), 6.5-6.9 (3 H, m, aromatic H's)	8.5 (CH_2CH_2), 15.1 (PhCH), 55.8 and 56.0 (OCH_3), 109.7 (C_3), 111.4 (C_2), 117.6 (C_1), 136.4 (C_4), 147.0 (C_1), 148.9 (C_2)
16	3005, 2945, 1525, 1278, 1244, 1147, 1044	192 (M^+ , 100), 164 (70), 163 (33), 161 (29), 149 (31), 147 (13), 135 (8), 133 (22), 131 (11), 121 (10), 107 (15), 103 (11)	0.5-1.0 (4 H, m, CH_2), 1.42 (3 H, t, $J = 6.9$ Hz, CCH_3), 1.5-2.1 (1 H, m, CH), 3.85 (3 H, s, OCH_3), 4.05 (2 H, q, OCH_2C), 6.5-6.9 (3 H, m, aromatic H's)	8.5 (CH_2CH_2), 14.9 (CCH_3), 15.1 (PhCH), 55.8 (OCH_3), 64.5 (OCH_2), 110.0 (C_2), 113.1 (C_1), 117.5 (C_3), 136.4 (C_4), 146.2 (C_1), 149.2 (C_2)
18	3020, 2975, 1523, 1259, 1183, 1038, 833	148 (M^+ , 100), 147 (51), 133 (30), 121 (33), 117 (44), 115 (19), 105 (33), 91 (31), 79 (27), 78 (22), 77 (46), 65 (15), 63 (20), 55 (13), 51 (32), 50 (14), 39 (49)	0.5-1.1 (4 H, m, CH_2), 1.6-2.1 (1 H, m, CH), 3.77 (3 H, s, OCH_3), 6.6-7.1 (4 H, m, aromatic H's)	8.5 (CH_2CH_2), 14.6 (PhCH), 55.3 (OCH_3), 114.2 (C_2 and C_5), 135.8 (C_6), 157.5 (C_1)

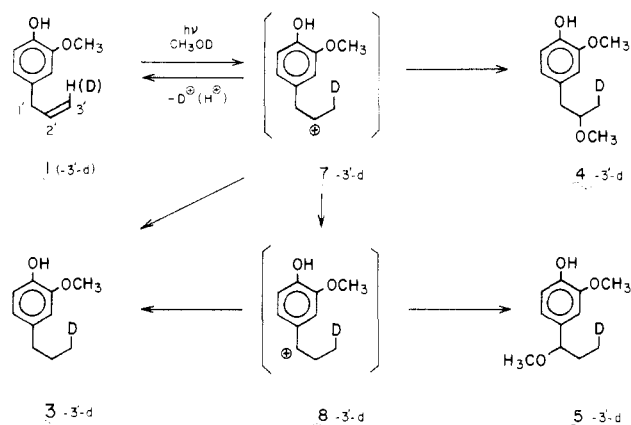


Figure 3. Postulated ionic process of compound 3 formation.

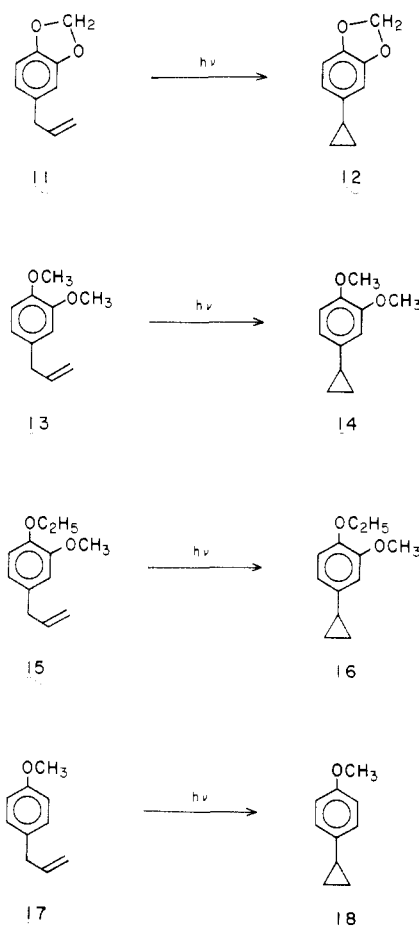


Figure 4. Eugenol-related compounds and their photochemical products (see Table II for chemical names).

products were methanol (solvent) addition products.

There are two possible mechanisms by which the photochemical reduction of eugenol may yield compound 3. One is a radical process that would be completely consistent with the behavior reported for methylcyclopentene (Kropp and Krauss, 1967) and 2-norbornenes (Kropp,

1969) (Figure 2). The other is an ionic process that involves hydride abstraction from methanol through carbocation intermediates 7 and 8 as shown in Figures 1 and 3 (Kropp, 1973). Eugenol irradiated in a methanol-*O-d* solution gave deuterium-incorporated compounds 1-5. The results of mass spectral analysis on the deuterium incorporated products are shown in Table III. The incorporation of deuterium into unreacted eugenol supports the postulation of an ionic process mechanism (Kropp, 1973). The unique fragment, m/z 151 (2%), appeared in the mass spectra of compound 3 (3-3'-*d* in Figure 3) recovered from the experiment conducted in the methanol-*O-d* solution indicates loss of $\text{CH}_2\text{D}\cdot$ (16) from the molecular ion $M^+ = 167$. The deuterium is, therefore, incorporated into the C_1 carbon atom of the propyl substituent. This result confirmed an ionic mechanism for compound 3 formation.

The formation of compound 5 is rather unusual but can be explained by hydride shift as shown in Figure 1. The irradiation of compound 2 did not give compound 5. It is clear, therefore, that compound 5 did not form through compound 2, even though alkylphenylcyclopropanes are known to undergo photocleavage to give alkenes, which can subsequently form methanol addition products (Salisbury, 1972).

Eugenol and Its Related Compounds in Acetonitrile Solution. The cyclopropane derivatives of eugenol and its related compounds possess an interesting floral and spicy odor (see Figure 4). The methanol addition products, however, did not possess odors of interest as flavor or fragrance agents. Acetonitrile, therefore, was used as a reaction solvent to avoid the formation of addition products.

Borchert et al. (1973) showed that safrole forms the highly reactive epoxide, which is associated with carcinogenic activity (Long et al., 1961), from the double bond on its side chain; thus, safrole was prohibited for use in food products. We suggest that the active side chain of eugenol and its related compounds be transformed into the non-hazardous yet flavor-retaining cyclopropane moiety, which would be valuable as possible flavor compounds.

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Received for review December 15, 1981. Revised manuscript received June 11, 1982. Accepted July 30, 1982.