Sensory Importance and Mechanism of Photochemical Conversion of Carvone to Carvonecamphor in Ethanol–Water Mixtures

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Approximate odor thresholds for carvonecamphor, with camphor odor, and for the ester [ethyl 2-[(1*R*,2*R*,4*R*,5*S*)-1,5-dimethyl-2-bicyclo[2.1.1]hexyl]acetate], with sweet odor, were determined to be 2200–4100 and 1.8–2.5 ppb, respectively, by gas chromatographic effluent sniffing. The quantum yield of photochemical conversion of carvone to carvonecamphor showed no wavelength dependence but increased with decreasing ethanol content in ethanol–water mixtures: 0.049 ± 0.008 mol·einstein^{-1} in 42% ethanol (apparent activation energy of 19 kJ·mol^{-1}) and 0.0033 ± 0.00015 mol·einstein^{-1} in neat ethanol. The quantum yield of further conversion of carvonecamphor to the ester was approximately 0.1 mol·einstein^{-1}. The triplet lifetime of carvone determined by laser flash spectroscopy in the absence of oxygen increased with decreasing ethanol content: 71 ns in neat, 76 ns in 80%, and 98 ns in 42% ethanol. Oxygen quenched the triplet excited state with k_{O_2} $\sim 3 \times 10^9$ L·mol^{-1}·s^{-1} whereas oxygen, piperylene, and diacetyl did not influence the photochemical conversion. Intramolecular electron transfer from an nπ* singlet state of carvone is suggested to be responsible for the photocycloaddition reaction of carvone.

Keywords: *(+)-Carvone; carvonecamphor; ethyl 2-[(1R,2R,4R,5S)-1,5-dimethyl-2-bicyclo[2.1.1]hexyl]-acetate; odor thresholds; gas chromatography–olfactometry; photocycloaddition*

INTRODUCTION

S-(+)-Carvone (**I**) is a monocyclic terpene with caraway flavor and is a main constituent of essential oils from caraway and dill seeds (Czygan, 1989; Blank and Grosch, 1991). Distillates of these seeds are important for the characteristic flavor of aquavits. Aquavits are traditionally marketed in transparent glass bottles, and light-induced conversion of carvone in aquavit and formation of carvonecamphor and other photoproducts will change the sensory impression of aquavit (Refsgaard et al., 1995). The photochemical conversion of carvone to carvonecamphor (**II**) in sunlight has been known since the turn of century (Ciamician and Silber, 1908), and later studies have revealed the presence of an ester derivative of carvonecamphor in the photolysis solution of carvone: ethyl 2-[(1*R*,2*R*,4*R*,5*S*)-1,5-dimethyl-2-bicyclo[2.1.1]hexyl]acetate (**III**) (Meinwald and Schneider, 1965; Malatesta et al., 1982; Tsipi et al., 1987) (Figure 1). Despite the importance for the shelf life of aquavit-type beverages, the mechanism of the photoconversion of carvone, including dependence on the wavelength of irradiation, temperature, and composition of the reaction medium, is only sparsely known. Accordingly, we have undertaken an investigation of the sensory importance of the photoproducts of carvone by use of gas chromatographic effluent sniffing techniques, and the kinetics and mechanism of the photochemical conversion in ethanol–water mixtures are studied by combining transient absorption laser flash spectroscopy and continuous wave photolysis.

MATERIALS AND METHODS

Chemicals. *S*-(+)-Carvone (96%), diacetyl (2,3-dioxobutane, 97%), 1-methylnaphthalene (98%), and piperylene (mixture of *cis-* and *trans-*isomers of 1,3-pentadiene, 90%) were
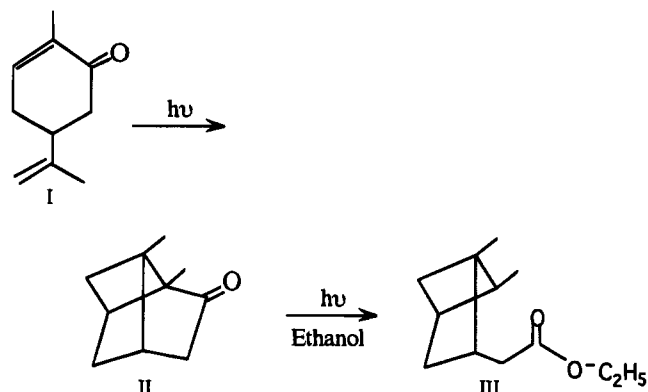

Figure 1. Photochemical conversion of (+)-carvone (**I**) to carvonecamphor (**II**) and ethyl 2-[(1*R*,2*R*,4*R*,5*S*)-1,5-dimethyl-2-bicyclo[2.1.1]hexyl]acetate (**III**).

from Aldrich Chemical Co. (Steinheim, Germany) and used without further purification. 4-Methyl-1-pentanol (97%) and 1,10-phenanthroline monohydrate of analytical grade were from Merck (Darmstadt, Germany). Potassium ferrioxalate was from K & K Laboratories (Cleveland, OH). Hexanal (98%) was from Merck, heptanal (95%), octanal (99%), dodecanal (92%), tridecanal (90%), and tetradecanal (80%) were from Aldrich, nonanal was from Roth (Karlsruhe, Germany), decanal (>99%) was from Sigma (St. Louis, MO), and undecanal (97%) was from Fluka (Buchs, Switzerland).

