some other C_9 components, e.g., (*Z*)-6-nonenal or (*Z*)-6-nonenyl acetate, which were described by Buttery et al. (1982) to possess strong melon-like aroma far below the level of detection used in this study, seems probable.

Registry No. 1, 629-59-4; 2, 544-76-3; 3, 593-45-3; 4, 112-95-8; 5, 71-43-2; 6, 108-88-3; 7, 80-56-8; 8, 127-91-3; 9, 123-35-3; 10, 138-86-3; 11, 3338-55-4; 12, 3779-61-1; 13, 586-62-9; 14, 3856-25-5; 15, 489-40-7; 16, 87-44-5; 17, 6753-98-6; 18, 23986-74-5; 19, 24703-35-3; 20, 473-13-2; 21, 39029-41-9; 22, 483-76-1; 23, 623-42-7; 24, 141-78-6; 25, 97-62-1; 26, 105-54-4; 27, 108-64-5; 28, 123-66-0; 29, 106-32-1; 30, 110-38-3; 31, 106-33-2; 32, 124-06-1; 33, 628-97-7; 34, 123-86-4; 35, 109-21-7; 36, 626-82-4; 37, 110-19-0; 38, 539-90-2; 39, 123-92-2; 40, 106-27-4; 41, 142-92-7; 42, 2639-63-6; 43, 3681-71-8; 44, 3681-82-1; 45, 2497-18-9; 46, 33467-74-2; 47, 16491-36-4; 48, 103-45-7; 49, 85762-16-9; 50, 85762-17-0; 51, 65405-80-3; 52, 85762-18-1; 53, 53398-87-1; 54, 5405-41-4; 55, 2305-25-1; 56, 53605-94-0; 57, 85762-19-2; 58, 85762-20-5; 59, 85762-21-6; 60, 96-22-0; 61, 66-25-1; 62, 6728-26-3; 63, 1335-39-3; 64, 110-43-0; 65, 18829-56-6; 66, 557-48-2; 67, 593-08-8; 68, 98-01-1; 69, 100-52-7; 70, 122-78-1; 71, 432-25-7; 72, 23726-93-4; 73, 79-77-6; 74, 71-36-3; 75, 78-92-2; 76, 78-83-1; 77, 556-82-1; 78, 115-18-4; 79, 71-41-0; 80, 6032-29-7; 81, 123-51-3; 82, 111-27-3; 83, 928-96-1; 84, 928-97-2; 85, 928-95-0; 86, 36653-82-4; 87, 60-12-8; 88, 98-55-5; 89, 138-87-4; 90, 78-70-6; 91, 1197-06-4; 92, 1197-07-5; 93, 19888-33-6; 94, 19888-34-7; 95, 1139-30-6; 96, 489-41-8; 97, 552-02-3; 98, 21284-22-0; 99, 481-34-5; 100, 50895-55-1; 101, 16641-47-7; 102, 96-48-0; 103, 108-29-2; 104, 695-06-7; 105, 104-50-7; 106, 698-76-0; 107, 82373-92-0; 108, 706-14-9; 109, 705-86-2; 110, 513-86-0; 111, 4077-47-8; 112, 2628-17-3; 113, 71750-42-0; 114, 95-16-9.

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Deterioration Mechansim of Lemon Flavor. 2. Formation Mechanism of Off-Odor Substances Arising from Citral

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p-Mentha-1,5-dien-8-ol (**3a**) and *p*-mentha-1(7),2-dien-8-ol (**3b**) were isolated from deteriorated citral as major components and were identified by IR, EI-MS, FI-MS, ^{1}H NMR, and ^{13}C NMR. When **3a** or **3b** was treated with aqueous citric acid, an equlibrium mixture of **3a**–**3b** isomers (55:45) resulted and both isomers were subsequently converted to *p*-cymen-8-ol (**6**) by disproportionation and redox reactions. Further, the more stable *p*-cymene (**9**) and α,*p*-dimethylstyrene (**8**), which are responsible for the off-odor of deteriorated lemon, were formed from **3** and **6**. This deterioration mechanism was also confirmed by mass chromatography studies. The existence of *p*-menth-1-ene-3,8-diol (extremely unstable in acidic conditions) was suggested by isolation of 3-ethoxy-*p*-menth-1-en-8-ol (**4**).

