

Photochemical Studies on Jasmin Oil

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Egyptian jasmin absolute oil was irradiated with a high-pressure mercury lamp (HPML) and low-pressure mercury lamp (LPML) for various periods of time. The volatile constituents of the irradiated samples were isolated and identified by the GC/MS technique. The *Z/E* isomerization reaction was observed in several constituents; certain amounts of naturally existing *cis* isomers were transformed into the *trans* isomers upon both HPML and LPML irradiation. Benzoic acid was recovered in fairly large quantities from the irradiated samples. The formation pathways of the major photochemical products, 3-methyl-2-(*trans*-2-pentenyl)-2-cyclopenten-1-one (isomerization), 2-(2-ethylcyclopropyl)-3-methyl-2-cyclopenten-1-one (di- π -methane rearrangement), benzoic acid (free radical mechanism), benzyl alcohol (α -hydrogen abstraction), and 2,3-butanediol (dimerization), are postulated.

The flower of jasmin, which is probably native to the Himalayas, has been used in India for ceremonial purposes and for the scenting of ointments for many years. The cultivation of jasmin began in Grasse, France (the world center of perfumery essence production), about 200 years ago when cosmetic products began to be produced on an industrial scale. Demand for and production of jasmin oil increased gradually up to the outbreak of World War II, but decreased drastically during the war. The essential oil of jasmin is still, however, one of the most important and indispensable flower essences used in cosmetic products today.

It has been noted that sunlight caused alteration of essential oil constituents (Garnero and Roustan, 1979). Jasmin oil, which possesses a light brown color, readily undergoes photochemical change and its quality diminishes. Cosmetic industries have been concerned about maintaining the quality of jasmin oil for many years.

The components of jasmin oil were reported in many literature citations (Polak, 1973; Kaiser and Lamparsky, 1974; Nofal et al., 1982). Some constituents such as benzyl acetate and benzyl benzoate are known to undergo photochemical reaction (Appleton et al., 1980).

In this study, natural jasmin oil and one of its major components, benzyl benzoate, were irradiated by high-pressure and low-pressure mercury lamps to investigate their photochemical products and reaction mechanisms.

EXPERIMENTAL SECTION

Photochemical Irradiation of Jasmin Oil. An ethanol solution (300 mL) containing 0.7 g of Egyptian jasmin absolute oil (obtained from a commercial source) was irradiated either by a high-pressure mercury lamp (HPML) with Pyrex filter for 7 h or a low-pressure mercury lamp (LPML) for 3 h under a nitrogen stream. After the irradiation, the reaction solutions were concentrated to 1 mL in volume by using a Kuderna-Danish evaporative concentrator. The concentrated samples were subjected to instrumental analyses (GLC, GC/MS).

Isolation and Identification of Components in the Samples. All samples were analyzed by using GC retention index and GC/MS techniques as described previously (Yamaguchi and Shibamoto, 1979, 1980; Toda et al., 1982). The gas chromatographic retention index (Kovats Index) and MS fragmentation pattern of each component were compared to those of the authentic compound to identify

the constituents of the samples.

A Hewlett-Packard Model 5710-A gas chromatograph equipped with a flame ionization detector, modified for capillary analyses, and 50 m \times 0.23 mm i.d. fused silica capillary column coated with Carbowax 20M was used. The injector temperature was 250 °C. Peak areas were integrated by using a Hewlett-Packard Model 3385-A automation system combined with the above gas chromatograph. A Hitachi Model RMU-6M combination mass spectrometer/gas chromatograph (Hitachi Model M-5201) equipped with Hitachi Model M-6010 and 10 II/A data system was used under the following conditions: ionization voltage, 70 eV; emission current, 80 μ A; ion acceleration voltage, 3100 V; ion source temperature, 200 °C.

