Photochemical Reaction of (Z)-Jasmonate under Various Conditions

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(Z)-Jasmonate (1) was irradiated with a 400 W high-pressure mercury lamp under various conditions. Under nitrogen, 1 was converted to the (E)-isomer (2), to di-π-methane rearrangement products (3 and 4) and intramolecular cyclo-adducts (5 and 6) in methanol and ethanol, and to 2, 3, and 4 in ethyl acetate. Under oxygen, 1 was broken down to hydroperoxides (7 and 8), its reduction products (9 and 10), and dehydrates (11 and 12). These compounds were further photooxidized to yield compounds 13—17, 19, and 20 in methanol or ethanol. In ethyl acetate, an intramolecular cyclo-adduct (22) was obtained, together with a diol (21) and photoreaction products 23 and 24, and 11, 13—18, and 20. Hydroperoxides (7 and 8) and their reduction products (9 and 10) were obtained by a photosensitized reaction with rose bengal under oxygen. (Z)-Jasmonate was converted to 2 so rapidly that suppressing the photoisomerization of 1 was difficult, except by cutting off the UV light.

(Z)-Jasmonate (1), which expresses a jasmine-like odor (diffuse warm-spicy and somewhat fruity when neat, and floral when diluted), is the principal aroma component in Jasmine oil, which is also one of the most popular natural materials for flavors and fragrances. Volatile-photosensitive compounds, which contribute to the odor of essential oils, flavors and fragrances, have often been observed. α,β-Unsaturated carbonyl compounds, which often generate the characteristic aroma, should affect the odor of an essential oil by photo-deterioration. It has been reported that citral in lemon oil was converted to cyclocitrinal, and that carvone in spearmint oil and nootkatone in grapefruit oil were also changed to intramolecular cyclo-adducts. However, these have only been studied under limited conditions. We reported earlier the photoreactions of nootkatone and perillaldehyde under various conditions which could simulate the actual application system. Jasmine oil is also photosensitive, and we have reported that the photoreaction of 1 gave (E)-Jasmonate (2), and di-π-methane rearrangement products 3 and 4 in ethanol under nitrogen. The warm-spicy, floral and fruity odor of 1 was changed to a floral and fruity note when 1 was isomerized to 2, and then a marked metallic note appeared in ethanol.

We report here the photoreaction of 1 under various conditions, in methanol or ethanol as protic solvents and in ethyl acetate as an aprotic solvent, in the absence of oxygen and dye, and in the presence of oxygen and/or dye. The photoproducts and photoreactivity of 1 are clarified, and we will discuss how 1 can be stabilized against light.

**Photoreaction of 1 under nitrogen**

Under nitrogen, 1 was irradiated by UV and visible light in methanol. The conversion of 1 and 2 in methanol (69%) was similar to that in ethanol (68%) after 20 h of photoirradiation as shown in Table 1 (entries 1 and 7). However, the conversion increased in ethyl acetate (83%)

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</table>

1. RB, rose bengal. 2. Calculated from the recovery of 1 and 2. 3. Diastereoisomers (4:1). 4. P, high molecular weight products (MW ≥350), % by weight. 5. Irradiation for 5h. 6. ≥435 nm, conversion of 1. 7. Containing the ester derivatives.

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entry 10). After the reaction mixture had been subjected to repeated chromatography (GPC and silica gel TLC), 3 (23%), 4 (18%), 5a (7%), 6a (2%), and 2, together with unreacted 1 (31%), were isolated (entry 1). By the same procedure as that just mentioned, 3 (28%), 4 (22%), 5b (7%), 6b (2%), and 2, together with unreacted 1 (32%), in ethanol, and 3 (42%), 4 (29%), and 2, together with unreacted 1 (17%), in ethyl acetate were isolated (entries 7 and 10). The molecular weight of the residue (P) was presumed to be ≥350 by gel filtration with HPLC on a JAIKEL-1H column, using polystyrene gel as the standard for calibration. The structure of each product was deduced from spectroscopic data as described later.

