Notes
Bull. Korean Chem. Soc. **2013**, Vol. 34, No. 6 1927
http://dx.doi.org/10.5012/bkcs.2013.34.6.1927

Insight into Bamboo Salt Effects on Hydrolysis of Organic Tri-esters

Woosik Hong, Jae-Hyun Joo,[†] Ok-Sang Jung, Suk-Hee Moon,[‡] and Kun-Young Park[†,*]

Department of Chemistry and [†]Department of Food Science and Nutrition, Pusan National University, Pusan 609-735, Korea
[*]E-mail: kunypark@pusan.ac.kr
[‡]Department of Food and Nutrition, Kyungnam College of Information and Technology, Pusan 617-701, Korea

Received March 19, 2013, Accepted March 27, 2013

Key Words : Alkaline pH, Bamboo salts, Hydrolysis, Organic tri-esters

Korean bamboo salts have been taken as both a popular health-food and a folk remedy because they have proven various therapeutic effects on inflammation, viral disease, diabetes, circulation disorders, and cancer,[1-5] even though its efficacy is not completely understood. Recently bamboo salt has been utilized as diverse additives for face cream, tooth paste, cosmetics, food additives, cleaning materials, and antibacteria.[6,7] Thus, food scientists are interested in basic research of bamboo salt effects. Bamboo salt has been known to contain various trace ions and to exhibit basic pH,[2,8] but, to date, its task-specific applications to chemical reactions remains unexplored except our previous report.[8] In order to investigate exact bamboo salt effects on hydrolysis process, the hydrolysis of new organic tri-esters using bamboo salt was achieved. This paper reports the bamboo salt effects on hydrolysis process of new organic tri-esters. The organic esters are widespread in nature and are widely used in the fragrance and flavor industry. Fats are also tri-ester compounds derived from glycerol and fatty acids.[9] Several billion kilograms of polyesters are produced annually, important products being polyethylene terephthalate, acrylate esters, and cellulose acetate.[10]

New tris(3-thiophenylmethyl)trimersic ester (L1) and tris(3-thiophenylethyl)trimersic ester (L2), were synthesized in high yields. They were recrystallized in a mixture of chloroform and methanol to obtain crystalline solids suitable for X-ray single crystallography. X-ray crystal structures along with their packing diagrams are shown in Figure 1. Each compound is a discrete molecule in solid state. The L1 approximates to a planar structure, and thus, packing diagram shows a layer-by-layer structure. In contrast, L2 was deviated from a planar plane owing to the longer ethylene chain. Their compositions and structures in solution were confirmed by chemical analysis, IR, ^{1}H NMR, and ^{13}C NMR. The products are soluble in common organic solvents such as acetone, chloroform, *N,N*-dimethylformamide, and dimethyl sulfoxide, but are insoluble in water, methanol, and ethanol. All products are stable even in solutions.