Kinetic Study of the Reactants and Products in an Irradiated Jasmin Oil. The quantitative fluctuations of some jasmin constituents upon photochemical irradiation were monitored by using the gas chromatographic internal standard method (Ettre, 1967). Tridecane standard solution was prepared by adding 100 μ g of tridecane into 10 mL of ethyl acetate. The standard solution (10 μ L each) was added to each irradiated sample, which had previously been concentrated to 200 μ L in volume by blowing a nitrogen gas, and the relative area of each objective gas chromatographic peak to that of the standard was plotted against an irradiation time (Figures 1-4).

Photochemical Irradiation of Benzyl Benzoate. An ethanol solution (300 mL) containing 1 g of benzyl benzoate was irradiated for 29 h under a nitrogen stream using a 10-W low-pressure mercury lamp. After the sample was concentrated to 1 mL in volume, the photochemical products were isolated and identified by the same method as for natural jasmin oil.

RESULTS AND DISCUSSION

Table I shows compounds identified in the original jasmin oil and the samples irradiated by LPML and HPML. The GC peak area percentages for each constituent in the three samples indicate that photochemical changes occurred.

The relative proportions of some components such as linalool (peak no. 13, Table I), benzyl acetate (18), benzyl alcohol (23), *cis*-3-hexenyl benzoate (33), eugenol (36), benzyl benzoate (65), and phytol (66) changed significantly. These compounds may be transformed into new compounds, as some new chemicals were found in the irradiated samples.

Ethyl benzyl ether was found in the sample irradiated with LPML; this is in line with Zimmerman and Sandel's (1963) report that 3-methoxybenzyl acetate in 50% aqueous ethanol yielded ethyl 3-methoxybenzyl ether upon photochemical irradiation. 1,2-Diphenyl ethanol (65)

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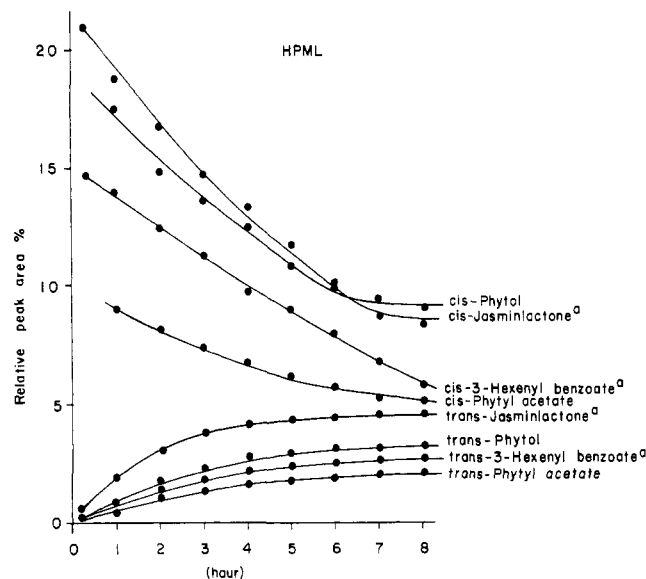


Figure 1. Quantitative changes of *Z/E* isomers in a jasmin oil upon HPML irradiation over time. (a) Actual value of peak area percent $\times 10$.