In each solvent, 1 was mainly converted to E-isomer 2 via an excited triplet state at first, and then 1 and 2 to the cyclopropyl derivatives (3 and 4) through di-π-methane rearrangement (entries 1, 7, and 10, and Fig. 1). Additionally, the intramolecular cyclo-adduct (B) would have been obtained, which was converted to octahydroptalene (5a or 5b) by solvent addition in the protic solvents (entries 1 and 7). Compounds 5a and 5b were obtained regio- and stereo-selectively. As 6a was obtained by photoradiating 5a, 5a and 5b were presumably converted to esters 6a and 6b via a biradical (C), and via a ketene (D) by a Norrish type 1 reaction.

**Photoreaction of 1 under oxygen**

Under oxygen, the conversion of 1 and 2 was increased in less-polar solvents (69% in methanol, 76% in ethanol, and 99% in ethyl acetate; entries 2, 8, and 11). Subsequent separation gave 3 (2%), 4 (1%), 5a (2%), 7 (1%), 8 (1%), 9 (2%), 10 (1%), 11 (5%), 12 (1%), 13 (3%), 14 (4%), 15 (6%, an acid (a) and ester (b)), 16 (3%), 17 (4%), 19 (1%), and 20 (10%, an acid (a) and ester (b)) in methanol (entry 2), whereas 3 (2%), 4 (1%), 5b (2%), 7 (1%), 8 (1%), 9 (2%), 10 (1%), 11 (5%), 12 (1%), 13 (2%), 14 (2%), 15 (4%, an acid (a) and ester (c)), 16 (3%), 17 (3%), 19 (2%), and 20 (11%, an acid (a) and ester (c)) were obtained in ethanol from 1 (entry 8). Products 21 (13%), 22 (4%), 23 (3%), and 24 (2%) were obtained in addition to 11 (8%), 13 (5%), 14 (5%), 15a (4%), 16 (1%), 17 (2%), 18 (1%), and 20a (7%) in ethyl acetate (entry 11).

(Z)-Jasmonate would have been oxygenated with a triplet oxygen via the excited triplet state of 1 to give a Schenck-type intermediate (E), which was then converted to hydroperoxides 7 and 8 by hydrogen abstraction in the protic solvent (entries 2 and 8, and Fig. 2). Hydroperoxides 7 and 8 were next converted to reduction products 9 and 10, and to dehydrates 11 and 12 in that solvent system, respectively. The reaction route for the photoproducts is presumed to be that mentioned later by the photoreaction of 9, 10, 12, 13, 14, and 21. Product 9 was photooxidized to give 13 and 14, which were further converted to 15—17, 20, and 18—20, respectively. Compound 10 was also photooxidized to give 15 and 17, while diketone 12 was changed to 15 and 16 by photooxidation. In ethyl acetate, a diastereomixture of diol 21 would have been obtained by the hydrolysis of an epoxide (G), which was derived from a Schenck-type intermediate (E) via F, in addition to 11, 13—18, and 20 (entry 11, and Fig. 3). An intramolecular cyclization reaction of 1 should also have occurred between the carbonyl group and double bond of the pentenyl
group. Compound 22 would then be formed by further oxidative cleavage of the cyclopentene ring. Under nitrogen, Z-E isomerization and a di-π-methane rearrangement reaction were preferable to the other reactions in every solvent. On the other hand, oxetane production proceeded in ethyl acetate under oxygen, despite the di-π-methane rearrangement reaction being suppressed by a triplet oxygen. Compounds 23 and 24 were obtained from 21 by photoirradiation and acetylation with Ac₂O/pyridine.$^{13}$

**Photosensitization of 1 with Rose Bengal (RB)**

Although 1 did not react under nitrogen (entry 4), 72% of 1 was degraded under oxygen (entry 5) by visible light irradiation (≥435 nm which did not excite 1 directly) for 20h in the presence of RB. The reaction mixture was subjected to column chromatography and TLC on silica gel to isolate 7 (30%), 8 (18%), 9 (5%), and 10 (5%; entry 5, and Fig. 2).

