Syntheses, crystal structure and antibacterial activities of mononuclear and tetranuclear di-*n*-butyltin(IV) complexes constructed from 2-(4-formyl-2-methoxyphenoxy)acetic acid

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Two new organotin(IV) carboxylates of composition *n*-$Bu_2Sn(O_2CCH_2OC_6H_3OCH_3\,CHO)_2$ (**1**) and {[*n*-$Bu_2Sn(O_2CCH_2OC_6H_3OCH_3CHO)_2]_2O\}_2$ (**2**) were obtained by the reaction of *n*-Bu_2SnO and 2-(4-formyl-2-methoxyphenoxy)acetic acid (LH). The compounds **1** and **2** have been characterised by elemental analysis and IR, ^{1}H NMR and X-ray crystallographic diffraction studies. The tin atom in **1** is found to adopt the skew-trapezoidal bipyramidal geometry in the polymeric chains. The compound **2** adopts a dimeric ladder structure and contains a tetranuclear tin framework with six distannoxane rings. The antibacterial activities decrease in the order **2** > **1** > $(n\text{-}Bu)_2SnO$ > LH.

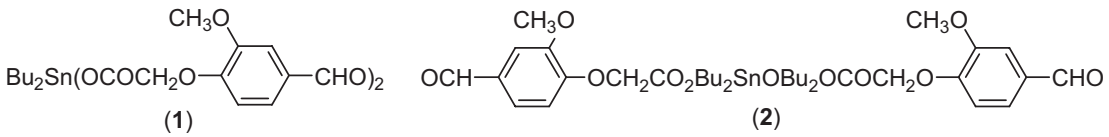
Keywords: organotin(IV) carboxylates, 2-(4-formyl-2-methoxyphenoxy)acetic acid, crystal structures, antibacterial activity

The increasing interest in organotin(IV) carboxylates in the last few decades is attributed to their significantly important applications in chemistry and biology.[1-4] As a part of the important applications, the synthesis and structural chemistry of organotin(IV) carboxylates have received considerable attention.[5,6] Depending on the type of carboxylic acid used and the stoichiometry of the reactants, various organotin carboxylates such as monomers, dimers, tetramers, oligomeric ladders and hexameric drums can be produced. Among these organotin carboxylates, the monomer with the general formula $R'_2Sn(O_2CR)_2$ adopts two types of crystal structure in the crystalline state.[5,6] The monomeric species have crystallographically imposed two-fold symmetry; the Sn atom exists in a skew-trapezoidal bipyramidal geometry with each basal plane being defined by two asymmetrically chelating carboxylate groups.[7] The second structural type is a polymeric complex; the Sn atom is seven-coordinate and exists in a distorted octahedral geometry.[8] The tetramer with the general formula $\{[R'_2Sn(O_2CR)]_2O\}_2$ adopts five types of crystal structure in the crystalline state.[5,6] All these structures involve a centrosymmetric structure built up around a planar, four-membered cyclic Sn_2O_2 unit in which the two exocyclic Sn atoms are five-coordinate. Each of the two exocyclic five-coordinate Sn atoms is bound to one bridging O atom of the four-membered ring, making these O atoms tri-coordinate. However, the different combinations based on the ligating mode between carboxylate groups and Sn atoms lead to particular carboxylate structures. As an extension of these studies, we have synthesised two new di-n-butyltin(IV) derivatives of 2-(4-formyl-2-methoxyphenoxy)acetic acid (LH) with quite different coordination modes, and their structures have been determined by single crystal X-ray diffraction. These compounds, **1** and **2**, exhibit good antibacterial properties.

In fact reactions of di-n-butyltin oxide with LH in a 1:2 and 1:1 molar ratio yield the corresponding mononuclear and tetranuclear di-n-butyltin carboxylates respectively, as described below. Attempts to produce various di-n-butyltin carboxylates, by changing molar ratio were unsuccessful.