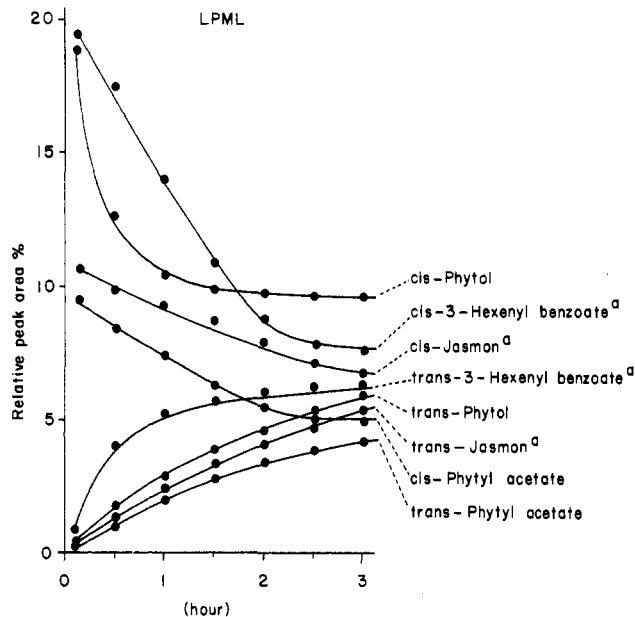


Figure 2. Quantitative changes of *Z/E* isomers in a jasmin oil upon LPML irradiation over time. (a) Actual value of peak area percent $\times 10$.

might be formed from benzyl benzoate (67) with ethanol via the benzyl radical. On the other hand, benzoic acid was produced via a hydrogen abstraction of the benzoyloxy radical, which was produced as the pair of the benzyl radical by the homolytic scission of benzyl benzoate. The details of these mechanisms will be discussed in the section on the photochemical reaction of benzyl benzoate.

Mihara and Shibamoto (1982) proposed that 4-cyclopropyl-2-methoxyphenol (41) was produced from eugenol (36) via di- π -methane rearrangement upon photochemical irradiation. The same rearrangement was observed in the case of 3-methyl-2-(*trans*-2-pentenyl)-2-cyclopenten-1-one (26) upon HPML irradiation; a certain amount of 2-(2-ethylcyclopropyl)-3-methyl-2-cyclopenten-1-one (24) was also formed.

It is noted that *trans,trans*- β -farnesene (20) disappeared upon LPML irradiation and decreased considerably upon HPML irradiation. Nevertheless, White and Gupta (1969) reported that β -farnesene gave a mixture of isomeric

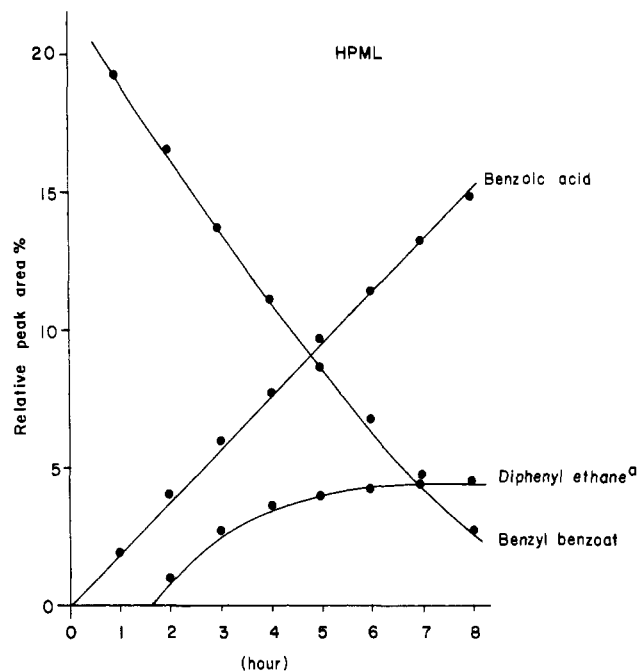


Figure 3. Quantitative changes of benzyl benzoate and its possible products in a jasmin oil upon HPML irradiation over time. (a) Actual value of peak area percent $\times 10$.