Hydroperoxides 7 and 8 were obtained by the ene reaction of 1 with a singlet oxygen. These hydroperoxides (7 and 8) were then reduced to 9 and 10. A comparison of the conversion in entry 6 (photoirradiation for 5h) with entries 3, 9, and 12 indicates that the jasmones were degraded relatively quickly in the presence of RB under oxygen. Thus, the RB photosensitization reaction for 20h would have slowed because of the dye-deterioration. In entries 2, 8, and 11, it is clear that 7 and 8 were not obtained by the photosensitized oxygenation reaction because there was no inhibition of the reaction by singlet oxygen quenchers.$^{14}$

**Structural elucidation of the photoproducts**

By high-resolution mass spectrometry (HRMS), the molecular formula of 5a was deduced to be C$_{12}$H$_{20}$O$_2$, which is equivalent to the methanol adduct of 1. Carbonyl (1735 cm$^{-1}$) and C-O (1105) absorption bands were observed in the IR spectrum. In the $^1$H-NMR spectrum of 5a, a pair of signals from the olefinic protons and olefinic
Photochemical Reaction of (Z)-Jasmone

Fig. 3. Proposed Reaction Pathways from 1 in EtOAc under Oxygen.

Fig. 4. NOEs (⦁) of Compounds 5a, 22, and 23.
methyl proton signals of 1 disappeared. Signals of a methine group (δ 3.31), which was substituted with a methoxy group (3.29), a methine group (1.59) substituted with an ethyl group [1.04 (t) and 1.50 (m)], an α-methylene proton (2.29) of a carbonyl group, and a methyl group (1.25) attached to a quaternary carbon were newly observed. These data suggested 5a to be an octahydropentalenone as shown in Fig. 1.† The stereochemistry was confirmed by a NOESY experiment (Fig. 4). A signal for 3a-CH3 showed an NOE cross peak to 6a-H, revealing that an octahydropentalenone ring was cis-fused. NOEs observed between 3a-CH3 and 2β-H, and between 6a-H and 6β-H supported this result. A signal for 5-H showed NOE cross peaks to 3z-H, 6z-H, and 4-CH2, revealing the cis relationship of 3a-CH3 and 4-CH2, and the cis relationship of 3a-CH3 and 5-CH2.

By HRMS, the molecular formula of 6a was calculated as C13H22O3, which is equivalent to the two molar methanol adduct of 1. The IR spectrum showed carbonyl (1740 cm⁻¹) and C-O (1180 and 1100 cm⁻¹) absorption bands. The presence of a methyl ester [δ 51.6 (q) and 174.8 (s)] and a methyl ether [δ 56.8 (q) and 88.6 (d)] were confirmed by the 13C-NMR spectrum. In the 1H-NMR spectrum, a methyl group (δ 3.67) and a methylene group (2.24) of a methyl ester, a singlet methyl (0.99), a methine group (1.38) substituted with an ethyl group, a methine group (3.46) substituted with a methoxy group (3.28), and a methylene group (1.60 and 1.87) were observed. These spectral data indicated 6a to be a methyl ester as shown in Fig. 1.

The structures of 5b and 6b were similar to those of 5a and 6a, except for the methoxy group altered to an ethoxy group.

The structures of 7—14 and 17 were easily deduced from spectroscopic data to be similar to 1 as shown in Table II (Fig. 2). Compounds 15a—c, 16, 18, 19, 20a—c, and 21
The molecular formula of 24 was the same as that of 23. Although most of the spectral data were similar to those for 23, signals for two acetoxyethylated methine protons (δ 4.98 and 5.11) and a methyl proton (1.46) attached to a quaternary carbon were observed in the 1H-NMR spectrum. Thus, 24 was determined to be an epoxide of diacetate 21. All of the spectral data for 24 were consistent with those derived from 21 by acetylation and epoxidation.  

The stereochemistry of the acetoxy group was not determined.

Conclusion

We clarified the photoactivity of (Z)-jasmonate (1) under various conditions. Photoisomerization of 1 and 2 could be prevented only by cutting off the light. Further photodegradation of 1 and 2, which expressed a similar odor to each other, was presumed to have mainly occurred by a light-induced radical reaction, the conversion being low in a protic solvent under nitrogen. Thus, photolysis of 1 and 2 would have been controlled in protic solvents without oxygen or by the addition of radical scavengers. In the presence of RB, the deterioration of 1 would be potentially suppressed under nitrogen or by adding singlet oxygen quenchers under oxygen.

