

## Note

### Unusual KMnO<sub>4</sub> oxidation product of $\beta$ -ionone

Shrivallabh P Kamat<sup>a\*</sup>, Asha M D'Souza<sup>a</sup>,  
Shashikumar K Paknikar<sup>b</sup>,

Mohan M Bhadbhade<sup>c</sup> & Rajesh G Gonnade<sup>c</sup>

<sup>a</sup>Department of Chemistry, Goa University, Goa 403 206, India

<sup>b</sup>Siddharth Chemicals, Kundai Industrial Estate, Kundai,  
Goa 403 115, India

<sup>c</sup>Center for Materials Characterization, National Chemical  
Laboratory, Pune 411 008, India

Email: shrivkamat@yahoo.com

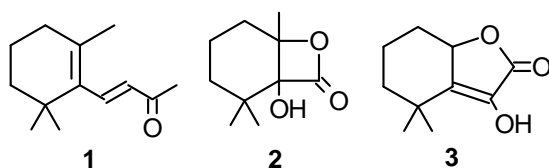
Received 25 July 2006; accepted (revised) 6 February 2007

KMnO<sub>4</sub> oxidation of  $\beta$ -ionone has been reinvestigated. The structure proposed for the hydroxyionolactone **3** obtained in this reaction is supported by MS, UV, IR, <sup>1</sup>H and <sup>13</sup>C NMR data and further confirmed by single crystal X-ray diffraction studies of the bromolactone **8**.

**Keywords:**  $\beta$ -ionone, KMnO<sub>4</sub> oxidation, hydroxyionolactone, bromolactone, crystal structure, X-ray diffraction

The hydroxyionolactone obtained<sup>1</sup> by KMnO<sub>4</sub> oxidation of  $\beta$ -ionone **1** was formulated<sup>2</sup> as  $\beta$ -lactone **2** which was further revised<sup>3</sup> to structure **3** on the basis of its elemental analysis, UV and IR spectral data. However, no mass, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded which would support the structure **3**. Moreover, formation of **3** by KMnO<sub>4</sub> oxidation of **1** seemed interesting from the mechanistic point of view. Therefore, we repeated the KMnO<sub>4</sub> oxidation of **1** and obtained hydroxyionolactone as a crystalline solid, m.p. 122°C.

All the structural features of **3** including the conjugated enol lactone butenolide part are consistent with the UV, IR, <sup>1</sup>H and <sup>13</sup>C NMR data. Its <sup>1</sup>H NMR showed three singlets ( $\delta$  1.19, 1.46, 1.53), each



\*A similar cleavage without participation of the carbonyl group has been reported earlier<sup>4</sup>.