Continuous Wave Photolysis. The carvone concentration was, if not otherwise stated, 4.0×10^{-4} mol·L^{-1} (0.060 g·L^{-1}), and ethanol-water mixtures were made from water with pH 6.0 (0.010 mol·L^{-1} phosphate buffer). The carvone solutions were exposed to monochromatic light selected from an Osram HBO 200 W/2 high-pressure Hg lamp (line spectrum) by means of an interference filter. The lamp was mounted as part of an optical train (Spindler und Hoyer, Göttingen, Germany), which also included a light condenser, a heat filter, a shutter connected to an electronic timer, and lenses focusing the light into a thermostated (25.0 ± 0.5 °C) 5 cm quartz cell containing the photolysis solution (12 mL), which was stirred by a magnetic bar. An Oriel 6035 low-pressure Hg–Ar penlight

lamp equipped with an Oriel 6041 short-wave filter from Oriel Corp. (Stratford, CT) mounted in a thermostated cell holder (25.0 ± 0.5 °C) was used as a diffuse light source for 254 nm irradiation of a 12 mL photolysis solution in a 5 cm quartz cell. Accurate light intensities were determined by ferrioxalate actinometry (Hatchard and Parker, 1956) for each photolysis experiment. All solutions were either air-saturated or degassed by bubbling with nitrogen for 30 min prior to photolysis. The spectrophotometric measurements were carried out on a Shimadzu UV 2101-PC scanning spectrophotometer (Kyoto, Japan).

Dark Reactions. Thermal reactions at 25 °C of carvone solutions excluded from light were monitored spectrophotometrically at regular intervals during the time span of the photolysis.

Laser Flash Photolysis. The experiments were conducted with a complete LKS.50 laser photolysis spectrometer from Applied Photophysics Ltd. (London, U.K.). Pulses (20 mJ, 8 ns duration) from a frequency-tripled (λ_{exc} = 355 nm) Spectron SL 800 Nd:YAG laser were directed onto the sample in a circular beam with a diameter of about 6 mm. At right angles to the laser, a 150 W xenon arc lamp equipped with an arc lamp pulser was used as the analyzing beam. This beam was directed through the sample, then through a monochromator with a bandpass of 4.7 nm, and onto a Hamamatsu 1P28 photomultiplier, whose current was transferred through a load resistor of 50 Ω to a Philips PM3323 digital oscilloscope measuring the resulting voltage at 2 ns/point. Data were transferred to an Archimedes 420/I computer and converted to ΔA. No data smoothing was performed. Nonlinear regression was carried out using the Marquardt algorithm based on the routine Curfit (Bevington, 1969). The parameters of eq 1 were fitted to the data:

$$A(t) = B \exp(-kt) + A_\infty \qquad (1)$$

The absorbances $A(t)$, $B \exp(-kt)$, and A_∞ are understood with $A = 0$ as the absorbance of the solution before the laser pulse (baseline). $A(t)$ is the observed absorbance at a time t. A_∞ is the absorbance at infinite time, $B + A_\infty$ is the absorbance difference at $t = 0$ immediately after the laser pulse, and k is the rate constant of the exponential decay. Magnetic stirring was used in all experiments. During acquisition of time traces the laser was fired at ≤0.5 Hz. Sixteen traces were averaged for each observation. The absorbance of the photolysis solution at the wavelength of irradiation was in the range A_{355} = 0.11–0.27.

Photochemical Products. After steady-state photolysis, the samples were kept at −18 °C until extraction. Four hundred microliters of an aqueous solution of 500 mg·L^{-1} 4-methyl-1-pentanol was added to a 10.0 mL sample as internal standard. The ethanol–water samples were extracted with 10.0 mL of diethyl ether–n-pentane (1:2 v/v) during magnetic stirring for 5 min. The two phases were separated in a separatory funnel, and the ether–pentane phase was concentrated to 200 μL under nitrogen. Ethanol samples were concentrated to 200 μL under nitrogen.

Carvone and photoproducts were separated on a DB-Wax column (30 m × 0.25 mm × 0.25 μm) from J&W Scientific (Folsom, CA). A Hewlett-Packard 5890A gas chromatograph (Avondale, PA) was used, and the conditions were as follows: 1:19 split ratio; injector temperature, 250 °C; flame ionization detector temperature, 250 °C; helium as carrier gas; column flow, 0.7 mL/min; temperature program, 60 °C for 10 min, 60–220 °C at 3 °C/min, and 220 °C for 45 min. Retention indices were calculated according to the methods of Dool and Kratz (1963) and Franke et al. (1993) with aldehydes as standard compounds.

Identification and Quantification. Carvonecamphor was identified from its mass spectrum (Ndiaye and Aaron, 1989; Refsgaard et al., 1995) and NMR data (Refsgaard et al., 1995) and the ester from its mass spectrum (Meinwald and Schneider, 1965; Meinwald et al., 1967; Tsipi et al., 1987; Ndiaye and Aaron, 1989). The volatile compounds were quantified relative to the internal standard with the assumption of equal extraction.

Gas Chromatography−Mass Spectrometry Analysis. GC−MS was performed on a system consisting of a Hewlett-Packard 5890 Series II gas chromatograph directly coupled to a JEOL JMS-AX505W mass spectrometer (JEOL Ltd., Tokyo, Japan) as described elsewhere (Refsgaard et al., 1995).