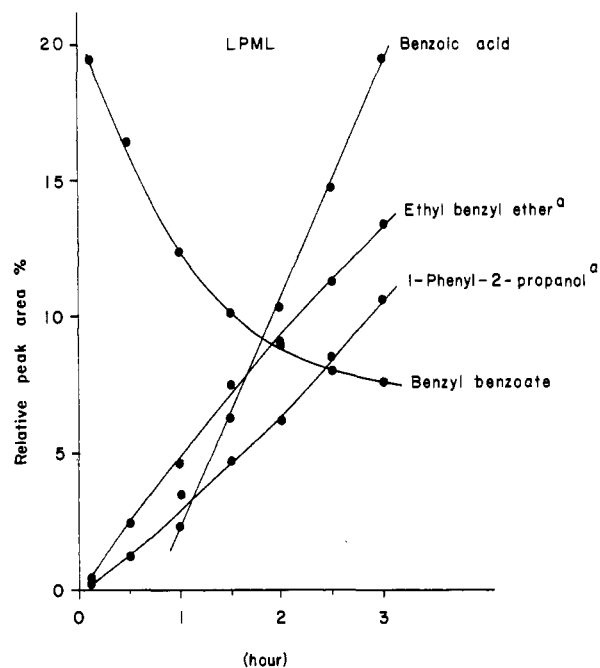


Figure 4. Quantitative changes of benzyl benzoate and its possible products in a jasmin oil upon LPML irradiation over time. (a) Actual value of peak area percent $\times 10$.

hydrocarbons upon sensitized or direct irradiation. No hydrocarbons which could be hypothesized to be β -farnesene derivatives were observed in the irradiated samples and no other reasonable proposed photochemical products of β -farnesene were found in the irradiated samples.

The compounds which contain a chain double bond underwent a *Z/E* isomerization reaction; they are 3-methyl-2-(*cis*-2-pentenyl)-2-cyclopenten-1-one (26), *cis*-3-hexenyl benzoate (33), *cis*-7-decen-5-olide (39), phytol acetate (59), geranyl linalool (59), and phytol (66). The *cis* isomer was present predominantly in the natural jasmin oil and the *trans* isomer was formed from the *cis* isomer