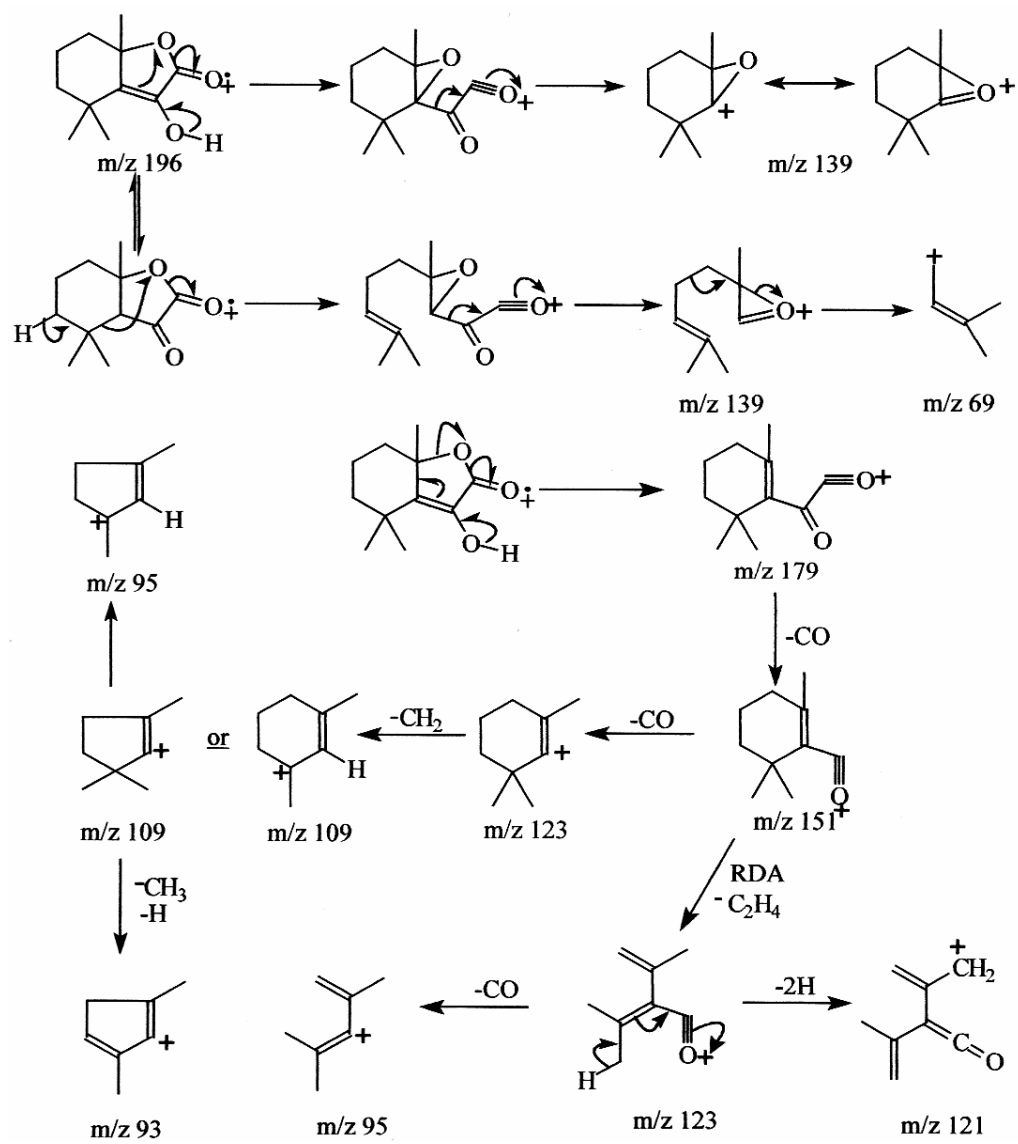
integrating for three protons corresponding to two tertiary methyl groups (gemdimethyl) at C<sub>4</sub> and a tertiary methyl at C<sub>7a</sub> respectively. The three methylene Hs appeared as multiplets in the region  $\delta$  1.5-2.27. The <sup>13</sup>C NMR signals for all the eleven carbons fully support the structure **3**. The DEPT and H decoupled <sup>13</sup>C NMR spectra exhibited three *sp*<sup>3</sup> methyls ( $\delta$  25.24, 25.66, 29.67), three *sp*<sup>3</sup> methylenes ( $\delta$  19.94, 39.03, 41.6) and five quaternary carbons ( $\delta$  35.81, 85.13, 133.39, 141.27, 170.07). The high resolution CIMS showed M<sup>+</sup> peak at *m/z* 219 (100% M<sup>+</sup> + Na) and 196 (M<sup>+</sup>), corresponding to the molecular formula C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>. The genesis of the major fragment ions is presented below in **Scheme I**.

Although Brooks and co-workers<sup>3</sup> have suggested the formation of **3** through the intermediate  $\alpha$ -keto acid **4**, it is not clear how **4** is formed. We believe that, the initially formed manganate ester **5** undergoes a cleavage\* to give the  $\alpha$ -keto aldehyde **7** via the Mn(III) complex **6**. Further oxidation of **7** to the  $\alpha$ -keto acid **4** followed by cyclization gives **3** (**Scheme II**).

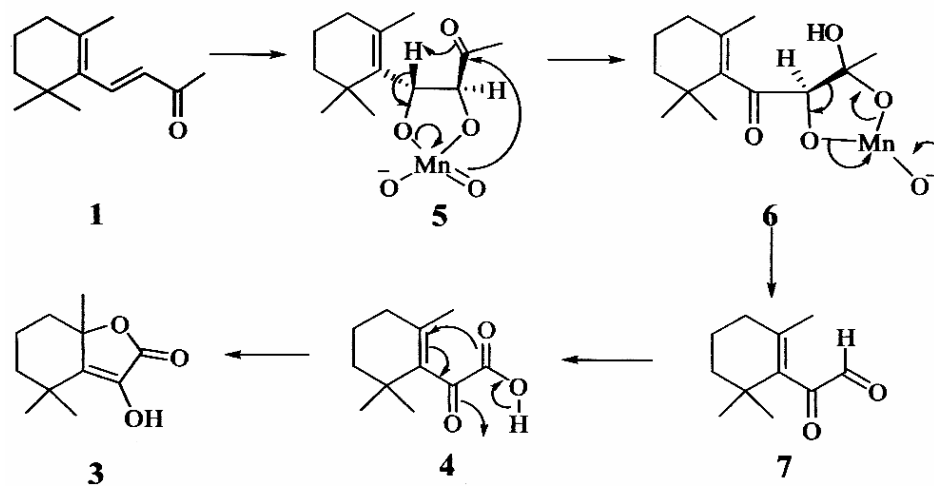
Hydroxyionolactone **3** is reported<sup>1</sup> to form a bromolactone **8** on treatment with hydrobromic acid under unstated<sup>1</sup> conditions and by the addition of bromine to the aqueous solution of the lactone **3**