GC−Olfactometry. (+)-Carvone (3.3 × 10^{-3} mol·L^{-1}) in 42% ethanol was irradiated for a week at 350 nm in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co., Branford, CT) and was extracted as described above. Carvonecamphor, carvone, and the ester were separated by gas chromatography on both the polar DB-Wax and the nonpolar HP-1 (25 m × 0.20 mm × 0.33 μm) capillary column and odors perceived at a sniffing port (olfactory detector outlet, OD-1, from SGE, Ringwood, Australia). A temperature program of 70 °C for 10 min, 70–220 °C at 10 °C/min, and 220 °C for 10 min was used. Four persons performed the olfactometric analysis, and the illuminated (+)-carvone solution was diluted with ether–pentane (1:2 v/v) until the lowest concentration at which an odor could be detected by GC−olfactometry was reached.

Approximate odor threshold values, T_x, of the photochemical products of carvone were determined by aroma extract dilution analysis as described by Ullrich and Grosch (1987):

$$T_x = T_{is}c_x^0 FD_{is}/c_{is}^0 FD_x \qquad (2)$$

T_{is} is the odor threshold of an internal standard, c_{is}^0 and c_x^0 are the starting concentrations of the internal standard and of the compound with unknown odor threshold, and FD$_{is}$ and FD$_x$ are the highest dilutions at which the internal standard and the compound with unknown threshold can be recognized. (+)-Carvone was used as internal standard.

Odor thresholds for (+)-carvone and photoproducts were also determined according to the method of Drawert and Christoph (1984):

$$SA = cVp(1 - 1/r) \qquad (3)$$

The stimulus amount (SA) in grams eluted from the sniffing port can be calculated from the concentration (c) in grams per liter of the solution with the volatile substance, the injected volume (V) in liters (2 × 10^{-6} L), and the purity (p) of the substance in percent, and the split ratio (r = 2) can be determined to the corresponding column temperature.

Calculations. The photodegradation quantum yield

$$\Phi_I = \frac{\text{mol of carvone degraded/s}}{\text{mol of photons absorbed by carvone/s}} = \frac{D_I}{Q_I} \qquad (4)$$

was calculated from concentration changes of carvone monitored by gas chromatography and the light intensity, I_0, as determined by actinometry and expressed in quanta·s^{-1}. The number of moles of carvone molecules degraded per second, D_I, was determined as

$$D_I = |\alpha|V \qquad (5)$$

where V is the volume of the photolysis solution in liters and $|\alpha|$ is the numerical slope of plots of carvone concentration against irradiation time. For calculation of the quantum yield for the conversion of carvone to carvonecamphor, $\Phi_{I \rightarrow II}$, the slope of plots of carvonecamphor concentration against irradiation time was used in eq 5, and for calculation of the quantum yield for formation of the ester, $\Phi_{II \rightarrow III}$, the ester concentration against irradiation time was applied. Plots of at least five determinations were used, and R^2 was always higher than 0.90. The number of moles of photons absorbed by carvone, Q_I, was calculated by

$$Q_I = \frac{I_0}{N_A} \frac{l\epsilon_{irr}c}{\bar{A}_{irr}}(1 - 10^{-\bar{A}_{irr}}) \qquad (6)$$

where N_A is Avogadro's number, $\bar{A}_{irr}$ is the absorbance at the wavelength of irradiation at the time $1/2(t_i + t_{i-1})$, l is the cell
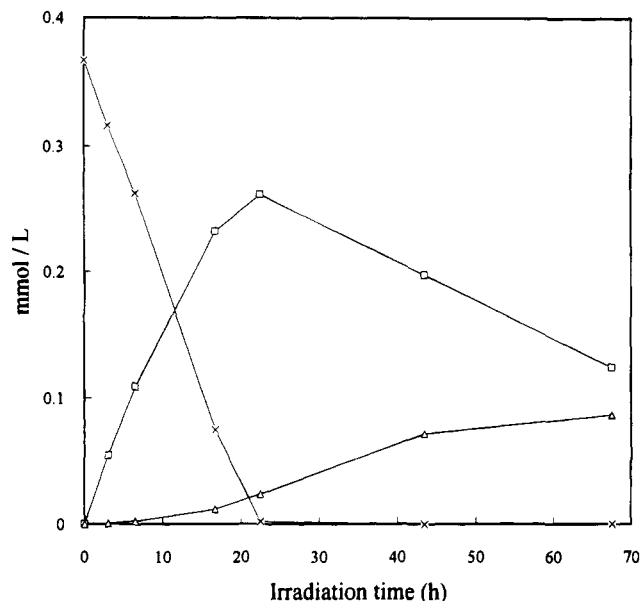
Figure 2. Concentration profile for continuous wave photolysis of 4.0×10^{-4} mol·L^{-1} carvone in degassed 42% ethanol for 254 nm irradiation ($I_0 = 2.2 \times 10^{17}$ quanta·s^{-1}·L^{-1}) at 25 °C based on GC analysis: ×, carvone; □, carvonecamphor; △, the ester. Absorption spectra of the photolysis solutions are shown in Figure 3.

length, c is the concentration, and ϵ_{irr} is the molar absorptivity of carvone at the irradiation wavelength. The factor $(l\epsilon_{irr}c)/\bar{A}_{irr}$ was different from unity in experiments in which quenchers other than oxygen were present in the photolysis solution. Quantum yields of formation of the ester were calculated in an analogous manner, using ϵ_{irr} for carvonecamphor in eq 6 by which the number of moles of photons absorbed by carvonecamphor was determined.

