Photo-oxygenation of α -Ionone[†]

By Kazuo INA and Hideo ETÔ

Department of Agricultural Chemistry, Shizuoka University, Iwata, Shizuoka-Ken

Received July 16, 1971

Photo-oxygenation of α -ionone was studied to clarify the relationship between the maturity of aroma and photo-oxygenative change of α -ionone. α -Ionone was converted to oxygenated derivatives which were identified as 2,3-epoxy- β -ionone, 3,4-epoxy- α -ionone, 4-keto- β -ionone (*trans*- and *cis*-form), 5-keto- α -ionone and 3,4-dihydroxy- α -ionone.

Several plants contain α -, β -, γ -, and dihydro-ionones in their blossoms, roots, stems, and fruits, and these compounds play a principal role as aroma.

Recently, some compounds which were suggested to be biochemically synthesized from ionones have been isolated from several species of plants^{1~2)} and insects.³⁾ They were actinidiolide (I), dihydroactinidiolide (II), loliolide (III), 2,3-epoxy- β -ionone (IV), theaspirone (V), 4-keto- β -ionone (VI) and allenic ketone (VII).

Isoe⁴⁾ and Mousseron-Canet⁵⁾ have demonstrated that β -carotene was converted to β -ionone and dihydroactinidiolide by photo-sensitized oxygenation. Büchi⁶⁾ and Mousseron-Canet⁷⁾ also found that isomerization of

trans- α -ionone to its *cis*-form occurred in a photosensitized reaction.

In previous papers^{8,9)} we reported the structures of 2,3-epoxy- β -ionone, theaspirone, dihydroactinidiolide and 4-keto- β -ionone isolated from the tea essential oil. Their structures suggested that they may be produced from ionones in tea leaves or during tea manufacture.

This report describes in detail the photo-oxygenation of α -ionone without a sensitizer to clarify the relationship between the maturity of aroma and photo-oxygenative conversion.

Photo-oxygenation of α -ionone was carried out at room temperature (20~25°C) under irradiation by a 10W-fluorescent lamp without a sensitizer. After two weeks the gaschromatography

[†] Studies on the Photo-oxygenation of Ionones.
Part II.

FIG. 1. Gaschromatogram of Irradiation Products of α -Ionone.

Column DEGS 10% on celite 545, 120~200°C (4°C/min) flow rate 14 ml/min N₂.

TABLE I. FRACTIONATION BY SILICA GEL COLUMN CHROMATOGRAPHY

Fraction No.	Solvents		Volume of solvents (ml)	Peak No.
	Pet. Ether;	Ether		
1~3	100	0	300	
4~9	99	1	600	
10~15	98	2	600	1
16~21	96	4	600	α -ionone
22~27	94	6	600	α -ionone
28~33	88	12	600	2, 3, 4
34~39	80	20	600	3, 4, 5, 9
40~45	70	30	600	5, 6, 7, 9
46~51	60	40	600	7, 8
52~57	50	50	600	9
58~63	40	60	600	9
64~73	0	100	1000	

matogram of the reactant showed that it contained nine fractions tentatively named as 1~9 (Fig. 1), and these fractions were separated by silica-gel column chromatography and preparative gaschromatography (Table I). In this separation 2,3-epoxy- β -ionone (peak 2, 3%), 3,4-epoxy- α -ionone (peak 3, 14%), *cis*-4-keto- β -ionone (peak 5, 3%), *trans*-4-keto- β -ionone (peak 6, 5%), 5-keto- α -ionone (peak 8, 9%), and 3,4-dihydroxy- α -ionone (peak 9, 22%) were identified, and approximately 33% of the starting material was recovered as shown in Table II.

TABLE II. COMPOSITION OF IRRADIATION PRODUCTS OF α -IONONE

Peak No.	Compound	Peak area percentage
1	Unknown	2
2	2,3-Epoxy- β -ionone	3
3	3,4-Epoxy- α -ionone	14
4	Unknown	3
5	<i>cis</i> -4-Keto- β -ionone	3
6	<i>trans</i> -4-Keto- β -ionone	5
7	Unknown	6
8	5-Keto- α -ionone	9
9	3,4-Dihydroxy- α -ionone	22
10	α -Ionone of starting material	33

The identification of these compounds with their authentic specimens was provided by comparison of their UV, IR, NMR and mass spectra.

From these data the main product for the photo-oxygenation of α -ionone was 3,4-dihydroxy- α -ionone, while 3,4-epoxy- α -ionone, 5-keto- α -ionone, *trans*-4-keto- β -ionone, *cis*-4-keto- β -ionone and 2,3-epoxy- β -ionone were obtained as minor components. These results suggested that the aroma of tea was formed during manufacture or aging.

The structures of the minor compounds, peak 1, 4 and 7 will be presented subsequently.

EXPERIMENTAL

Spectral analyses

The NMR spectra were measured with a HITACHI R-20B or a JNM -C-60HL in deuterio-chloroform with tetramethylsilane as an internal reference. The mass spectra were measured with a HITACHI RMS-4 or a SHIMAZU LKB-9000.