(ref 3). However, the bromolactone obtained using these methods melted over a range (166-73°C) and was considered to be a mixture of stereoisomers<sup>3</sup>. The bromolactone **8** was prepared in 92% yield by generating bromine *in-situ* using potassium bromate and hydrobromic acid in glacial acetic acid<sup>5</sup> (**Scheme III**).

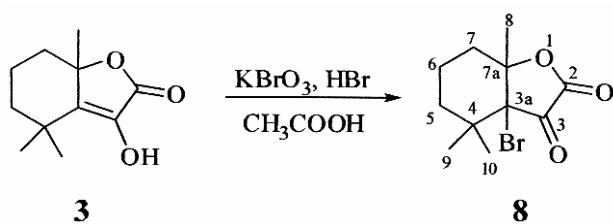
Compound **8**, a pale yellow crystalline solid that melted at 214°C with decomposition was analyzed for C<sub>11</sub>H<sub>15</sub>O<sub>3</sub>Br (MS). The IR spectrum showed the presence of carbonyl band at 1790 cm<sup>-1</sup> and the absence of the hydroxyl functionality. The <sup>1</sup>H NMR spectrum of **8** could nicely account for all the 15 H present as 3 methyls (9 H) and 3 methylenes (6 H) as follows:  $\delta$  1.29 (s, 3H, C<sub>4</sub>-CH<sub>3</sub>), 1.46 (s, 3H, C<sub>4</sub>-CH<sub>3</sub>), 1.53-1.75 (m, 4H, C<sub>5</sub>, and C<sub>6</sub> H), 1.79 (s, 3H, C<sub>8</sub>-H), 2.48 (m, 1H, C<sub>7</sub>-H), 2.52 (m, 1H, C<sub>7</sub>-H). The H decoupled <sup>13</sup>C NMR spectrum of **8** showed distinct 11 signals. Further support to the structure was found in



Scheme I—Mass spectral fragmentation of 3



Scheme II



Scheme III

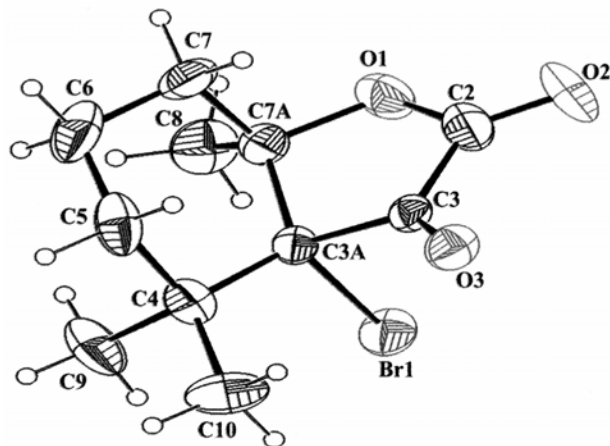


Figure 1—Perspective view of the bromolactone 8

the mass spectral data. The characteristic feature of EIMS is the fragment ions  $m/z$  202, 204 and 187, 189 obviously indicating the presence of bromine atom in these fragment ions.

Although, the spectral data of **8** obtained by our method is in agreement with the structure, the melting point ( $214^{\circ}\text{C}$ ) does not tally with that reported by earlier workers ( $166\text{--}73^{\circ}\text{C}$ )<sup>1,3</sup> and is attributed to the presence of only the *cis*-isomer which is confirmed by single crystal X-ray analysis of **8**. The crystal structure (**Figure 1**) clearly indicated that the six membered ring exists in a perfect chair conformation and the two substituents (Br and  $\text{CH}_3$ ) at the junction carbons (**3a** and **7a**) are *cis* to each other.

## Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded on a Shimadzu 8101-A FTIR spectrophotometer;  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WT 300 MHz FT NMR spectrophotometer in  $\text{CDCl}_3$  with TMS as an internal standard and chemical shifts are recorded in  $\delta$  values. All yields refer to pure isolated products.

**3-Hydroxy-4,4,7a-trimethyl-5,6,7,7a-tetrahydro-1-benzofuran-2(4H)-one 3.** A solution of potassium permanganate (10.0 g, 63.3 mmol) in water

(150 mL) was added dropwise, in 4.5 hr, to a stirred solution of  $\beta$ -ionone (5.0 g, 26 mmol) in acetone (55 mL) and water (15 mL) at  $0\text{--}5^{\circ}\text{C}$ , and was not allowed to exceed  $6^{\circ}\text{C}$  during the addition. The mixture was kept overnight at room temperature. To the reaction mass was added sodium acetate (1.25 g) and then treated with  $\text{SO}_2$  gas (prepared by the action of dil HCl on  $\text{Na}_2\text{SO}_3$ ) until a clear pale yellow solution was obtained. It was then saturated with NaCl and extracted with ether ( $4 \times 25$  mL). The combined ether extracts were treated with saturated  $\text{NaHCO}_3$  solution ( $4 \times 25$  mL). Acidification of the alkaline phase followed by ether extraction afforded yellow oil (1.87 g), which was subjected to steam distillation. The steam volatile fraction was discarded and the residue remaining in the flask on cooling gave a waxy solid (0.509 g, 10%). Recrystallization from hot water, afforded colourless cubic plates of **3** having m.p.  $121^{\circ}\text{C}$  (Lit. ref.  $3$   $122^{\circ}\text{C}$ ), which was further purified by sublimation under reduced pressure, however the m.p. did not change. IR (KBr): 3340 (OH), 2925, 1735, 1455, 1465, 1400, 1390, 1330, 1310, 1270, 1240, 1210, 1110, 1035, 900, 780, 650  $\text{cm}^{-1}$ ; UV (ethanol): 238 nm [Lit<sup>3</sup> UV (ethanol): 238 nm];  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.19 (s, 3H,  $\text{C}_4\text{-CH}_3$ ), 1.45 (s, 3H,  $\text{C}_4\text{-CH}_3$ ), 1.53 (s, 3H,  $\text{C}_{7a}\text{-CH}_3$ ), 1.5–2.21 (m, 6H,  $\text{C}_5$ ,  $\text{C}_6$  and  $\text{C}_7\text{-H}$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.9 (C-6), 25.2 (C-8), 25.7 ( $\text{C}_4\text{-CH}_3$ ), 29.7 ( $\text{C}_4\text{-CH}_3$ ), 35.8 (C-4), 39.0 (C-5), 41.6 (C-7), 85.1 (C-7a), 133.9 (C-3), 141.3 (C-3a), 170.1 (C-2); CIMS:  $m/z$ , (relative intensity) 219 ( $\text{M}^+ + \text{Na}$ , 100), 197 ( $\text{M}^+ + 1$ , 55), 179 (29), 151 (36), 139 (17), 123 (37), 121 (29), 109 (23), 95 (26), 93 (13), 69 (17%).

**3a-Bromo-4,4,7a-trimethylhexahydro-1-benzofuran-2,3-dione 8.** Potassium bromate (0.085 g, 0.5 mmol) was added to a solution of **3** (0.07 g, 0.36 mmol) in acetic acid (2 mL). To this mixture was added with stirring 48% HBr (0.3 mL) and then stirred at room temperature for 10 min. Water (10 mL) was added to the reaction mixture and a pale yellow solid separated out, was filtered, washed with dilute  $\text{NaHSO}_3$  ( $3 \times 2$  mL), water ( $3 \times 2$  mL) and dried to give **8** (0.09 g, 92%). Recrystallization from petroleum ether containing traces of benzene, gave pale yellow crystalline solid, which melted with decomposition at  $214^{\circ}\text{C}$  (Lit. ref.  $3$   $166\text{--}73^{\circ}\text{C}$ , from ether and petroleum ether). IR (KBr): 2940, 1790, 1775, 1455, 1385, 1310, 1270, 1245, 1160, 1145, 1060, 1035, 900, 875, 805, 705, 690  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