RESULTS

Carvonecamphor was the main product in all continuous wave photolyses. For 334 and 366 nm irradiation, the ester could not be detected after 24 h of irradiation. In contrast to this, the ester was detected as a photoproduct at 254 and 313 nm irradiation. Formation of the ester was, however, delayed, with a rate approximately proportional to the concentration of carvonecamphor in the photolysis solution, as illustrated in Figure 2 for an experiment with 254 nm irradiation of carvone in 42% ethanol. These observations indicate that the ester is formed from carvonecamphor in ethanol—water mixtures rather than directly from carvone and are in agreement with the fact that carvonecamphor is optically transparent for wavelengths above 340 nm (Figure 3). As may be seen in Figure 2, carvone was completely converted after 22.5 h of exposure to 254 nm light to the main product, carvonecamphor, which had the absorption spectrum shown in Figure 3.

The quantum yields of disappearance of carvone in 42% ethanol and the quantum yields of formation of carvonecamphor were found to be almost identical and to be independent of the wavelength of irradiation (254, 313, 334, or 366 nm), as may be seen in Table 1. An average value for these experimental conditions of 0.049 ± 0.008 mol·einstein^{-1} was calculated. The quantum yield of formation of the ester from carvonecamphor in 42% ethanol was $\Phi_{II \to III} = 0.11$ mol·einstein^{-1} at 254 nm irradiation and $\Phi_{II \to III} = 0.071$ mol·einstein^{-1} at 313 nm irradiation.

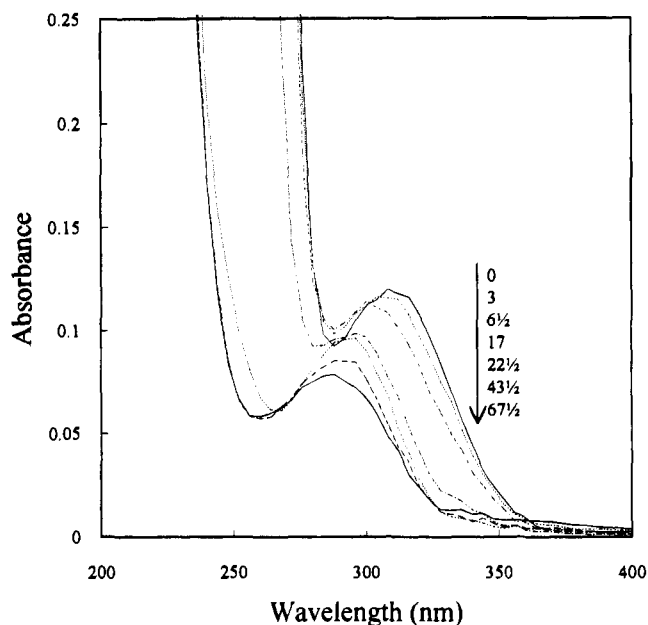Quantum yields for degradation of carvone at 366 nm irradiation in 42% ethanol and of formation of carvone-

Figure 3. Spectral changes during 254 nm photolysis at 25 °C of 4.0×10^{-4} mol·L^{-1} carvone in degassed 42% ethanol: UV-visible absorption spectrum prior to light exposure and after 3, 6.5, 17, 22.5, 43.5, and 67.5 h of light exposure ($I_0 = 2.2 \times 10^{17}$ quanta·s^{-1}·L^{-1}). Concentrations of carvone, carvonecamphor, and the ester in each of the photolysis solutions are shown in Figure 2.

camphor were found not to change significantly with the carvone concentration in the interval 2.7×10^{-4} to 2.7×10^{-3} mol·L^{-1}. The formation of carvonecamphor in 42% ethanol was found to be independent of the light intensity at 366 nm irradiation in the interval 1.89×10^{17} to 3.70×10^{18} quanta·s^{-1}·L^{-1}. We found increasing quantum yields with increasing temperature. The quantum yields were 0.026 mol·einstein^{-1} at 5 °C and 0.057 mol·einstein^{-1} at 35 °C. The apparent activation energy for the carvone cycloaddition was 19 kJ·mol^{-1}, calculated by use of quantum yields instead of rate constants in the Arrhenius equation.

Quenching experiments were conducted to determine the multiplicity of the photoreactive state of carvone, i.e., singlet or triplet reactivity. As may be seen in Table 1, the triplet quenchers oxygen, diacetyl, and piperylene did not quench the quantum yields of the transformation of carvone to carvonecamphor. This insensitivity to the presence of triplet quenchers provides circumstantial evidence for a singlet state as the photoreactive state in the cycloaddition. The quantum yields increased with addition of diacetyl, which may have acted as an electron acceptor sensitizer, whereas 1-methylnaphthalene, which is a good electron donor, had a slight quenching effect on the cycloaddition of carvone in 42% ethanol.

Laser flash photolysis of carvone in degassed 42% and degassed 100% ethanol at 355 nm led to the transient spectra shown in Figure 4. The absorption maximum is red-shifted 28 nm compared to the singlet—singlet absorption spectrum of the ground-state carvone, and the transient may be assigned as a triplet state of carvone (Malatesta et al., 1982). The lifetime of the carvone triplet was determined from the trace of absorbance at the absorption maximum (345 nm) versus time, cf. eq 1. Typical decays of the lowest triplet of carvone in neat, 80%, and 42% ethanol are shown in Figure 5. Equation 1 gave an adequate description of the time trace, and τ was found to increase with