Table I. Compounds Identified in Jasmin Oil and Its Irradiated Samples

gas chromatographic peak no.	compounds	peak area %			Kovats index	
		natural jasmin oil	irradiated by		I_{unknown}^b	I_{known}^c
			LPML	HPML		
1	unknown	0.05	a	a	1300	
2	<i>cis</i> -3-hexenyl acetate	0.05	a	a	1316	1313
3	<i>cis</i> -3-hexenol	0.07	a	a	1352	1351
4	unknown	a	a	0.06	1369	
5	unknown	a	0.09	a	1376	
6	unknown	a	a	0.25	1400	
7	unknown	a	a	0.05	1413	
8	ethyl benzyl ether	a	0.24	a	1421	1421
9	unknown	0.07	a	a	1440	
10	unknown	a	0.08	a	1446	
11	unknown	a	a	0.05	1450	
12	2,3-butanediol	a	0.10	a	1492	1491
13	linalool	4.62	3.83	1.83	1511	1513
14	unknown	a	0.09	a	1567	
15	methyl benzoate	0.05	a	a	1574	1573
16	caryophyllene	0.08	a	a	1580	1581
32	<i>trans</i> -3-hexenyl benzoate	a	0.67	0.36	2046	2051
33	<i>cis</i> -3-hexenyl benzoate	1.20	0.48	1.24	2072	2074
34	unknown	a	a	0.13	2079	
35	6,10,14-trimethylpentadecan-2-one	0.81	0.65	1.09	2096	2096
36	eugenol	2.01	0.99	0.22	2100	2100
37	<i>trans</i> -7-decen-5-olide	a	1.04	0.47	2161	
38	methyl palmitate	1.33	0.79	1.78	2177	
39	<i>cis</i> -7-decen-5-olide	1.92	2.67	3.42	2184	
40	unknown	0.27	a	1.24	2210	
41	4-cyclopropyl-2-methoxyphenol	a	0.39	a	2225	2228
42	unknown	a	0.59	0.14	2235	
43	isophytol	8.47	12.65	15.16		
44	2-pentenylcyclopentanone-3-acetic acid methyl ester	0.91	10.45	0.52	2273	2272
45	unknown	0.08	a	a	2289	
46	unknown	0.07	a	a	2300	
47	unknown	0.08	a	a	2314	
48	benzoic acid	a	2.27	3.11	2338	2336
49	indol	1.24	a	0.52	2350	2346
50	unknown	a	a	0.40	2362	
17	unknown	a	a	0.06	1676	
18	benzyl acetate	18.82	7.63q	4.79	1689	1688
19	unknown	0.08	a	0.01	1700	
20	<i>trans,trans</i> - β -farnesene	0.86	a	0.10	1723	1727
21	benzyl propionate	0.05	a	a	1766	1769
22	1-phenyl-2-propanol	a	1.41	0.07	1773	1771
23	benzyl alcohol	1.65	2.26	0.97	1813	1813
24	2-(2-ethylcyclopropyl)-3-methyl-2-cyclopenten-1-one	a	a	1.09	1856	1851
25	3-methyl-2-(<i>trans</i> -2-pentenyl)-2-cyclopenten-1-one	a	0.11	0.18	1877	1873
26	3-methyl-2-(<i>cis</i> -2-pentenyl)-2-cyclopenten-1-one	2.15	0.26	0.17	1886	1887
27	unknown	0.60	1.42	0.84	1916	
28	unknown	0.39	0.15	0.15	1965	
29	unknown	0.25	a	0.16	1985	
30	<i>p</i> -cresol	0.41	0.38	0.28	1998	2001
31	diphenyl ethane	a	0.67	0.35	2036	2040
51	methyl <i>N</i> -methylanthranilate	0.66	a	a	2376	2372
52	unknown	a	0.43	0.45	2385	
53	geranyl linalool (photoinduced reaction isomer)	a	0.93	0.67	2395	2398
54	methyl oleate	0.90	0.82	1.42	2403	2400
55	unknown	0.33	0.82	0.38	2408	
56	<i>trans</i> -phytyl acetate	1.06	4.91	3.34	2438	2439
57	geranyl linalool (photoinduced reaction isomer)	0.38	0.71	1.21	2444	2456
58	unknown	a	1.36	1.33	2454	2456
59	geranyl linalool + <i>cis</i> -phytyl acetate	10.50	7.61	14.34	2491	2492
60	unknown	a	0.46	a	2507	
61	unknown	a	0.32	0.73	2510	
62	methyl linolate	3.45	1.56	2.16	2513	
63	unknown	a	a	0.35	2518	
64	<i>trans</i> -phytol	a	7.72	4.86	2530	2525
65	benzyl benzoate	13.29	8.50	9.73	2540	2537
66	<i>cis</i> -phytol	14.17	10.24	13.73	2573	2570
67	1,2-diphenyl ethanol	a	0.40	a		
68	unknown	1.07	1.15	1.13		

^a Peak area percent less than 0.01. ^b Kovats index of unknown peak. ^c Kovats index of authentic compound.

by photochemical irradiation.

To a certain degree, HPML irradiation and LPML irradiation gave different results. The amount of 6,10,14-

trimethylpentadecan-2-one (35) and isophytol (43) decreased more with HPML irradiation than with LPML irradiation. On the other hand, the quantities of indole