So far, studies on the fate of citral under acidic conditions have been carried out in connection with the deterioration flavor of alcoholic lemon beverages or concentrated lemon juice (Iwata et al., 1968; Iwata and Yamamoto, 1978; Kimura and Iwata, 1978a,b; Kimura et al., 1981, 1982). Citral, one of the significant components of lemon oil (Ikeda et al., 1962; Lund and Bryan, 1976), was rapidly cyclized to give *p*-cymene (**9**) and α,*p*-dimethylstyrene (**8**) in Scheme I, which are responsible for lemon off-odor (Iwata and Yamamoto, 1978).

Compound **8** has been isolated and identified as an acid-catalyzed cyclization product of citral and in the distilled essential lime oil (Loori and Cover, 1964; Slater and Watkins, 1964).

These have been several recent publications on the cyclization of citral (Baines et al., 1970; Clark et al., 1977; McHale et al., 1979). However, unequivocal evidence to confirm the deterioration mechanism still appears to be lacking, since pure compounds (**3a** and **3b**) were not used to precisely elucidate the individual pathway. We deal here with the detailed identification of intermediates of off-odor substances arising from citral and with the further fate of such intermediates in an aqueous citric acid solution.

EXPERIMENTAL SECTION

Instrumentation. Analyses by gas–liquid chromatography (GLC) were performed on a JEOL JGC-20KFP equipped with glass capillary SCOT column (30 m × 0.28 mm i.d.), coated with DEGS. The oven temperature was programmed from 50 to 160 °C at 3 °C/min. The injector

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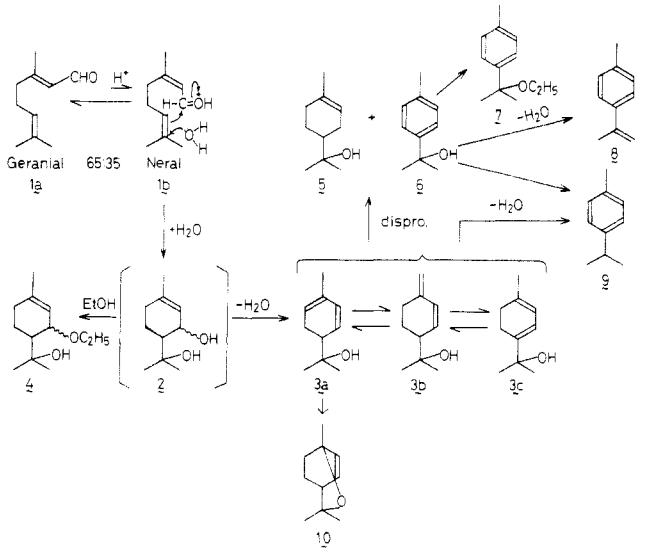
Scheme I. Deterioration Mechanism of Citral in an Acid Aqueous Solution



and detector were maintained at 250 °C. A flow rate of 1.25 mL/min nitrogen was employed. GC–mass spectra were determined on a JEOL JMS-D300 spectrometer at an ionizing voltage of 30 eV. Mass chromatography (MC) was carried out by using a JEOL JMA-2000 mass data analysis system. Field ionization mass spectra were measured on JEOL JMS-01SG-2 spectrometer. IR spectra were recorded on a Hitachi IR spectrometer, Model 285. NMR spectra were obtained on a JEOL FX-200 FT with ^1H NMR at 200 MHz and ^{13}C NMR at 50 MHz. HPLC analyses were carried out with a Shimadzu LC-3A equipped with the SPD-1 UV-detector (254 nm) on a ZORBAX SIL (15 cm × 4.6 mm i.d.) column. The solvent was *n*-hexane–isopropyl alcohol (98:2 v/v) and the flow rate was 1.5 mL/min.