Table 1. Quantum Yields at 25 °C of the Cycloaddition of Carvone (I) To Give Carvonecamphor (II) in the Presence of Triplet Quenchers

solvent	λ_{irr} (nm)	oxygen (%)	quencher	$\Phi_{I \to II}{}^{a}$ (mol·einstein^{-1})	$\Phi^{+}{}_{I \to II}/\Phi^{-}{}_{I \to II}{}^{b}$
42% ethanol	254	0		0.049	
	254	21		0.059	1.2
	313	0		0.044	
	334	0		0.060	
	366	21		0.043	
	366	21	piperylene[c,d]	0.052	1.2
	366	21	1-methylnaphthalene[e]	0.036	0.84
	366	21	diacetyl[f]	0.093	2.1
100% ethanol	254	0		0.0035	
	254	21		0.0032	1.1
	366	21		0.0034	
	366	21	piperylene[c]	0.0045	1.3
	366	21	1-methylnaphthalene[e]	0.0034	1.0
	366	21	diacetyl[f]	0.011	3.4

[a] Standard deviation on quantum yields was 15% or less. [b] Ratio between quantum yield for I → II with triplet quencher present and quantum yield for I → II without triplet quencher present. [c] 5.9×10^{-4} mol·L^{-1} piperylene, triplet energy, $E_T = 247$ kJ·mol^{-1} (Kellogg and Schwenker, 1964). [d] Piperylene had no quenching effect on the quantum yield, $\Phi_{I \to II}$, in the concentration interval 1.5×10^{-4} to 1.5×10^{-3} mol·L^{-1}. [e] 4.2×10^{-4} mol·L^{-1} 1-methylnaphthalene, triplet energy, $E_T = 254$ kJ·mol^{-1} (Lewis and Kasha, 1944). [f] 7.0×10^{-4} mol·L^{-1} diacetyl, triplet energy, $E_T = 236$ kJ·mol^{-1} (Lewis and Kasha, 1944; Sidmann and McClure, 1955).

Figure 5. Typical decays at 345 nm of the lowest excited triplet of carvone in 100%, 80%, and 42% ethanol. The carvone concentration was 1.3×10^{-4} mol·L^{-1} in degassed solutions, and 355 nm excitation was used.

k_{obs} is the rate coefficient for decay of excited triplet carvone in the presence of oxygen, k_0 is the rate coefficient for spontaneous decay of excited triplet carvone in the absence of oxygen, and [O$_2$] is the oxygen concentration. The k_{O_2} calculated from eq 7 for carvone in neat, 80%, and 42% ethanol are given in Table 2. We cannot currently explain the nonmonotonic dependence of k_{O_2} on ethanol concentration.

Sensory Importance of the Photocycloaddition of Carvone. Carvonecamphor had a camphor-like odor, and the odor of the ester we will describe as sweet. We found approximate odor thresholds of 2200−4100 ppb for carvonecamphor and 1.8−2.5 ppb for the ester by use of gas chromatographic effluent sniffing on the nonpolar column HP-1 (Table 3). Some differences in the flavor dilution factors were found between the four assessors: 4−16 for carvone and carvonecamphor and 5600−7800 for the ester. These differences are due to individual variation.

Some odorants are better resolved and less absorbed by polar than nonpolar columns or vice versa (Blank et
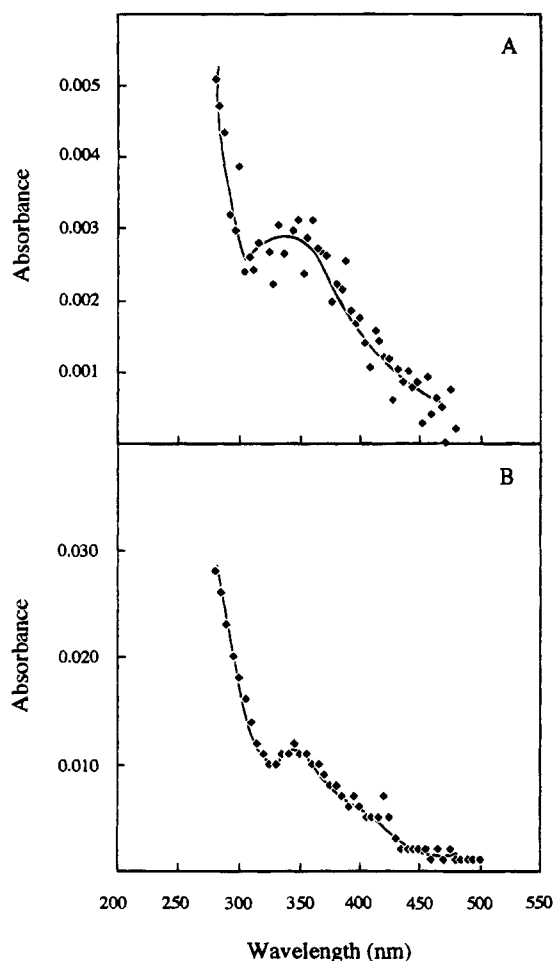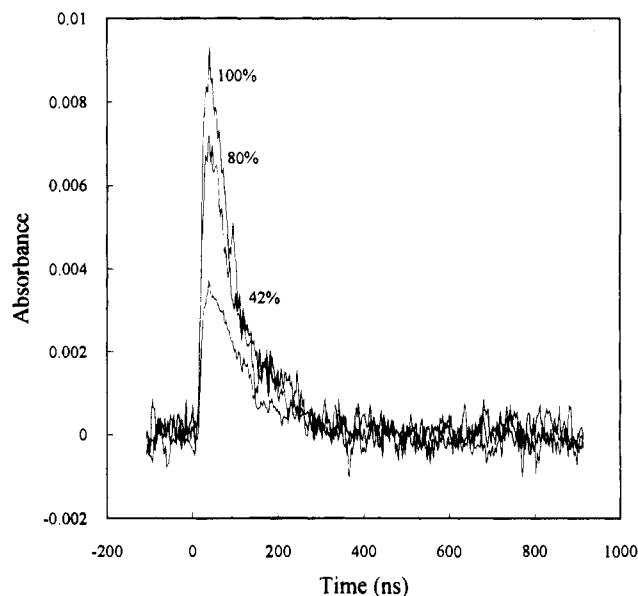
Figure 4. Transient absorption spectra of triplet carvone in (A) 42% ethanol and (B) 100% ethanol as obtained by laser flash photolysis spectroscopy 70 ns after laser flash. The carvone concentration was 1.3×10^{-4} mol·L^{-1} in degassed solutions, and 355 nm excitation was used.