(300 MHz, CDCl<sub>3</sub>):  $\delta$  1.29 (s, 3H, C<sub>4</sub>-CH<sub>3</sub>), 1.46 (s, 3H, C<sub>4</sub>-CH<sub>3</sub>), 1.53-1.75 (m, 4H, C<sub>5</sub> and C<sub>6</sub> Hs), 1.79 (s, 3H, C<sub>7a</sub>-CH<sub>3</sub>), 2.48 (m, 1H, H-7b), 2.52 (m, 1H, H-7a); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  18.6 (C-6), 23.8 (C-8), 26.3 (C<sub>4</sub>-CH<sub>3</sub>), 27.1 (C<sub>4</sub>-CH<sub>3</sub>), 36.8 (C-7), 38.9 (C-4), 42.1 (C-5), 80.0 (C-7a), 85.4 (C-3a), 159.8 (C-2), 183.0 (C-3); EIMS:  $m/z$ , (relative intensity) 274.2, 276.2 (M<sup>+</sup>), 204.2, 202.2 (36), 187.1, 189.1 (87), 167.2, 152.2, 151.2 (72), 123.2 (100), 107.2 (79), 93.1 (27), 81.1 (54), 79.1 (27), 55.1 (23), 53.1 (26), 43.1 (55%).

### Crystallographic data

Single crystals of the bromolactone **8** were obtained from petroleum ether containing traces of benzene. X-ray intensity data for **8** were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromatized (Mo K $\alpha$  = 0.71073 Å) radiation at room temperature (293  $\pm$  2 K). All the data were corrected for Lorentzian polarization and absorption effects using Bruker's SAINT and SADABS programs. SHELXS-97 and SHELXL-97 programs<sup>6</sup> were used for crystal structure solution and full-matrix least-squares refinement on  $F^2$ . Hydrogen atoms were positioned and refined using the riding model. The perspective view<sup>7</sup> of the molecule is shown in **Figure 1**. Crystal data: C<sub>11</sub>H<sub>15</sub>BrO<sub>3</sub>, M = 275.14, crystal system monoclinic, space group  $P2_1/n$ , crystal size 0.83  $\times$  0.82  $\times$  0.34 mm<sup>3</sup>,  $a$  = 7.6212(14) Å,  $b$  = 11.581(2) Å,  $c$  = 13.207(3) Å,  $\beta$  = 93.974(4)°, T = 297(2)K,  $V$  = 1162.8(4) Å<sup>3</sup>,  $\mu$  = 3.520 mm<sup>-1</sup>, D<sub>cal</sub> = 1.572 g cm<sup>-3</sup>,  $Z$  = 4,  $F(000)$  = 560, reflections collected = 5011, unique reflections = 1964, refined parameters = 139, observed reflections = 1487,  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0611,  $WR2$  = 0.1731, Goodness of fit = 1.039, Absorption correction multi-scan, Index

ranges =  $-7 \leq h \leq 9$ ,  $-13 \leq k \leq 13$ ,  $-15 \leq l \leq 15$ ,  $T_{\min}$  = 0.1582,  $T_{\max}$  = 0.3764,  $\Delta\rho_{\max}$ ,  $\Delta\rho_{\min}$  = 1.209, -0.673 e Å<sup>-3</sup>

### Supplementary material

Crystallographic data (excluding structure factors) for the structure of compound **8** reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 614663. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144 1223 336033 or email: deposit@ccdc.cam.ac.uk]

### Acknowledgement

We thank Dr C G Naik, NIO, Goa, for recording NMR data and Dr Ratnakar Asolkar, University of Gottingen, Germany and Dr Manoj Samant, ICT, Hyderabad for recording MS data on our samples.

### References

- 1 Tiemann, *Ber*, 31, **1898**, 857.
- 2 (a) Simonsen J L, *The Terpenes*, Vol I, 2<sup>nd</sup> edn, (Cambridge University Press, London), **1953**, 128.  
(b) Rodd, *Chemistry of Carbon Compounds*, Vol II, (Elsevier Publishing Co, Amsterdam), **1953**, 503.
- 3 Brooks C J W, Eglinton G & Magrill D S, *J Chem Soc*, **1961**, 308.
- 4 ApSimon J W, Chau A S Y, Craig, W G & Krehm H, *Canadian Journal of Chemistry*, 45, **1967**, 1439.
- 5 Schatz P F, *J Chem Edu*, 73 (3), **1996**, 267.
- 6 Sheldrick G M, SHELXS-97 and SHELXL-97 programs for crystal structure solution and refinement, University of Göttingen, Germany, **1997**.
- 7 Johnson C K, ORTEP III, report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, **1976**.