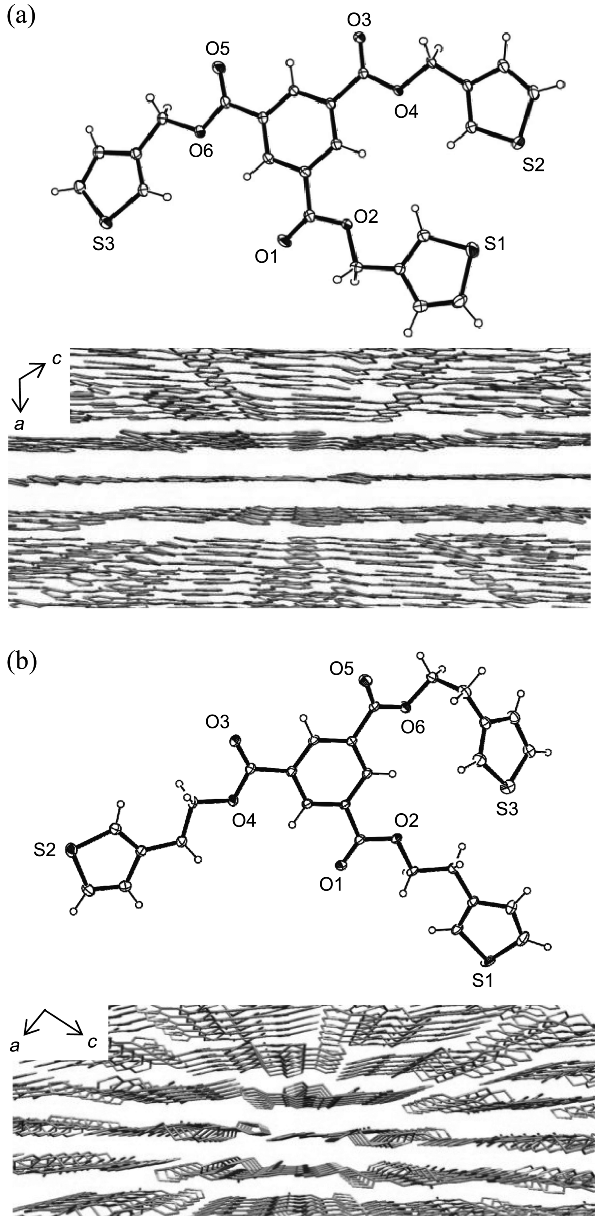


Figure 1. ORTEP drawings (top) and packing diagrams (bottom) of L1 (a) and L2 (b). The hydrogen atoms in each packing diagram were omitted for clarity.

The morphologies of the bamboo salt and its recrystallized salt were designated in Figure 2, and their elemental analyses results *via* SEM-EDX were listed in Table S1. The bamboo salt effects on hydrolysis were carried out relative to those of strong acids, bases, and without-bamboo salt. The

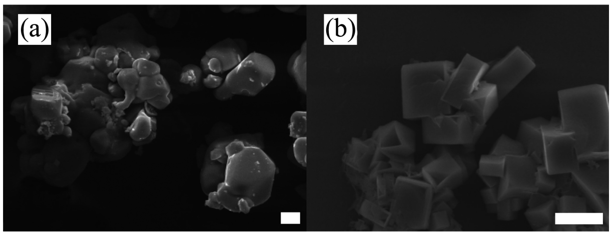


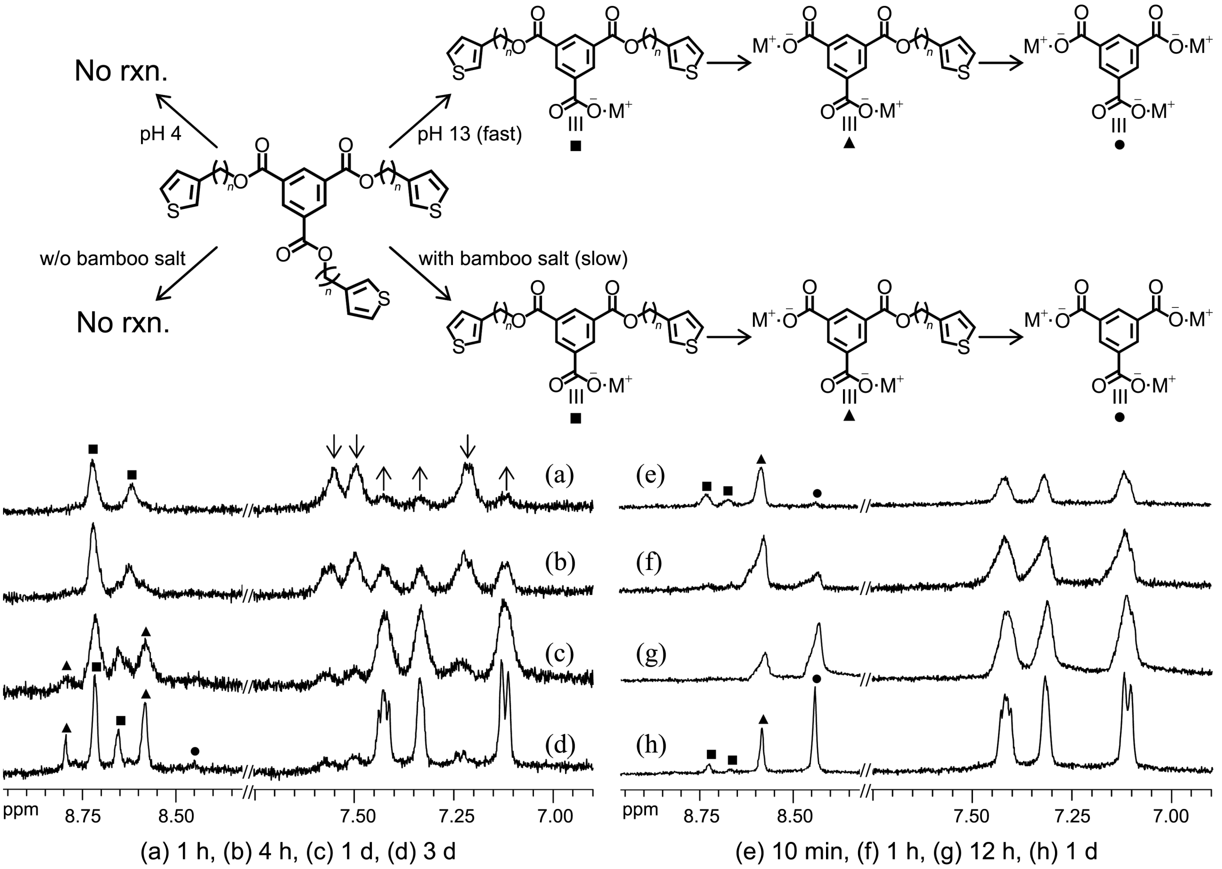
Figure 2. SEM image of bamboo salt (a) and its recrystallized salt (b). Scale bar = 10 μm.