decreasing ethanol content in ethanol−water mixtures (Table 2). In oxygen saturated neat ethanol, the lifetime was $\tau = 23.9 \pm 1.5$ ns, corresponding to an oxygen quenching rate constant, $k_{O_2} = 3.2 \times 10^9$ L·mol^{-1}·s^{-1} as calculated from

$$k_{obs} = k_0 + k_{O_2}[O_2] \qquad (7)$$

Photochemical Conversion of Carvone to Carvonecamphor

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Table 2. Lifetime of the Lowest Triplet Excited State of (+)-Carvone in Ethanol−Water Mixtures at 25 °C following Laser Flash Photolysis at 355 nm

ethanol (%)	$[O_2]^a \times 10^{-3}$ (mol·L^{-1})	τ (ns)	$k_{O_2}{}^b$ (L·mol^{-1}·s^{-1})
100			3.2×10^9
	0.0	70.9 ± 1.7	
	1.8	41.1 ± 0.9	
	8.3	23.9 ± 1.5	
80			1.5×10^{10}
	0.0	76.3 ± 1.5	
	0.25	59.0 ± 1.0	
	1.2	31.7 ± 1.8	
42			2.3×10^9
	0.0	98.0 ± 2.0	
	0.81	77.3 ± 1.4	
	3.9	52.6 ± 1.3	

^{a} Solubility data from Battino (1981). For other partial pressures of O_2 than 0.21 atm, it was assumed that Henry's law holds. ^{b} Oxygen quenching rate constants, k_{O_2}, calculated according to eq 7.

al., 1992), and therefore the sniffing analyses on the nonpolar column were repeated using a polar column (DB-Wax). The results obtained on the polar column were comparable with those reported in Table 3 for the nonpolar column. Carvone and its photoproducts could in general be detected by odor in lower concentrations on the nonpolar column than on the polar column.

DISCUSSION

Photochemical transformation of carvone to carvonecamphor and the ester will change the sensory impression of caraway-flavored products. Since quantum yields for transformation are moderately high, the ester with its low odor threshold will contribute to sensory changes during storage of caraway-flavored alcoholic beverages exposed to light. Moreover, the loss of carvone is itself undesirable in this type of product.

The odor threshold values determined according to the two methods described by Ullrich and Grosch (1987) and Drawert and Christoph (1984) are of the same magnitude. The large variation of the values is due to biological variation. Ullrich and Grosch (1987) recommend that the internal standard chosen should be a substance with an odor threshold value similar to that expected for the unknown. Although we did not expect similar thresholds for carvone and its photoproducts, we have used (+)-carvone as internal standard. The use of eq 2 was only expected to provide relative or approximative odor threshold values for carvonecamphor and the ester.

Whether the ester is a direct photoproduct of carvone or a photoproduct of carvonecamphor has been discussed. Zandomeneghi et al. (1980) and Malatesta et al. (1982) proposed that the ester is formed directly from carvone by exposure to light. However, both the con-
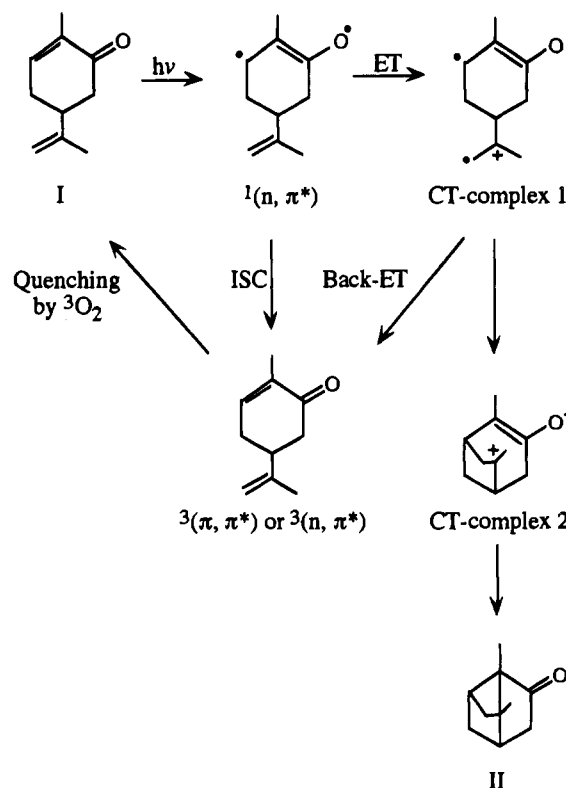

Figure 6. Proposed reaction sequence for photochemical conversion of carvone (**I**) to carvonecamphor (**II**) in ethanol and ethanol−water mixtures.

secutive kinetics shown in Figure 2 for the photoconversion and the fact that the ester was not formed by 334 and 366 nm irradiation of carvone, at which wavelengths carvonecamphor does not absorb light, indicate that the ester is formed from carvonecamphor rather than from carvone. Moreover, it is difficult to formulate a reaction mechanism that will account for a one-step rearrangement of carvone to yield the ester. By contrast, α-cleavage of the carbonyl group of carvonecamphor followed by intramolecular hydrogen abstraction to produce a ketene intermediate, which is then trapped by ethanol to give the ester, appears to be a plausible mechanism, cf. Figure 7 (Meinwald and Schneider, 1965).