Extraction and Isolation. Citral (6 g) in 30 mL of ethanol was shaken with 160 mL of 5% citric acid solution (pH 1.8) at 38 °C for 9 days. The reaction mixture was extracted with ether (200 mL × 3). The ethereal layer was washed by cold 1 N sodium hydroxide (50 mL × 2) and brine (100 mL × 2) to give a neutral fraction (5.9 g). The neutral fraction was chromatographed on neutral aluminum oxide (Merck, activity III) with mixtures of a *n*-hexane–ether gradient as an elution solvent. Each fraction was rechromatographed on a Celite 545–silica gel (1:1 w/w) or a 10% $AgNO_3$–SiO_2 column with the same solvent. The isomers of the intermediates were separated by HPLC.

***p*-Mentha-1,5-dien-8-ol (3a).** IR (film) 3380 (OH), 2950, 2920 and 1440 (CH_2), 1365 and 1360 cm^{-1} (isopropyl); ^1H NMR ($CDCl_3$) δ 1.21 (3 H, s, CH_3), 1.22 (3 H, s, CH_3), 1.58 (1 H, s, variable OH), 1.73 (3 H, s, CH_3C=), 5.47 (1 H, br s, C=CH), 5.84 (2 H, m, CCH=CH); ^{13}C NMR ($CDCl_3$) δ 20.9 (C-7, q), 26.9 (C-9, q), 29.7 (C-10, q), 31.8 (C-3, t), 43.3 (C-4, d), 72.4 (C-8, s), 124.3 (C-5 and C-6, d), 128.9 (C-2, d), 136.3 (C-1, s); FI-MS *m/z* (rel intensity) 153 ($M^+ + 1$, 12), 152 (M^+, 100); EI-MS *m/z* (rel intensity) 137 ($M^+ - CH_3$, 0.1), 134 ($M^+ - H_2O$, 0.1), 94 (72), 79 (53), 59 [$(CH_3)_2C - OH)^+$, 100].

***p*-Mentha-1(7),2-dien-8-ol (3b).** IR (film) 3380 (OH), 2970 and 1445 (CH_2), 1375 and 1365 (isopropyl), 879 cm^{-1} (*exo*-methylene); ^1H NMR ($CDCl_3$) δ 1.18 (3 H, s, CH_3), 1.23 (3 H, s, CH_3), 1.57 (1 H, s, variable OH), 4.79 (2 H, s, $=CH_2$), 5.91 (1 H, d, J = 10.3 Hz, CCH=), 6.24 (1 H, dd, J = 10.3 Hz, CCH=C*H*); ^{13}C NMR ($CDCl_3$) δ 24.8 (C-5, t), 26.1 (C-9, q), 27.9 (C-10, q), 30.2 (C-6, t), 47.3 (C-4, d), 72.7 (C-8, s), 110.5 (C-7, t), 130.9 (C-2 and C-3, d), 143.0 (C-1, s); FI-MS *m/z* (rel intensity) 152 (M^+, 100), 135 (16), 94 (42), 93 (35), 59 [$(CH_3)_2C$–$OH)^+$, 83]; EI-MS *m/z* (rel intensity) 137 ($M^+ - CH_3$, 0.5), 134 ($M^+ - H_2O$, 0.4), 94 (46), 79 (44), 59 (100).

Table I. Aluminum Oxide Column Chromatography of Deteriorated Citral

fraction no.	solvent	compounds, peak no.[a]
1	hexane	2, 3
2	hexane	4, 6
3	hexane-ether (95:5)	7, 8, 9, 10, 11
4	hexane-ether (90:10)	1, 16′
5	hexane-ether (70:30)	15, 18
6	hexane-ether (50:50)	14, 17, 19

[a] Peak numbers are from Figure 1.