The stretching frequencies of interest are those associated with the C=O, COO, Sn–O–Sn, Sn–O and Sn–C groups. The disappearance of a broad band due to the COOH group in the region 3200–2800 cm^{-1} of the ligand is indicative of the deprotonation of the carboxylic acid. In the IR spectra of **1** and **2**, the stretching modes of acyl C=O are observed at 1764 and 1694 cm^{-1}, respectively. The $\Delta\nu(\nu_{as}(COO)–\nu_{sym}(COO))$ value is used to determine the nature of bonding of carboxylate to tin(IV) complexes.[9] It is generally believed that the different values in $\Delta\nu$ between asymmetric ($\nu_{as}(COO)$) and symmetric ($\nu_{sym}(COO)$) absorption frequencies can distinguish the ligating mode of a carboxylate moiety, that is, the value smaller than 200 cm^{-1} indicates that the carboxylate moiety is bidentate, while the value larger than 200 cm^{-1} indicates that the carboxylate moiety is unidentate. The absorption frequencies of $\nu_{as}(COO)$ and $\nu_{sym}(COO)$ bands were observed at 1598 and 1422 cm^{-1} for **1**, the $\Delta\nu = \nu_{as}(COO)–\nu_{sym}(COO)$ value of **1** falls at 176 cm^{-1}, indicative of possibly distorted chelate coordination of the carboxylate group. The two peaks of the COO absorption bands were observed at 1674, 1588 cm^{-1}[$\nu_{as}(COO)$] and at 1506, 1380 cm^{-1}[$\nu_{sym}(COO)$] for **2**, respectively. The appearance or shifts of these absorptions in spectrum of **2** indicate that there is interaction between carboxylate group and the metal ions in two distinct ligating modes. The difference $\Delta[\nu_{as}(COO)–\nu_{sym}(COO)]$ between these frequencies for **2** is close to that found for a unidentate chelate mode (ca 208 cm^{-1}) and a bridging bidentate carboxylato groups (ca 168 cm^{-1}), respectively.[10,11] A band at 648 cm^{-1} for **2** is assigned to ν(Sn–O–Sn), which indicates an Sn–O–Sn bridged structure for **2**. The absorption bands at 542 and 468 cm^{-1} for compound **1**, 546 and 481 cm^{-1} for **2** are assigned to ν(Sn–C) and ν(Sn–O), respectively.[12,13]

The data for the ^{1}H NMR spectra are summarised in the experimental section. It is observed that the COOH resonance appearing at 11–13 ppm as a singlet for LH disappears when LH participates in coordination to the Sn atoms in **1** and **2**. The acyl (CHO) protons in complexes **1** and **2** exhibit resonance at 9.87 and 9.85 ppm, respectively. The n-butyl protons in complexes **1** and **2** show multiple resonances for the –CH_2–



(**1**) (**2**)

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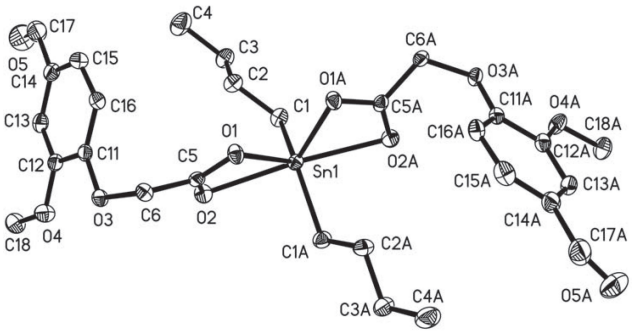

Fig. 1 The ORTEP drawing of compound **1**.

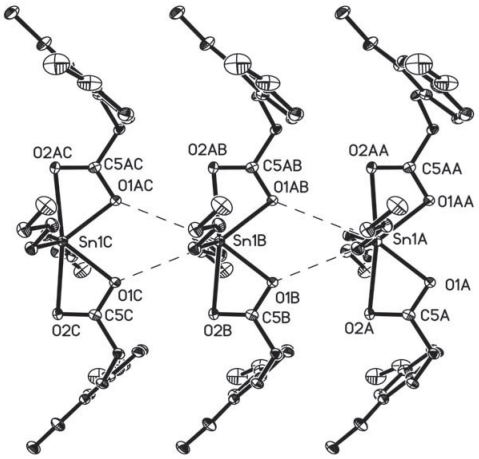

Fig. 2 The polymeric chains of compound **1**.