Brackmann and Schäfer (1982) and Malatesta et al. (1982) have suggested that the triplet state of carvone is involved in the photochemical cycloaddition of carvone in ethanol. Conjugated dienes such as 2,5-dimethyl-2,4-hexadiene and 1-methylnaphthalene were reported to quench triplet carvone (Zandomeneghi et al., 1980; Malatesta et al., 1982). We have found that the rate constant for quenching of excited triplet carvone by oxygen is 3.2×10^9 L·mol^{-1}·s^{-1} in neat ethanol (Table 2), which is close to the diffusion limit. This value is comparable to 2.5×10^9 L·mol^{-1}·s^{-1} obtained for 1-meth-

Table 3. Approximate Odor Thresholds for Carvonecamphor and the Ester Determined by Aroma Extract Dilution Analysis

	RI^a		FD^b				concn (g·L^{-1})	$T_x{}^c$ (ppb)	AS^d (ppb)	odor description
	np	p	assessor 1	assessor 2	assessor 3	assessor 4				
carvonecamphor	836	1037	16	12	4	6	0.291	2200 ± 190	4100 ± 2500	camphor-like
S-(+)-carvone	929	1228	16	10	4	6	0.0109	85^e	158 ± 90	caraway
ester	1019	1118	7800	7000	7200	5600	0.169	1.8 ± 0.55	2.5 ± 0.37	sweet

^{a} Retention indices on np (nonpolar HP-1) column and p (polar DW-Wax) column calculated as described under Materials and Methods. ^{b} Flavor dilution factors by use of the nonpolar HP-1 column. ^{c} Approximate odor threshold values determined from eq 2. ^{d} Approximate odor threshold values determined from eq 3 and by use of 100 mL as an arbitrary respiration volume per stimulus (Drawert and Christoph, 1984). ^{e} Odor threshold for (+)-carvone in water (Leitereg et al., 1971).
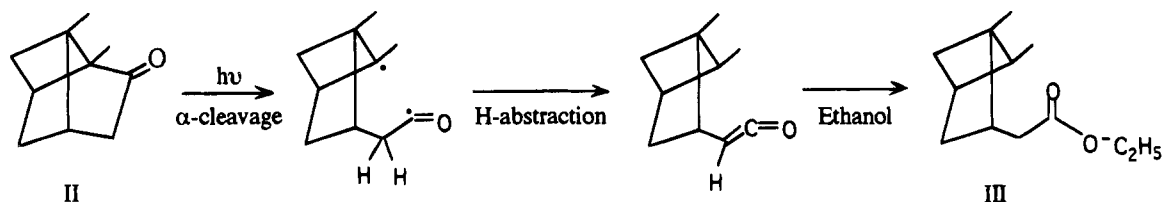
Figure 7. Reaction sequence for photoinduced formation of the ester (**III**) from carvonecamphor (**II**) (Meinwald and Schneider, 1965).

ylnaphthalene quenching of triplet carvone in neat ethanol (Malatesta et al., 1982). We found that the triplet quenchers oxygen, diacetyl, and piperylene, which all have smaller triplet energies (E_T) than carvone (259 kJ·mol^{-1}; Malatesta et al., 1982), had no quenching effect on the degradation and conversion quantum yields of carvone (Table 1) in contrast to the effect of the lifetime of the triplet state. This provides strong evidence for a mechanism in which the internal cyclization takes place from an excited singlet state.

Tsipi et al. (1987) have also reported that oxygen does not quench the photocycloaddition and propose accordingly that the nπ^* singlet state is responsible for the photocyclic reaction of carvone in water−ethanol mixtures. The assignment of singlet reactivity is further substantiated by the observed hypsochromic shift of the n → π^* transition for decreasing ethanol content in the mixture. The concomitant increase in molar absorptivity may result from charge transfer from the isolated double bond, which becomes more favorable as the solvent polarity increases.

Exciplex formation might explain the more efficient photoconversion of carvone to carvonecamphor with increasing polarity of the solvent. The normal temperature dependence of the quantum yields, i.e., a moderate increase with increasing temperature, corresponding to an apparent energy of activation of 19 kJ·mol^{-1} as determined in the present study, suggests, however, that formation of an exciplex was not involved in the conversion. We propose that the enhanced quantum yields of product formation in the presence of diacetyl (Table 1) are due to an electron transfer reaction between excited-state diacetyl and ground-state carvone.

A mechanism for the carvone transformation based on our present observations is shown in Figure 6. Carvone is excited by light absorption, and an nπ^* singlet state of carvone is formed immediately. The excited singlet can by electron transfer be converted to the charge transfer CT-complex 1 shown in Figure 6. CT-complexes will be stabilized by increasing polarity of the solvent, i.e., by increasing water content of a water−ethanol mixture. Specifically, increasing polarity will stabilize CT-complex 2 relative to the carvone triplet state. Hence, an increase in solvent polarity will make the rate constant of conversion of CT-complex 1 to CT-complex 2 increase but cause the rate constant of back-ET to decrease. As a result, the quantum yield $\Phi_{I \rightarrow II}$ will increase with increasing solvent polarity. The cycloaddition is, however, only a minor decay route for the ^{1}(n, π^*)-state process during which the tricyclic carvonecamphor is formed, as evidenced by the moderately small photoreaction quantum yields. In contrast, the intersystem crossing quantum yield (singlet → triplet) is close to unity for carvone (Malatesta et al., 1982).