3-Ethoxy-*p*-menth-1-en-8-ol (4a and 4b). IR (film) 3470 (OH), 2970, 2920, and 1440 (CH_2), 1380 and 1370 (isopropyl), 1075 cm^{-1} (ether); ^1H NMR ($CDCl_3$) δ 1.17 (3 H, CH_3), 1.23 (3 H, s, CH_3), 1.23 (3 H, t, J = 6.8 Hz, $-OCH_2CH_3$), 1.70 (3 H, br s, CH_3C=), 1.96 (1 H, s, variable OH), 3.44 and 3.49 (1 H, two q, J = 6.8 Hz, diastereomeric $-OCHHCH_3$, H-$11_{b,b'}$), 3.76 and 3.80 (1 H, two q, diastereomeric $-OCHHCH_3$, H-$11_{a,a'}$), 4.14 (0.5 H, br d, J = 7.8 Hz, *trans*-CH–OEt), 5.20 (0.5 H, br s, *cis*-CH–OEt), 5.48 (1 H, br s, C=CH); ^{13}C NMR ($CDCl_3$) δ 15.6 (C-12, q), 23.0 (C-7, q), 24.4 (C-10, q), 24.7 (C-9, q), 29.5 (C-5, t), 30.9 (C-6, t), 48.7 (C-4, d), 62.8 (C-11, t), 73.1 (C-8, s), 78.2 (C-3, d), 121.2 (C-2, d), 137.6 (C-1, s); FI-MS *m/z* (rel intensity) 199 ($M^+ + 1$, 56), 198 (M^+, 17), 180 ($M^+ - H_2O$, 94), 135 (100), 94 (17), 68 (15), 59 [$(CH_3)_2C$–$OH)^+$, 31]; EI-MS *m/z* (rel intensity) 180 ($M^+ - H_2O$, 16), 165 ($M^+ - H_2O - CH_3$, 11), 140 (16), 112 (60), 94 (100), 79 (56), 59 (53), 43 (39).

2,3-Dehydro-1,8-cineole (10). A sufficient amount of dehydrocineole (**10**) was not isolated to measure a NMR spectrum because of a minor product. However, it was identified by comparing with the GC and MS data of Clark et al. (1977): EI-MS *m/z* (rel intensity) 152 (M^+, 7), 124 (23), 109 (100), 94 (26), 91 (13), 79 (37).

Fate of Intermediates in Citric Acid Aqueous Solutions. *p*-Mentha-1,5-dien-8-ol (**3a**) or *p*-mentha-1-(7),2-dien-8-ol (**3b**) (5 mg each) dissolved in 2.5 mL of ethanol was incubated in 10 mL of 5% citric acid aqueous solution at 38 °C in the presence of oxygen or nitrogen (oxygen free). The reaction products were extracted with *n*-hexane after 3, 8, 15, 72, 120, and 168 h. The extracts were identified by GLC, GC–MS, and mass chromatography.

Effect of Antioxidants for Deterioration Mechanism of Citral. Citral (100 mg) and antioxidants dissolved in 10 mL of ethanol were added to 15 mL of 7% citric acid aqueous solution: 2,6-di-*tert*-butyl-*p*-cresol (BHT), 5 mg; 2- and 3-*tert*-butyl-4-hydroxyanisoles (BHA), 5 mg; *n*-propyl gallate, 2.5 mg; *dl*-α-tocopherol, 5 mg; nordihydroguaiaretic acid, 2.5 mg. *n*-Tritriacontan-16,18-dione (2 mg) isolated from the leaf wax of *Eucalyptus* leaves (Osawa and Namiki, 1981) was also used as an antioxidant. Each mixture was incubated at 38 °C. The deterioration products were quantitatively determined in 3, 7, 14, 21, and 28 days.