CH_2–CH_2– skeleton in the range of 1.31–1.77 and 1.28–1.58 ppm and clear triplets for the terminal methyl groups at 0.88 and 0.85 ppm, respectively.

The ORTEP drawing and the polymeric chains of **1** are shown in Figs 1 and 2, respectively. The molecular structure of **2** is shown in Fig. 3. The selected bond lengths and angles are listed in Table 1. Compound **1** reveals a monomeric molecular structure. The carboxylate groups on the LH act as bidentate chelating agents, forming an equatorial plane around the tin atom with four asymmetrically coordinated oxygen atoms.

Table 1 Selected bond lengths (Å) and angles (°) of compounds **1** and **2**

		1	
Sn(1)–C(1)	2.108(3)	O(1)–C(5)	1.294(3)
Sn(1)–O(1)	2.149(2)	O(2)–C(5)	1.235(3)
Sn(1)–O(2)	2.4936(18)	C(5)–C(6)	1.511(4)
C(1)–Sn(1)–C(1A)	139.43(18)	C(1A)–Sn(1)–O(2A)	86.12(9)
C(1)–Sn(1)–O(1)	113.09(10)	O(1)–Sn(1)–O(2A)	132.62(7)
C(1A)–Sn(1)–O(1)	98.01(10)	O(1A)–Sn(1)–O(2A)	55.83(7)
C(1)–Sn(1)–O(1A)	98.01(10)	O(2)–Sn(1)–O(2A)	171.36(9)
C(1A)–Sn(1)–O(1A)	113.09(10)	C(5)–O(1)–Sn(1)	98.93(18)
O(1)–Sn(1)–O(1A)	79.89(10)	C(5)–O(2)–Sn(1)	84.54(16)
C(1)–Sn(1)–O(2)	86.12(9)	O(2)–C(5)–O(1)	120.4(3)
C(1A)–Sn(1)–O(2)	90.89(9)	O(2)–C(5)–C(6)	122.3(3)
O(1)–Sn(1)–O(2)	55.83(7)	O(1)–C(5)–C(6)	117.2(3)
O(1A)–Sn(1)–O(2)	132.62(7)	O(3)–C(6)–C(5)	111.0(2)
C(1)–Sn(1)–O(2A)	90.89(9)		
		2	
Sn(1)–O(1A)	2.092(2)	Sn(2)–O(7)	2.261(2)
Sn(1)–O(1)	2.111(2)	O(2)–C(1)	1.274(4)
Sn(1)–C(31)	2.131(3)	O(3)–C(1)	1.237(4)
Sn(1)–C(41)	2.136(4)	O(3)–Sn(1A)	2.559(3)
Sn(1)–O(7)	2.436(2)	O(7)–C(3)	1.300(4)
Sn(1)–O(3A)	2.559(3)	O(8)–C(3)	1.226(4)
Sn(2)–O(1)	2.030(2)	C(1)–C(2)	1.517(5)
Sn(2)–C(61)	2.116(3)	O(4)–C(2)	1.429(4)
Sn(2)–C(51)	2.120(4)	C(3)–C(4)	1.497(5)
Sn(2)–O(2)	2.174(2)	O(9)–C(4)	1.437(4)
O(1A)–Sn(1)–O(1)	74.85(9)	O(1)–Sn(2)–O(7)	73.31(8)
O(1A)–Sn(1)–C(31)	102.75(12)	C(61)–Sn(2)–O(7)	90.53(11)
O(1)–Sn(1)–C(31)	112.18(13)	C(51)–Sn(2)–O(7)	93.53(11)
O(1A)–Sn(1)–C(41)	110.91(12)	O(2)–Sn(2)–O(7)	168.17(9)
O(1)–Sn(1)–C(41)	103.64(12)	Sn(2)–O(1)–Sn(1A)	136.26(11)
C(31)–Sn(1)–C(41)	135.93(16)	Sn(2)–O(1)–Sn(1)	117.99(10)
O(1A)–Sn(1)–O(7)	142.85(9)	Sn(1A)–O(1)–Sn(1)	105.15(9)
O(1)–Sn(1)–O(7)	68.35(8)	C(1)–O(2)–Sn(2)	129.5(2)
C(31)–Sn(1)–O(7)	86.80(11)	C(1)–O(3)–Sn(1A)	129.1(2)
C(41)–Sn(1)–O(7)	83.22(12)	C(3)–O(7)–Sn(2)	139.3(2)
O(1A)–Sn(1)–O(3A)	82.73(8)	C(3)–O(7)–Sn(1)	119.3(2)
O(1)–Sn(1)–O(3A)	156.22(8)	Sn(2)–O(7)–Sn(1)	98.14(8)
C(31)–Sn(1)–O(3A)	80.16(12)	O(3)–C(1)–O(2)	125.8(3)
C(41)–Sn(1)–O(3A)	76.85(12)	O(3)–C(1)–C(2)	117.2(3)
O(7)–Sn(1)–O(3A)	134.41(8)	O(2)–C(1)–C(2)	117.0(3)
O(1)–Sn(2)–C(61)	105.63(12)	O(4)–C(2)–C(1)	113.9(3)
O(1)–Sn(2)–C(51)	110.14(12)	O(8)–C(3)–O(7)	123.0(3)
C(61)–Sn(2)–C(51)	143.66(15)	O(8)–C(3)–C(4)	117.7(3)
O(1)–Sn(2)–O(2)	95.23(9)	O(7)–C(3)–C(4)	119.3(3)
C(61)–Sn(2)–O(2)	95.53(11)	O(9)–C(4)–C(3)	112.0(3)
C(51)–Sn(2)–O(2)	87.54(12)		