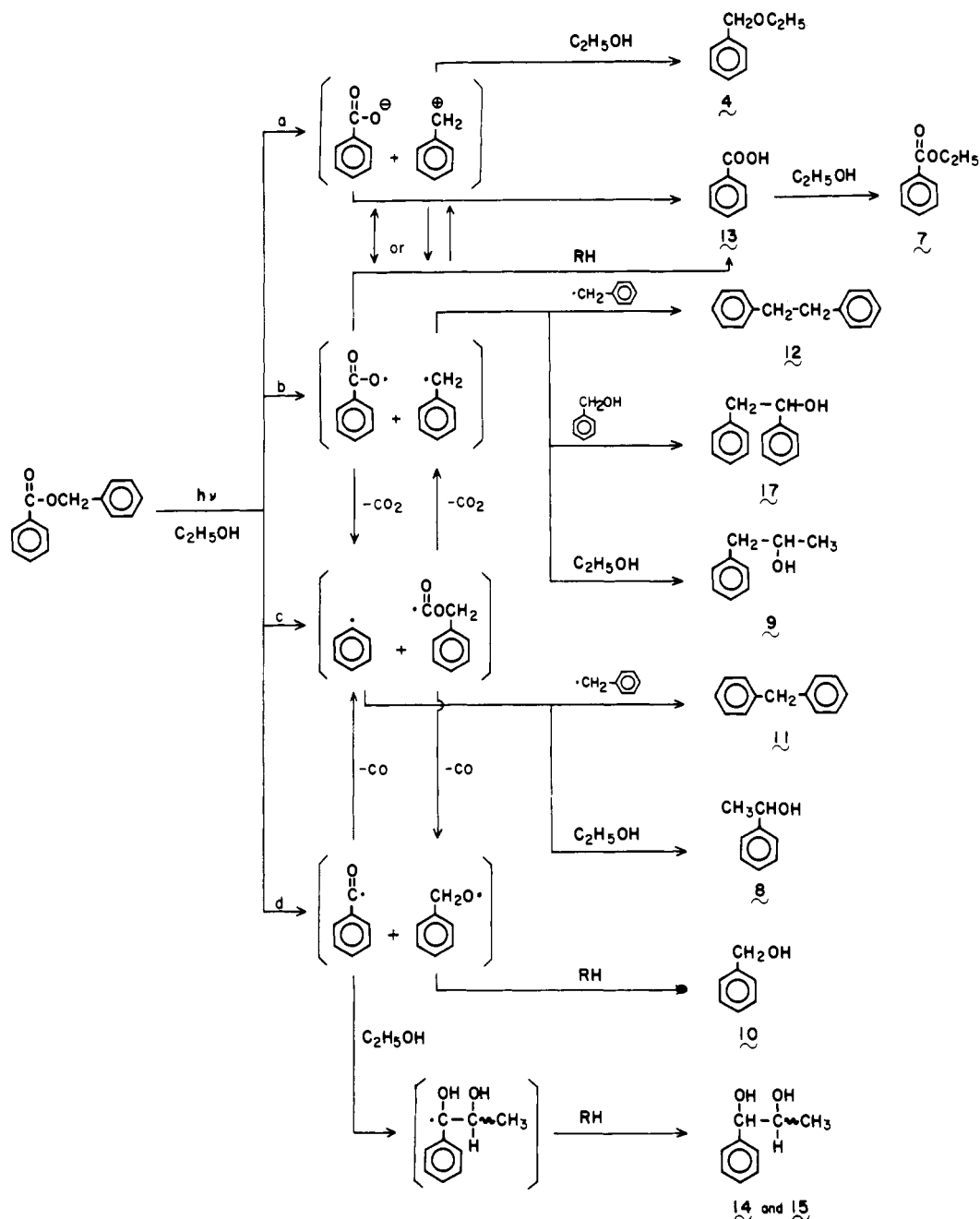


Figure 5. Proposed mechanisms of photolysis of benzyl benzoate in ethanol.

(49) and methyl linolenate (62) were diminished by LPML irradiation more than by HPML irradiation.

Quantitative Changes in Specific Constituents over Time. The compounds exhibiting significant quantitative changes as the irradiation period increased in length are shown in Figures 1–4. Apparent correlations between *Z/E* isomers are observed; *cis*- and *trans*-phytols and *cis*- and *trans*-phytyl acetates in Figures 1 and 2; *cis*- and *trans*-jasminolactones (*cis*- or *trans*-7-decen-5-olide) in Figure 1; *cis*- and *trans*-3-hexenyl benzoates in Figures 1 and 2; *cis*- and *trans*-jasnone [3-methyl-2-(*cis*- or *trans*-2-pentenyl)-2-cyclopenten-1-one] in Figure 2. *Cis* isomers, which were constituents of the natural oil, decrease and *trans* isomers, which were photochemical products, increased over time.