RESULTS AND DISCUSSION

Identification of Intermediates from Deteriorated Citral. A gas chromatogram of citral incubated in aqueous citric acid for 9 days is shown in Figure 1; a large amount of intermediates **3a** and **3b** (peaks 14 and 17) had accumulated at this stage. The deteriorated citral was fractionated on an aluminum oxide column in *n*-hexane–ether (Table I). Peaks 14 and 17 in the fraction 6 were re-

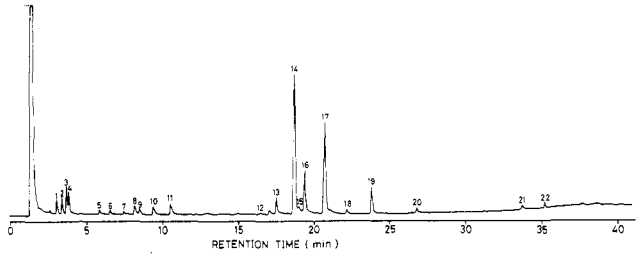


Figure 1. Gas chromatogram of deteriorated citral in a citric acid aqueous solution in 9 days with shaking. Peaks: 1, 2,3-dehydro-1,8-cineole; 2, *p*-mentha-1,5,8-triene; 3, *p*-mentha-1,4-diene; 4, *p*-cymene; 5, unknown; 6, α,*p*-dimethylstyrene; 7–10, M^+ 180; 11, 8-ethoxy-*p*-cymene; 12, α-terpineol; 13, neral; 14, *p*-mentha-1,5-dien-8-ol; 15, *p*-mentha-1,3-dien-8-ol; 16, geranial; 16′, piperitone; 17, *p*-mentha-1(7),2-dien-8-ol; 18, 3-ethoxy-*p*-menth-1-en-8-ol; 19, *p*-cymen-8-ol; 20, M^+ 226; 21 and 22, M^+ 268. Conditions: A glass capillary SCOT column (30 m × 0.28 mm i.d.) coated with DEGS. Column temperature, 50–160 °C (program rate, 3 °C/min). Flow rate (N_2), 1.25 mL/min.

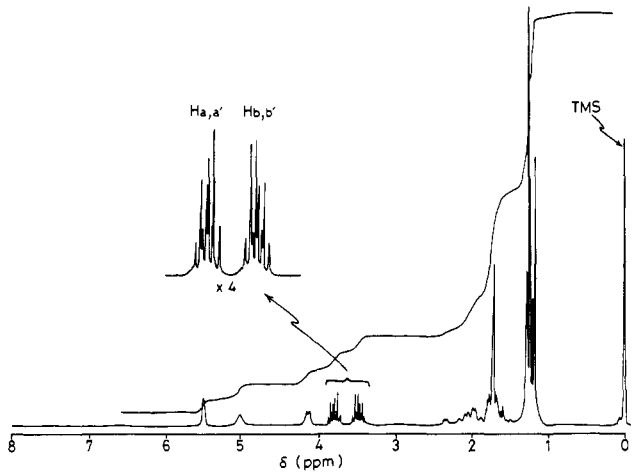
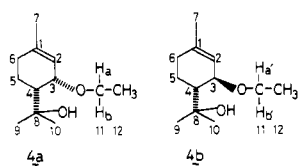


Figure 2. ^1H NMR (200 MHz) spectrum of 3-ethoxy-*p*-menth-1-en-8-ol.

chromatographed on a 10% $AgNO_3$–SiO_2 column and by HPLC. Isolated peaks 14 (12 mg) and 17 (23 mg) were analyzed by EI-MS, FI-MS, IR, ^1H NMR, and ^{13}C NMR. Peaks 14 and 17 were identified as *p*-mentha-1,5-dien-8-ol (**3a**) and *p*-mentha-1(7),2-dien-8-ol (**3b**) by interpretation of EI-MS, FI-MS, IR, ^1H NMR, and ^{13}C NMR spectra and comparison of published data, respectively. *p*-Mentha-1,5-dien-8-ol (**3a**) was extremely unstable in the presence of air at room temperature and was easily changed to *p*-cymen-8-ol (**6**).