1. α -Ionone was placed in a plate of 18 cm diameter and was continuously exposed to irradiation by a 10W-fluorescent lamp without a sensitizer. After two weeks about 70% of the α -ionone was converted to several compounds. A gaschromatogram of the irradiation ionone is shown in Fig. 1. The reactant was subjected to silica-gel column chromatography

with the solvent system as indicated in Table I. The eluate was finally separated into ten fractions (Table II).

2. *2,3-Epoxy- β -ionone* (peak 2). The compound was a colorless crystal of mp $47\sim 48^\circ\text{C}$. Two absorption peaks of the IR spectrum at 1630 cm^{-1} and 1680 cm^{-1} and UV $\lambda_{\text{max}}^{\text{EtOH}}$ $234\text{ m}\mu$ ($\epsilon=12,000$) suggested the existence of $\text{C}=\text{C}-\text{C}-\text{O}$ group in the compound. The

parent peak of the mass spectrum was 208 mass unit, suggesting its molecular formula to be $\text{C}_{13}\text{H}_{20}\text{O}_2$. The NMR data suggested the following linkages; gem. $-\text{CH}_3$, $\delta 0.95$, 1.15 ppm (6H, d), $-\text{C}-\text{CH}_3$, $\delta 1.17\text{ ppm}$ (3H, s), $-\text{CH}_2-$, $\delta 1.4\sim 1.8\text{ ppm}$ (6H, m), $-\text{C}-\text{CH}_3$,

$\delta 2.2\text{ ppm}$ (3H, s), $\text{C}=\text{C}$ $\delta 6.16$ and 6.85 ppm (1H, d, $J=16\text{ Hz}$).

From these data this compound was assigned as 2,3-epoxy- β -ionone.

3. *3,4-Epoxy- α -ionone* (peak 3). This compound was presumed to be an isomer of peak 2 from the mass parent peak m/e 208 ($\text{C}_{13}\text{H}_{20}\text{O}_2$). It is suggested from the following NMR data that the compound is

α -type; epoxy-H, $\delta 2.95\text{ ppm}$ (1H, broad t), $-\text{C}-\text{C}-$, $\delta 5.80\sim 6.78\text{ ppm}$ (2H, ABX type, $J_{\text{trans}}=16\text{ Hz}$).

Comparison of the retention time and mass spectra of the compound with those of an authentic specimen confirmed it to be 3,4-epoxy- α -ionone.

4. *cis-4-Keto- β -ionone* (peak 5). In the mass spectrum the parent peak was shown to be 206 mass unit, indicating the molecular formula to be $\text{C}_{13}\text{H}_{18}\text{O}_2$. The structure of this compound was confirmed to be *cis*-4-keto- β -ionone from the following data; IR, 1700 , 1670 , 1630 and 1610 cm^{-1} , NMR, gem- CH_3 $\delta 1.17\text{ ppm}$ (6H, s), $-\text{C}-\text{CH}_3$ $\delta 1.56\text{ ppm}$ (3H, s), $-\text{CH}_2-$ $\delta 1.89\text{ ppm}$ (2H, t), $\text{C}-\text{CH}_3$ $\delta 2.15\text{ ppm}$ (3H, s), $\text{C}-\text{CH}_2-$

$\delta 2.42\text{ ppm}$ (2H, t), $-\text{C}=\text{C}-$ $6.12\sim 6.42\text{ ppm}$ (2H, AB type 12 Hz), and UV* $\lambda_{\text{max}}^{\text{EtOH}}$ $227\text{ m}\mu$ ($\epsilon=7000$), and $273\text{ m}\mu$ ($\epsilon=10,000$).

* *cis*- α -Ionone,⁽⁶⁾ UV $\lambda_{\text{max}}^{\text{EtOH}}$ $224\text{ m}\mu$ ($\epsilon=6550$), *trans*- α -ionone,⁽⁶⁾ UV $\lambda_{\text{max}}^{\text{EtOH}}$ $228\text{ m}\mu$ ($\epsilon=16,700$).

5. *trans-4-Keto- β -ionone* (peak 6). The parent peak of this compound was 206 mass unit, and the molecular formula of this compound was deduced as $\text{C}_{13}\text{H}_{18}\text{O}_2$. The structure of this compound was confirmed to be *trans*-4-keto- β -ionone from following data; IR, 1700 , 1680 and 1615 cm^{-1} UV $\lambda_{\text{max}}^{\text{EtOH}}$ $221\text{ m}\mu$ ($\epsilon=11,800$) and $273\text{ m}\mu$ ($\epsilon=10,000$), and NMR gem. $-\text{CH}_3$ $\delta 1.20\text{ ppm}$ (6H, s), $\text{C}=\text{C}-\text{CH}_3$ $\delta 1.75\text{ ppm}$ (3H, s), ring $-\text{CH}_2-$ $\delta 1.85\text{ ppm}$ (2H, m), $-\text{C}=\text{C}-$ $\delta 6.07\text{ ppm}$ (1H, d, $J=16\text{ Hz}$, β -type), and $\delta 7.11\text{ ppm}$ (1H, d, $J=16\text{ Hz}$, β -type).