One of the most important findings of this study was that benzoic acid, the precursor of which could be benzyl benzoate, formed in relatively large quantities. Figures 3 and 4 indicate that benzyl benzoate produced benzoic acid upon either HPML or LPML irradiation. Further

investigation on benzoic acid formation from benzyl benzoate was performed and will be discussed in the following section.

Photolysis of Benzyl Benzoate in Ethanol. The products identified in the irradiated benzyl benzoate are shown in Table II. The proposed formation pathways of the major photochemical products are presented in Figure 5.

The production of benzyl ethyl ether (4) suggested the formation of a benzyl cation and a benzoate anion via an ionic transformation of the electronically excited state (Zimmerman and Sandel, 1963, pathway a). Since hydrogen abstraction from the α -carbon of alcohol is much more facile than from oxygen (Kharasch et al., 1951), benzyl ethyl ether would not be formed via the free radical mechanisms shown in pathway b (Figure 5).

Benzoic acid (13) produced in fairly large quantities (peak area percent is 17). The compounds which could be proposed to be formed via a free radical mechanism [pathway b, 1,2-diphenylethane (12), 1,2-diphenylethanol

Table II. Compounds Identified in the Irradiated Benzyl Benzoate

peak no.	compound	peak area %	I_{unknown}	I_{known}
1	acetaldehyde	0.01	500	500
2	unknown	0.01	585	
3	unknown	0.02	810	
4	benzyl ethyl ether	1.13	1424	1421
5	2,3-butanediol (diastereomer)	6.67	1490	1492
6	2,3-butanediol (diastereomer)	7.62	1526	1522
7	ethyl benzoate	0.22	1640	1641
8	1-phenylethanol	0.80	1764	1765
9	1-phenyl-2-propanol	19.38	1778	1779
10	benzyl alcohol	17.19	1822	1823
11	diphenylmethane	1.67	1980	1984
12	1,2-diphenylethane	2.31	2069	2072
13	benzoic acid	16.97	2336	2340
14	1-phenyl-1,2-propanediol (diastereomer)	3.90	2339	2343
15	1-phenyl-1,2-propanediol (diastereomer)	5.21	2361	2365
16	benzyl benzoate	13.53	1563	2566
17	1,2-diphenylethanol	2.60		

(17), and 1-phenyl-2-propanol (9)] were found in large amounts; it is reasonable, therefore, to conclude that pathway b is more predominant than pathway a for benzoic acid formation. Benzoic acid reacted subsequently with ethanol to give ethyl benzoate (7). Zimmerman and Sandel (1963), who obtained benzyl alcohol (peak no. 10 in Table II, peak area percent = 17) from a photolysis of benzyl halide and benzyl acetate in aqueous alcohol or dioxane solutions, proposed that benzyl alcohol was formed via benzyl cation. On the other hand, Appleton et al. (1980) reported that benzyl alcohol was not detected in the irradiated alcohol solution of benzyl halides or benzyl acetate. Benzyl alcohol, which was one of the major photochemical products in this study, may be formed from a benzyl cation reacted with water which is present in ethanol in small quantities (less than 0.5%). The formation of benzyl alcohol did not, however, increase with the addition of water (10%). The major benzyl alcohol formation pathway might, therefore, be pathway d; a benzyloxyl radical formed by irradiation and subsequently an α -hydrogen abstracted from alcohol to give benzyl alcohol. Pryor (1966) proposed the same formation mechanism of alcohol through an alkyloxyl radical intermediate in the thermal decomposition of dialkyl peroxide.