hydrolysis process was monitored on the increase of hydrolyzed species *via* ^{1}H NMR peaks (Figure 3). L1 (30 mg, 0.06 mmol) was dissolved in a saturated bamboo salt (30 mg) solution of CD_3OD and D_2O (1:1, 5 mL) at 60 ºC. At range of 1-4 h, the mono-hydrolyzed species is predominant, and after 1 day, the mono-hydrolyzed species and di-hydrolyzed species coexist in the solution, and after 3 days, the tri-hydrolyzed species appears (mono-, di-, and tri-hydrolyzed species exists in the mole ratio of 51:41:8). Such facts can be explained by a three-step hydrolysis of L1. In contrast, the hydrolysis reaction using strong alkaline (pH = 13) is much faster (mono-, di-, and tri-hydrolyzed species exists in the mole ratio of 15:38:47) than the hydrolysis with bamboo salts: after 1 day, the tri-hydrolyzed species is predominant in the reaction solution. At pH = 14, the hydrolysis reaction was completed to produce only the tri-hydrolyzed species within 1 h (Supporting Information). Thus, the hydrolysis is very sensitive to pH in aqueous solution. That is, the weak basic bamboo salt is very useful to control such a sensitive hydrolysis of polyesters. The similar hydrolysis reaction using HCl solution (pH = 3) or without bamboo salts does not occur. The hydrolysis rate of L1 is slightly higher than that of L2 under the same condition (Supporting Information). The bamboo salt is a significant reagent on step-wise hydrolysis of organic polyesters. Under basic conditions, hydroxide acts as a nucleophile, while an alkoxide is the leaving group, which is a process of saponification.

In conclusion, weak alkaline properties of bamboo salts are proved to be an interesting task-specific hydrolysis material for the partial hydrolysis of organic polyesters. This is the first application of bamboo salt to organic polyester compounds. Further experiment on the components and reactions will contribute to the development of hydrolysis of some extended organic compounds.

Experimental

Typical Preparation of Bamboo Salts (Taesung Food Inc.). They are stuffed inside bamboo and covered with yellow mud, the products are then baked with pine wood and pine resin at about 1000 to 1500 °C for 8-10 h in a kiln, and then powdered. It is repeatedly stuffed inside the bamboo and baked. Finally, it is baked at about 1300 to 2000 °C.



(a) 1 h, (b) 4 h, (c) 1 d, (d) 3 d

(e) 10 min, (f) 1 h, (g) 12 h, (h) 1 d

Figure 3. Schematic diagram of hydrolysis (top) and ^{1}H NMR spectral change (bottom) of L1 in a mixture of D_2O and CD_3OD (v/v = 1:1) with bamboo salt (a)-(d) and with NaOH (pH = 13) (e)-(h) at 60 ºC. n = 1 (L1) and 2 (L2); $M^+ = H^+$ or Na^+.