FIG. 2. Mass Spectra of *trans* and *cis*, 4-Keto- β -ionone.

(A) *trans* form, (B) *cis* form.

6. *5-Keto- α -ionone* (peak 8). The mass parent peak of this compound was 206 mass unit, and the molecular formula was deduced as $\text{C}_{13}\text{H}_{18}\text{O}_2$. The following spectral data suggested the existence of α,β -unsaturated carbonyl (IR; 1700 , 1680 and 1630 cm^{-1}), UV $\lambda_{\text{max}}^{\text{EtOH}}$ $238\text{ m}\mu$ ($\epsilon=15,000$). The NMR data suggested the following linkages; gem. $-\text{CH}_3$, $\delta 1.00$, 1.06 ppm (3H, each s), $-\text{C}-\text{C}-\text{CH}_3$, $\delta 1.89\text{ ppm}$ (3H, d, $J=1.0\text{ Hz}$), $-\text{C}-\text{CH}_3$, $\delta 2.21\text{ ppm}$ (3H, s), $-\text{CH}_2-\text{C}=\text{C}-$

δ 2.64 ppm (2H, m), $\text{H}-\text{C}=\text{C}-\text{H}$, δ 5.89 ppm (1H, m), $\text{H}-\text{C}=\text{C}-\text{H}$, δ 6.06 ppm (1H, d, $J=16$ Hz, α -type), 6.75 ppm (1H, d, $J=16$ Hz).

From these data this compound was assigned as 5-keto- α -ionone.

7. *3,4-Dihydroxy- α -ionone* (peak 9). This compound was a colorless plate crystal of melting point $132\sim 134^\circ\text{C}$. IR bands at 3500, 3350, 1655 and 1620 cm^{-1} and a UV $\lambda_{\text{max}}^{\text{EtOH}}$ at $232\text{ m}\mu$ ($\epsilon=11,600$) suggested the existence of the hydroxy group and α,β -unsaturated carbonyl. Spectral analysis was performed on the monoacetylated compound which was treated by acetic anhydride and pyridine. The existence of the tertiary hydroxy group in the compound was suggested by the following fact that IR bands at 3500 and 3350 cm^{-1} shifted to 3400 cm^{-1} as shown in Fig. 3. The NMR

data suggested the following linkages; gem. $-\text{CH}_3$, δ 0.85, 1.00 ppm (3H, each s), $-\text{C}-\text{CH}_3$, δ 1.07 ppm (3H, s), $-\text{O}-\text{C}-\text{CH}_3$, δ 2.02 ppm (3H, s), $-\text{C}-\text{CH}_3$,

δ 2.23 ppm (3H, s), $-\text{OH}^*$ δ 3.98 ppm (1H, m), $-\text{C}-\text{C}-\text{H}$, δ 5.97 ppm (1H, d, $J=16$ Hz), δ 7.05 ppm (1H, d, $J=16$ Hz).

Based on these data this compound was assigned as 3,4-dihydroxy- α -ionone.

Acknowledgements. The authors should like to express their thanks to Professor Y. Sakato, Shizuoka Eiwa Women's University, and to Professors T. Mitsui and H. Fukami, Kyoto University, for their helpful discussions in the course of this work. The authors are also indebted to Dr. T. Ueno, Kyoto University, for the measurement of mass spectra and Dr. T. Katagiri, Shizuoka University, for the measurement of NMR.

REFERENCES

- 1) T. Sakan, S. Isoe and S. Be Hyeron, *Tetrahedron Letters*, **1967**, 1623.
- 2) R. Hoges and A. L. Porte, *Tetrahedron*, **20**, 1463 (1964).
- 3) J. Meinwald, K. Erickson, M. Hartshorn, Y. C. Meinwald and T. Eisner, *Tetrahedron Letters*, **1968**, 6041.
- 4) S. Isoe, S. Be Hyeron and T. Sakan, *Tetrahedron Letters*, **1969**, 279.
- 5) M. Mousseron-Canet, T. C. Mani and J. P. Dalle, *Bull. Soc. Chim. France*, **2**, 608 (1967).
- 6) G. Büchi and N. C. Yang, *Helv. Chim. Acta*, **160**, 1388 (1955).
- 7) M. Mosseron-Canet and M. M. P. Legendre, *Bull. Soc. Chim. France*, **1961**, 1509.
- 8) K. Ina, Y. Sakato and H. Fukami, *Tetrahedron Letters*, **1968**, 2777.
- 9) K. Ina and H. Etô, *Agr. Biol. Chem.*, **35**, 962 (1971).

* Hydroxy: Optical rotation measurement has not been made yet.

FIG. 3. IR and NMR Spectra of 3,4-Dihydroxy- α -ionone.

(a) dihydroxy, (b) mono hydroxy mono acetate. —, sample, ----, authentic specimen.

Authentic specimen was synthesized as follows;

epoxy- α -ionone $\xrightarrow[\text{alcohol}]{\text{H}_2\text{SO}_4}$ 3,4-dihydroxy- α -ionone.