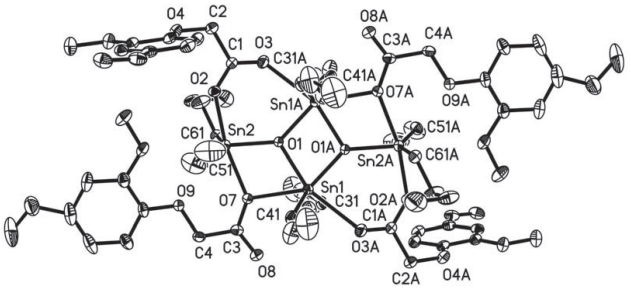

Fig. 3 The molecular structure of compound **2**.

The butyl groups lie in axial positions (C(1)–Sn(1)–C(1A) 139.43(18)), thereby completing six-coordination about the Sn atom, but they are distorted some 41.57° from a true trans position, being somewhat pinned back over the open space left by the equatorial groups. The geometry about the tin atom in **1** is best described as skew-trapezoidal bipyramid. One oxygen atom of the carboxylate of HL coordinates strongly to the Sn atom (Sn–O 2.149(2) Å), and the other carbonyl oxygen atom is much more weakly bound to the Sn atom (Sn–O 2.4936(18) Å) (Table 1). The oxygen atoms strongly bound the Sn atom lie cis to each another with a very acute O–Sn–O angle (79.89(10)°), while the weakly bound oxygen atoms lie only 8.64° from being linearly disposed to each another, thereby leaving one side of the Sn atom quite open.[14]

The most interesting aspect of the structure concerns the intermolecular weak Sn···O interactions, which help the construction of the polymeric chains (Fig. 2). The two weak Sn···O bond lengths are equal at 3.521 Å, which is less than the sum of the van der Waals radii (3.58 Å).[15] It appears that the interaction is very weak. Thus it may be concluded that the tin atom is best described as pseudo-eight-coordinate.[16]