Peak 18 (25 mg) was isolated from fraction 5 by rechromatography on a Celite 545–silica gel (1:1 w/w) column. The FI-mass spectral fragmentation (m/z 199, 198, 180, and 59) indicated a molecular formula of $C_{12}H_{22}O_2$ with an hydroxyisopropyl group. The ^1H NMR spectrum of peak 18 is shown in Figure 2. The spectrum indicated a mixture of two stereoisomers despite one peak on the GC trace and one spot on a thin-layer chromatogram. A broad doublet at δ 4.14 (0.5 H, J = 7.8 Hz) was attributed to the pseudoaxial proton attached to C-3 of structure **4b** (trans



4a **4b**

isomer). A broad singlet at δ 5.20 (0.5 H) was assigned to the pseudoequatorial proton attached to C-3 in structure

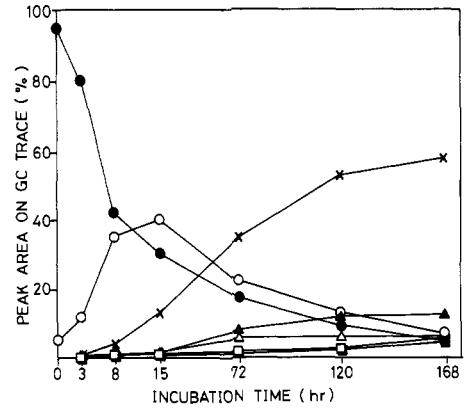


Figure 3. Time course changes of deterioration products from *p*-mentha-1(7),2-dien-8-ol incubated in a citric acid aqueous solution. (●) *p*-Mentha-1(7),2-dien-8-ol; (○) *p*-mentha-1,5-dien-8-ol; (□) *p*-cymene; (■) α,*p*-dimethylstyrene; (△) 8-ethoxy-*p*-cymene; (▲) α-terpineol; (×) *p*-cymen-8-ol.

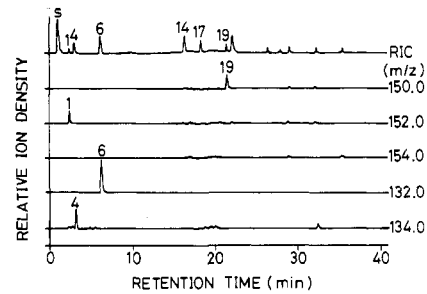
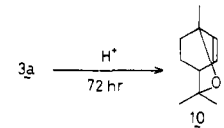


Figure 4. Mass chromatograms of deterioration products from *p*-mentha-1,5-dien-8-ol incubated in a citric acid aqueous solution for 3 days. Peaks: s, solvent; 1, 2,3-dehydro-1,8-cineole; 4, *p*-cymene; 6, α,*p*-dimethylstyrene; 14, *p*-mentha-1,5-dien-8-ol; 17, *p*-mentha-1(7), 2-dien-8-ol; 19, *p*-cymen-8-ol.

4a (cis isomer). The complex signals of 3.5–4.0 were due to methylene protons of ethoxy groups because of coupling with the methyl group (J = 6.8 Hz). The H-11_a and H-$11_{a'}$ signals appeared at lower field (δ 3.76 and 3.80) as a double quartet, while the H-11_b and H-$11_{b'}$ shifted to higher field (δ 3.44 and 3.49) as a double quartet. Since C-3 of **4a** and **4b** is asymmetric and cannot rotate freely, H-11_a and H-$11_{a'}$ or H-11_b and H-$11_{b'}$ were observed separately. Therefore, the structure of peak 18 was deduced as 3-ethoxy-*p*-menth-1-en-8-ol (**4a** and **4b**).

The other components were identified by comparison of GC retention time and mass spectrometric fragmentation with those of standard compounds or published data.