On the basis of the combined photophysical and photochemical investigations of carvone, it may be

concluded that addition of herbs with natural triplet quenchers, such as carotenoids, or exclusion of oxygen from carvone-containing foods or beverages will have no effect in preventing the photochemical conversion of carvone to carvonecamphor. A direct prevention of photocycloaddition of carvone is possible by exclusion of light at wavelengths below 380 nm by use of glass with UV absorber incorporated. It should also be noted that the photochemical conversion of carvone to carvonecamphor is slowed by decreasing polarity, i.e., by increasing alcohol percentage in aquavit.

LITERATURE CITED

Battino, R. Oxygen and Ozone. In *Solubility Data Series*; Pergamon: Oxford, England, 1981; Vol. 7, pp 196−197.

Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1967.

Blank, I.; Grosch, W. Evaluation of potent odorants in dill seed and dill herb (*Anethum graveolens L.*) by aroma extract dilution analysis. *J. Food Sci.* **1991**, *56* (1), 63−67.

Blank, I.; Sen, A.; Grosch, W. Potent odorants of the roasted powder and brew of Arabica coffee. *Z. Lebensm. Unters. Forsch.* **1992**, *195*, 239−245.

Brackmann, U.; Schäfer, F. P. Photocyclization of carvone to carvone camphor using rare gas halide laser. *Chem. Phys. Lett.* **1982**, *87* (6), 579−581.

Ciamician, C.; Silber, P. Chemical effects of light. *Chem. Ber.* **1908**, *41*, 1928−1935.

Czygan, F.-C. Kümmel. In *Teedrogen, Ein Handbuch für die Praxis auf wissenschaftlicher Grundlage*; Wichtl, M., Ed.; Wissenschaftliche Verlagsgesellschaft: Stuttgart, Germany, 1989; pp 292−293.

Dool, H. V. D.; Kratz, P. D. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *J. Chromatogr.* **1963**, *11*, 463−471.

Drawert, F.; Christoph, N. Significance of the sniffing-techique for the determination of odour threshold and detection of aroma impacts of trace volatiles. In *Analysis of Volatiles*; Schreier, P., Ed.; de Gruyter: Berlin, Germany, 1984; pp 269−291.

Franke, J. P.; Bogusz, M.; de Zeeuw, R. A. An overview on the standardization of chromatographic methods for screening analysis in toxicology by means of retention indices and secondary standards. *Fresenius' J. Anal. Chem.* **1993**, *347*, 67−72.

Hatchard, C. G.; Parker, C. A. A new sensitive chemical actinometer II. Potassium ferrioxalate as a standard chemical actinometer. *Proc. R. Soc. London A* **1956**, *235*, 518−536.

Kellogg, R. E.; Schwenker, R. P. "Temperature effect" on triplet state lifetimes in solid solutions. *J. Chem. Phys.* **1964**, *41* (9), 2860−2863.

Leitereg, T. J.; Guadagni, D. G.; Harris, J.; Mon, T. R.; Teranishi, R. Evidence for the difference between the odours of the optical isomers (+)- and (−)-carvone. *Nature* **1971**, *230*, 455−456.

Lewis, G. N.; Kasha, M. Phosphorescence and the triplet state. *J. Am. Chem. Soc.* **1944**, *66*, 2100–2116.

Malatesta, V.; Willis, C.; Hackett, P. A. Laser-induced cycloadditions: The carvone photoisomerization. *J. Org. Chem.* **1982**, *47*, 3117–3121.

Meinwald, J.; Schneider, R. A. Photochemical synthesis and reactions of carvonecamphor. *J. Am. Chem. Soc.* **1965**, *87* (22), 5218–5229.

Meinwald, J.; Schneider, R. A.; Thomas, A. F. Stereospecific hydrogen transfer in the photolysis of carvonecamphor. *J. Am. Chem. Soc.* **1967**, *89* (1), 70–73.

Ndiaye, S. A.; Aaron, J. J. Photoisomerization of carvone: Solvent dependence and evaluation for the photochemical storage of light energy. *J. Photochem. Photobiol. A: Chem.* **1989**, *49*, 259–268.

Refsgaard, H. H. F.; Brockhoff, P. M.; Poll, L.; Olsen, C. E.; Rasmussen, M.; Skibsted, L. H. Light Induced Sensory and Chemical Changes in Aquavit. *Lebensm. Wiss. Technol.* **1995**, in press.

Sidman, J. W.; McClure, D. S. Electronic and vibrational states of biacetyl and biacetyl-d_6. I. Electronic states. *J. Am. Chem. Soc.* **1955**, *77* (4), 6461–6470.

Tsipi, D.; Gegiou, D.; Hadjoudis, E. The intramolecular photocycloaddition carvone → carvonecamphor. *J. Photochem.* **1987**, *37*, 159–166.

Ullrich, F.; Grosch, W. Identification of the most intense volatile flavour compounds formed during autoxidation of linoleic acid. *Z. Lebensm. Unters. Forsch.* **1987**, *184*, 277–282.

Zandomeneghi, M.; Cavazza, M.; Moi, L.; Pietra, F. Laser photochemistry: The intramolecular cyclization of carvone to carvonecamphor. *Tetrahedron Lett.* **1980**, *21*, 213–214.