The structure of compound **2** is centro-symmetric with a central rhombus cyclic Sn_2O_2 unit, in which the four tin atoms are linked by two bridging carboxyl groups while the remaining two carboxyl groups act as monodentate ligands to the exocyclic tin atoms. Five distannoxane rings are presented to the dimeric tetraorganodistannoxanes with planar symmetric arrangement and the two endocyclic tin atoms (Sn(1) and Sn(1A)) exhibit six-coordination with distorted octahedral geometry. The quadrangular plane about Sn(1) is defined by C(31), C(41), O(7) and O(1A) atoms and the axial positions are occupied by the O(1) and O(3A) atoms [O(1)–Sn(1)–O(3A) 156.22(8)°]. The two exocyclic tin atoms (Sn(2) and Sn(2A)) exhibit five-coordination with distorted trigonal bipyramidal geometry. As for the Sn(2) atom, the trigonal plane is defined by C(51), C(61) and O(1) atoms and the axial positions are occupied by the O(2) and O(7) atoms [O(2)–Sn(1)–O(7) 168.17(9)°], and the Sn(2) atom lies 0.0868 Å out of the trigonal plane in the direction of the O(2) atom. The two O atoms of the $Bu_4Sn_2O_2$ unit are tridentate, of which O(1) atom links three Sn(1), Sn(1A) and Sn(2) atoms and O(1A) links three Sn(1), Sn(1A) and Sn(2A) atoms. The bond distances of Sn(1)–O(1), Sn(1)–O(1A) and Sn(2)–O(1) are 2.111(2), 2.092(2) and 2.030(2) Å, respectively. The Sn(1), O(1), Sn(1A), O(1A) atoms form an endocyclic four-membered central rhombus ring, while the Sn(1), O(1), Sn(2), O(7) and Sn(1A), O(1A), Sn(2A), O(7A) atoms form two exocyclic four-membered chelating ring. The Sn(1A), O(1), Sn(2), O(2), C(1), O(3) and Sn(1), O(1A), Sn(2A), O(2A), C(1A), O(3A) form two exo-cyclic six-membered chelating ring. Additional links between the endo- and exo-cyclic Sn atoms are provided by bidentate and monodentate carboxylate ligands that form essentially symmetrical bridges (Sn(1)–O(3A) 2.559(3), Sn(2)–O(2) 2.174(2), Sn(1)–O(7) 2.436(2) and Sn(2)–O(7) 2.261(2) Å).

Table 2 Antibacterial screening results of compounds **1** and **2**

Compound*	Zone of inhibition/mm	
	Colon bacillus	Hay bacillus
Ethanol	2.0	1.5
LH	2.1	1.7
n-Bu_2SnO	4.6	3.9
1	8.2	7.5
2	13.4	11.6

*Concentration used: 200 μgml^{-1} in ethanol solution.

In addition, the endocyclic Sn(1) makes a close contact of 3.361 Å with the O(8) atom and exocyclic Sn(2) makes a close contact of 3.189 Å with the O(11) atom. The two contacts are significantly less than the sum of the van der Waals radii[15] (3.58 Å). It is observed that the bond angle of the C(51)–Sn(2)–C(61) is 143.66(15)°, which is 7.73° larger than that of C(31)–Sn(1)–Sn(41) (135.93(16)°). It appears that the intramolecular interaction is very weak. Thus it may be concluded that the exocyclic tin atom Sn(1) is best described as pseudo-seven-coordinate, and the endocyclic Sn(2) as pseudo-six-coordinate.[16]

It is interesting to note that the compound **2** adopts dimeric ladder structures and contains a tetranuclear tin framework with six distannoxane rings, the four tridentate O atoms with four Sn atoms form ten significant Sn–O bonds with the bond lengths in the range of 2.030(2)–2.436(2) Å. It is noteworthy that O(7) and O(7A) atoms function in the bidentate ligand (through one O atom only) rather than in bidentate bridging mode.

Antibacterial screening results are listed in Table 2. Table 2 shows the zone of inhibition for 200 μg/ml test solutions (ethanol as the solvent) on the two bacteria, colon and hay bacillus. The compounds **1** and **2** exhibit good antibacterial activities, while the antibacterial properties decrease in the order of **2** > **1** > $(n\text{-}Bu)_2SnO$ > LH. The antibacterial activities to hay bacillus are significantly less than those to colon bacillus.