Fate of Intermediates in Citric Acid Aqueous Solutions. Figure 3 shows the time course of deterioration products from *p*-mentha-1(7),2-dien-8-ol (**3b**) incubated in aqueous citric acid. At the first stage, compound **3b** rapidly decreased and *p*-mentha-1,5-dien-8-ol (**3a**) was



produced by isomerization of **3b**, the equilibrium reaching a ratio of 55 to 45. Both terpene alcohols decreased with the equilibrium ratio after 15 h. On the other hand, *p*-cymen-8-ol (**6**), α-terpineol (**5**), and 8-ethoxy-*p*-cymene (**7**) increased as shown in Figure 3. After that, *p*-cymene (**9**) and α,*p*-dimethylstyrene (**8**) were formed. In the case of compound **3a**, a similar deterioration process to that of compound **3b** as shown in Figure 4 was observed except for following facts. 2,3-Dehydrocineole (**10**) temporarily

increased to 10% of total products on GC trace. Under oxygen-free conditions, the deterioration mechanism was not much different from that in the presence of oxygen, although the reaction rate was slower under the former condition.

Deterioration Mechanism of Citral. Clark et al. (1977) have subjected a mixture of **3a** and **3b** to air oxidation at 5 °C and found that they are transformed to the aromatic alcohol (**6**) as the major product. We compared the difference between the presence and absence of oxygen in deterioration products from **3a** or **3b** in aqueous citric acid. Both **3a** and **3b** gave *p*-cymen-8-ol (**6**) with disproportionation and redox reactions, followed by *p*-cymene (**9**) and α,*p*-dimethylstyrene (**8**) as the final stable products. These reaction processes did not depend on presence of oxygen, in spite of the formation of oxidation products, since antioxidants such as BHT, BHA, α-tocopherol, and so on were not effective in decreasing the amount of oxidative products (**6**, **8**, and **9**) from citral in aqueous citric acid.

Clark et al. (1977) and McHale et al. (1979) have reported that **3a**, **3b**, and *p*-menth-2-ene-1,8-diols (cis and trans) were major products even in the early stages of the reaction. Under our reaction conditions (see Experimental Section), the diols were not detected, although we examined in detail the changes in deterioration products as a function of time.

Scheme I shows the deterioration mechanism of citral in acid aqueous solutions. Citral (1) was cyclized to diastereoisomeric diols (**2**) from the *Z* isomer, holding the equilibrium between the *E*/*Z* isomers with a ratio of 65 to 35. The diols (**2**), which are extremely unstable in aqueous acid solution and not isolable, were immediately dehydrated to give monoterpene alcohols (**3a**, **3b**, and **3c**). Nishimura et al. (1982) have isolated *p*-menthane-3,8-diols (cis and trans) as biologically active compounds from *Eucalyptus citriodora* leaves. Both saturated compounds were very stable under the same acidic conditions as reported here. It is considered that *p*-menth-1-ene-3,8-diols (**2**) are much more labile than *p*-menthane-3,8-diols due to the allylic alcohol function. Instead of diols (**2**), monoethers (**4**) were isolated as a mixture of stereoisomers. In a previous paper (Kimura et al., 1982), we have reported **3c** as an intermediate produced from deteriorated citral, but **3a** and **3b** seem to be, if anything, major and significant intermediates in the present investigation. These intermediates were transformed to **5**, **6**, and **7** by disproportionation and redox reactions between two different molecules and subsequently to more stable aromatic compounds (**8** and **9**) which are responsible for the off-odor of deteriorated lemon.

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Registry No. 1, 5392-40-5; **2**, 6252-34-2; **3a**, 1686-20-0; **3b**, 65293-09-6; **4**, 85612-20-0; **5**, 10482-56-1; **6**, 1197-01-9; **7**, 68279-51-6; **8**, 1195-32-0; **9**, 99-87-6; **10**, 66113-06-2; BHT, 128-37-0; BHA, 25013-16-5; *n*-propyl gallate, 121-79-9; *dl*-α-tocopherol, 10191-41-0; nordihydroguaiaretic acid, 500-38-9; *n*-tritriacontan-16,18-dione, 24514-86-1; *p*-mentha-1,5,8-triene, 21195-59-5; *p*-mentha-1,4-diene, 99-85-4; neral, 106-26-3; *p*-mentha-1,3-dien-8-ol, 82538-84-9; geranial, 141-27-5; piperitone, 89-81-6.

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