Experimental

Reagent and apparatus. (Z)-Jasmonate (1) was purified to 97% (GC) by HPLC (GPC). NMR spectra were obtained in CDCl3 with TMS as an internal standard on a Bruker AM 400 spectrometer. The 13C and 1H-NMR spectral signal assignments of 5–24 were made on the basis of homo- and heteronuclear COSY and J-spectra. IR spectra were measured with a Hitachi 260-10 spectrometer, and mass spectra were recorded at 20 eV with a Hitachi M-80B spectrometer. Isolation of the photoproducts was performed by HPLC with a JAIKC-80R[JAIigel-1H column (Japan Analytical Industry), 20 mm diameter, 60 mm; CHCl3 solvent at 3 ml/min]. HPLC analyses were performed on an HP 1090 HPLC instrument equipped with a photodiode array detector. The photolysis was monitored by reverse-phase HPLC with a CAPCELL PAK C18 5 μm)-column (SHISEIDO, 4.6 mm diameter, 250 mm), using a constant elution gradient from 10% (v/v) CH3CN in water to CH3CN at a constant flow rate of 1 ml/min. GC analyses were carried out on a Hitachi 163 gas chromatograph equipped with a carbawax 20M capillary column (0.25 mm i.d. × 50 m).

Photoreaction of 1 under nitrogen. An MeOH solution (300 ml) containing 1 (1 g) and irradiated for 20 h under a stream of nitrogen with a water-cooled 400 W high-pressure mercury lamp (Riko UVL-400HA) in a Pyrex container. After evaporation of the solvent, the residual oil was subjected to HPLC. The eluate was fractionated to FA-1 (1:250, 350, 230–230) and FA-4 (<180). A colorless oil 6a (33 mg) was purified from FA-2, which was subjected to silica gel TLC (EtOAc-n-hexane = 1:1). Compound 5a (87 mg) was isolated from FA-3 as a colorless oil, while FA-4 was chromatographed on silica gel (EtOAc-n-hexane (1:5) to give 3 (200 mg); Rf = 0.48) and an Rf = 0.38 fraction, which was separated to yield 4 (180 mg), 1 and 2 (310 mg) by HPLC. No further purification of 1 and 2 was carried out. EtOH and ETOAc solutions of 1 were treated by the same method as that just described, the yield of each product being shown in Table I.

Octahydrotropolone (5a). HR-El-MS m/z (M+): calcd. for C17H22O5, 292.1643; found, 292.1479; IR [cm-1] νmax (film): 1735, 1105, 990; NMR δH (CDCl3, δ) 1.04 (3H, t, J = 7.4 Hz), 1.25 (3H, s), 1.50 (2H, m), 1.59 (IH, 0.7, 8.0, 8.3 Hz), 1.60 (1H, ddd, J = 1.3, 3.2, 9.3, 13.3 Hz), 1.75 (1H, ddd, J = 1.3, 11.2, 13.3 Hz), 1.81 (1H, ddd, J = 7.5, 11.1, 13.3 Hz), 2.12 (1H, ddd, J = 4.6, 6.9, 13.3 Hz), 2.24 (1H, ddd, J = 3.2, 8.3, 18.3 Hz), 2.29 (1H, m), 2.40 (1H, ddd, J = 1.3, 9.3, 11.2, 18.3 Hz), 3.29 (3H, s), 3.31 (1H, ddd, J = 6.9, 7.5, 8.0 Hz); NMR δC (CDCl3): 13.5 (q), 21.5 (t), 27.7 (q), 29.4 (t), 32.9 (q), 37.8 (t), 48.1 (s), 56.9 (d), 57.2 (d), 57.3 (q), 87.1 (d), 221.2 (s).