Synthesis of Tris(3-thiophenylmethyl)trimersic Ester (L1). Triethylamine (16.5 mmol, 2.32 mL) was added to a stirred mixture of 1,3,5-benzenetricarbonyl trichloride (5 mmol, 1.38 g) and 3-thiophenemethanol (15.8 mmol, 1.52 mL) in chloroform (120 mL) at 60 ºC. The reaction mixture was refluxed for 24 h. The solution was filtered, and added methanol (300 mL). Colorless crystals of L1 were obtained in 2 days in an 80% yield. mp 91-92 °C. Anal. Calcd for $C_{24}H_{18}O_6S_3$: C, 57.81; H, 3.64%. Found: C, 57.20; H, 3.74%. IR (KBr pellet, cm^{-1}): 3089 (w), 2933 (w), 1720 (s), 1324 (s), 1247 (s), 1166 (m), 1012 (m), 763 (m), 663 (w), 576 (w). ^1H NMR ($CDCl_3$, δ): 8.88 (s, 3H), 7.40 (s, 3H), 7.34 (d, J = 4.8 Hz, 3H), 7.18 (d, J = 4.8 Hz, 3H), 5.41 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 164.82, 136.33, 134.95, 131.31, 127.82, 126.55, 125.06, 62.45.

Synthesis of Tris(3-thiophenylethyl)trimersic Ester (L2). L2 was prepared in the same manner as the above L1, except that 3-thiopheneethanol was employed instead of 3-thiophenemethanol. Colorless crystals of L2 were obtained in 2 days in a 74% yield. mp 58-59 °C. Anal. Calcd for $C_{27}H_{24}O_6S_3$: C, 59.98; H, 4.47%. Found: C, 60.10; H, 4.74%. IR (KBr, cm^{-1}): 3419 (br), 3103 (w), 2962 (w), 1722 (s), 1371 (m), 1332 (m), 1249 (s), 1149 (m), 989 (m), 740 (m), 638 (w), 592 (w). ^1H NMR ($CDCl_3$, δ): 8.82 (s, 3H), 7.30 (d, J = 4.5 Hz, 3H), 7.09 (s, 3H), 7.04 (d, J = 4.8 Hz, 3H), 4.59 (t, J = 6.9 Hz, 6H), 3.16 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 164.84, 137.70, 134.62, 128.28, 125.96, 131.89, 65.55, 29.69.

Crystallographic Structure Determination. All X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector at 170 K. The cell parameters and orientation matrix were obtained by means of the collection and processing of thirty-six frames of 2D diffraction images. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected by the multi-scan method (SADABS). The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least-squares techniques (SHELXL 97). The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal parameters along with procedural information on the data collection and structure refinement are listed in Table S2. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-929573 and 929574 for L1 and L2, respectively). The data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments. This research was supported by the research grant (#911004-02-1-HD110) from the projects for the 'Globalization of Korean Foods', which is gratefully appreciated.

Supporting Information. Crystal refinement parameters for L1 and L2, SEM-EDX data of bamboo salt and its recrystallized salt, ^1H NMR spectra showing the complete hydrolysis of L1 at pH 14, and partial ^1H NMR spectra showing hydrolysis of L2 in a saturated bamboo salt.

References

1. Hwang, K.-M.; Jung, K.-O.; Song, C.-H.; Park, K.-Y. *J. Med. Food* **2008**, *11*, 717.
2. Shin, H.-Y.; Lee, E.-H.; Kim, C.-Y.; Shin, T.-Y.; Kim, S.-D.; Song, Y.-S.; Lee, K.-M.; Hong, S.-H.; Kim, H.-M. *Immunopharmacol. Immunotoxicol*. **2003**, *25*, 377.
3. Shin, H.-Y.; Na, H.-J.; Moon, P.-D.; Shin, T; Shin, T.-Y.; Kim, S.-H. *J. Ethnopharmacol.* **2004**, *91*, 153.
4. Yang, J. S.; Kim, O. H.; Chung, S. Y.; Yoo, T. M.; Roh, Y. N.; Yi, S. Y.; Chung, M. W.; Ahn, M. R.; Choi, H. J.; Rheu, H. M. *J. Appl. Pharm*. **1999**, *7*, 178.
5. Kim, H.-Y.; Lee, E.-S.; Jeong, J.-Y.; Choi, J.-H.; Choi, Y.-S.; Han, D.-J.; Lee, M.-A.; Kim, S.-Y.; Kim, C. J. *Meat Science* **2010**, *86*, 960.
6. Jung, R. H. *Bamboo Salt*; Milalbook, 1966.
7. Korean Food Standard Codex, Korea Food & Drug Administration, 2009.
8. Kim, S. M.; Joo, J. H.; Jung, O.-S.; Moon, S. H.; Park, K.-Y. *Bull. Korean Chem. Soc.* **2012**, *33*, 2753.
9. Beal, G. D. *Organic Syntheses* **1941**, *1*, 538.
10. Riemenschneider, W.; Bolt, H. M. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2005.