Diphenylmethane (11) and 1-phenylethanol (8) were apparently formed from a phenyl radical which was produced by direct homolytic fission of benzyl benzoate (pathway c), from the benzoyloxyl radical (pathway b), or from the benzoyl radical (pathway d). 1-Phenyl-1,2-propanediols (14, 15) could also form from a benzoyl radical (pathway d).

Most radicals ($R\cdot$) produced by the irradiation of benzyl benzoate abstract the α -hydrogen from ethanol to produce 1-hydroxyl-1-ethyl radical. Acetaldehyde (1) and 2,3-butanediols (5, 6) could be formed from a 1-hydroxylethyl radical via disproportionation and the dimerization reaction, respectively (proposed mechanisms shown in Figure 6).

The major photochemical reaction process of benzyl benzoate in ethanol was homolytic fission, producing benzoyloxyl and benzyl radicals (pathway b); this contributed 57% of the overall reaction products. The for-

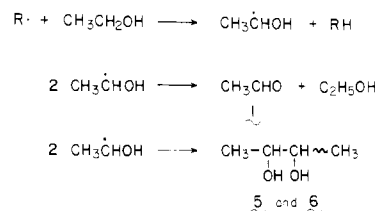


Figure 6. Proposed formation mechanisms of acetaldehyde (1) and 2,3-butanediols (5, 6).

mation of benzoyl and benzyloxyl radicals (pathway d) contributed 38% of the overall reaction products. The contribution of the phenyl radical (pathway c, 3%) and ionic species (pathway a, 2%) was considerably lower. The results of this study agreed with Cristol and Greenwald (1976), who performed direct irradiation of benzyl chloride in ethanol.

Further clarification of these photochemical products is necessary to achieve good quality control in the use of essential oils for the food and cosmetic industries.

Registry No. Benzyl benzoate, 120-51-4; *cis*-3-hexenyl acetate, 3681-71-8; *cis*-3-hexenol, 928-96-1; linalool, 78-70-6; methyl benzoate, 93-58-3; caryophyllene, 87-44-5; benzyl acetate, 140-11-4; *trans*- β -farnesene, 18794-84-8; benzyl propionate, 122-63-4; benzyl alcohol, 100-51-6; 3-methyl-2-(*cis*-2-pentenyl)-2-cyclopenten-1-one, 488-10-8; *p*-cresol, 106-44-5; *cis*-3-hexenyl benzoate, 25152-85-6; 6,10,14-trimethylpentadecan-2-one, 502-69-2; eugenol, 97-53-0; methyl palmitate, 112-39-0; *cis*-7-decen-5-olide, 25524-95-2; isophytol, 505-32-8; 2-pentenylcyclopentanone-3-acetic acid methyl ester, 85135-70-2; indole, 120-72-9; methyl *N*-methylantranilate, 85-91-6; methyl oleate, 112-62-9; *trans*-phytyl acetate, 10236-16-5; *cis*-phytyl acetate, 5016-85-3; methyl linolate, 112-63-0; *cis*-phytol, 5492-30-8; ethyl benzyl ether, 539-30-0; 2,3-butanediol, 513-85-9; 1-phenyl-2-propanol, 698-87-3; 2-(2-ethylcyclopropyl)-3-methyl-2-cyclopenten-1-one, 85135-71-3; 3-methyl-2-(*trans*-2-pentenyl)-2-cyclopenten-1-one, 6261-18-3; 1,2-diphenylethane, 103-29-7; *trans*-3-hexenyl benzoate, 75019-52-2; *trans*-7-decen-5-olide, 25524-96-3; benzoic acid, 65-85-0; geranylinalool, 1113-21-9; *trans*-phytol, 150-86-7; 1,2-diphenylethanol, 614-29-9; acetaldehyde, 75-07-0; ethyl benzoate, 93-89-0; 1-phenylethanol, 98-85-1; diphenylmethane, 101-81-5; 1-phenyl-1,2-propanediol, 1855-09-0.

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