Octahydrotropolene (5b). HR-El-MS m/z (M+): calcd. for C16H22O4, 270.1447; found, 270.1479; IR [cm-1] νmax (film): 1735, 1105, 990; NMR δH (CDCl3, δ) 1.04 (3H, t, J = 7.4 Hz), 1.25 (3H, s), 1.50 (2H, m), 1.59 (IH, 0.7, 8.0, 8.3 Hz), 1.60 (1H, ddd, J = 1.3, 3.2, 9.3, 13.3 Hz), 1.75 (1H, ddd, J = 1.3, 11.2, 13.3 Hz), 1.81 (1H, ddd, J = 7.5, 11.1, 13.3 Hz), 2.12 (1H, ddd, J = 4.6, 6.9, 13.3 Hz), 2.24 (1H, ddd, J = 3.2, 8.3, 18.3 Hz), 2.29 (1H, m), 2.40 (1H, ddd, J = 1.3, 9.3, 11.2, 18.3 Hz), 3.29 (3H, s), 3.31 (1H, ddd, J = 6.9, 7.5, 8.0 Hz); NMR δC (CDCl3): 13.5 (q), 21.5 (t), 27.7 (q), 29.4 (t), 32.9 (q), 37.8 (t), 48.1 (s), 56.9 (d), 57.2 (d), 57.3 (q), 87.1 (d), 221.2 (s).

Table III. NMR Spectral Data for 22

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Photoreaction of 1 in MeOH and EtOH under oxygen. After photoradiation 1 in MeOH under a stream of oxygen, the reaction mixture was treated by the same method as that already described, and 3 (18 mg), 4 (11 mg), 5 (20 mg), 7 (14 mg), 8 (10 mg), 9 (20 mg), 10 (8 mg), 11 (55 mg), 12 (7 mg), 13 (38 mg), 14 (46 mg), 15a (16 mg), 15b (37 mg), 16 (24 mg), 17 (30 mg), 19 (6 mg), 20a (37 mg), and 20b (36 mg) were all isolated as oils, except for 11 (mp 44–46°C) by HPLC (CHCl3) and silica gel TLC [EtOAc–n-hexane (2:1)]. By the same method as that used with MeOH, 3–5, 7, 17–19, and 20 were isolated from EtOH.

Photoreaction of 1 in EtOAc under oxygen. Under the same conditions as those used with MeOH, compounds 11 (83 mg), 15c (14 mg), 15a (35 mg), 16 (7 mg), 17 (13 mg), 18 (9 mg), 20a (52 mg), 21 (160 mg), 22 (a colorless oil, 53 mg), and residues (66 mg) were isolated by HPLC (CHCl3) and silica gel TLC [EtOAc–n-hexane (2:1)]. The residues were acetylated with Ac2O/pyridine and subsequently isolated by silica gel TLC [EtOAc–n-hexane (1:1)] to give 23 (33 mg) and 24 (28 mg) as oils.

Oxibicyclohexane (22). HR-ESI-MS m/z (M+): calculated for C29H37O2, 496.2688; found, 496.2692.

21. Dio1 (21) (10 mg) was acetylated with Ac2O/pyridine and then epoxidized with m-chloroperbenzoic acid to give 24 (6 mg).

Photoreaction of 5a, 9, 10, 12, 13, 14, and 21. Each compound (5a in MeOH under nitrogen; 9, 10, 12, 13, and 14 in MeOH under oxygen; 21 in EtOAc under oxygen; each 5–10 mg) was irradiated with a 400 W high-pressure mercury lamp for 2–7 h in a Pyrex tube (12 mm i.d. × 150 mm). After concentrating, the reaction mixture was analysed by GC/MS and HPLC and H-NMR.

Photossensitization with RB. An MeOH solution (300 mL) containing 1 (1.0 g) and RB (0.05 g) was irradiated with light at above 435 nm (400 W high-pressure mercury lamp; 33 mKNO3 solution of 1 cm thickness as a filter) for 20 h under a stream of O2. The solvent was removed, and the residual mixture was subjected to silica gel TLC with EtOAc–n-hexane (1:1). Compounds 7 (358 mg, Rf = 0.28), 8 (220 mg, Rf = 0.36), 9 (50 mg, Rf = 0.17), and 10 (57 mg, Rf = 0.13) were isolated.

References