Experimental

Elemental analyses were carried out on a Perkin-Elmer PE 2400 CHN instrument and gravimetric analysis carried out for Sn. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 MHz spectrometer. IR spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400–4000 cm^{-1} range).

2-(4-Formyl-2-methoxyphenoxy)acetic acid was obtained from commercial sources and used without further purification. The bacterial subcultures for colon and hay bacillus were obtained from the School of Life Sciences of Northeast Normal University, People's Republic of China.

Synthesis of compound **1**: A mixture of di-n-butyltin oxide (1.24 g, 5.0 mmol) and LH (2.10 g, 10.0 mmol) in 80 ml benzene was refluxed for 6 h and the binary azeotrope water/benzene was distilled off with a Dean–Stark funnel. The resulting clear solution was reduced under rotary evaporation at reduced pressure to a small volume. The residue was recrystallised from ethanol to yield 2.31 g of **1** as white crystalline solid. Single crystals suitable for X-ray analysis were obtained by slow evaporation of ethanol solution at room temperatue. Yield 71%, m.p. 153–154°C. Anal. Found (Calc) for $C_{28}H_{36}O_{10}Sn$: C, 51.7 (51.64), H, 5.6 (5.57), Sn, 18.25 (18.23)%. IR(KBr, cm^{-1}): ν(C=O) 1764, ν_{asym} (COO) 1598, ν_{sym}(COO) 1422, ν(Sn–C) 542, ν(Sn–O) 468. ^{1}H NMR ($CDCl_3$, ppm): δ 0.88 (t, 6H, –C–CH_3), 1.31–1.77 (m, 12H, –$CH_2CH_2CH_2$–), 3.96 (s, 6H, –OCH_3), 4.85 (s, 4H, –OCH_2COO), 6.85–7.45 (m, 6H, Ph), 9.87 (s, 2H, –CHO).

Synthesis of the compoud **2**: Di-n-butyltin oxide reacts with LH in 1:1 molar ratios to form **2** in a similar procedure to the above. Yield 64%, m.p. 126–128°C. Anal. Found (Calc) for $C_{72}H_{108}O_{22}Sn_4$: C, 48.1 (48.03), H, 6.1 (6.05), Sn, 26.3 (26.37)%. IR(KBr, cm^{-1}): ν(C=O) 1694, ν_{asym} (COO) 1674, 1588, ν_{sym}(COO) 1506, 1380, ν(Sn–O–Sn) 648, ν(Sn–C) 546, ν(Sn–O) 481 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 0.85 (t, 24H, –C–CH_3), 1.28–1.58 (m, 48H, –$CH_2CH_2CH_2$–), 3.94 (s, 12H, –OCH_3), 4.75 (s, 8H, –OCH_2COO), 6.83–7.43 (m, 12H, Ph), 9.85 (s, 4H, –CHO).

Crystal data (**1**): $C_{28}H_{36}O_{10}Sn$, Mr = 651.26, monoclinic, C2/c, a = 28.789(2) Å, b = 4.8867(4) Å, c = 20.1544(16) Å, β = 93.6380(10)°, V = 2829.7(4) Å^3, Z = 4, F(000) = 1336, Dx = 1.529 g cm^{-3}, μ = 0.958 mm^{-1}, T = 293(2) K, R_1 = 0.0348, wR_2 = 0.0635. (**2**): $C_{72}H_{108}O_{22}Sn_4$, Mr = 1800.34, triclinic, Pτ, a = 12.7883(8) Å, b = 13.5584(9) Å, c = 14.1763(9) Å, α = 113.9010(10)°, β = 93.3200(10)°, γ = 113.4910(10)°, V = 1989.2(2) Å^3, Z = 1, F(000) = 916, Dx = 1.503 g cm^{-3}, μ = 1.310 mm^{-1}, T = 273(2) K, R_1 = 0.0330, wR_2 = 0.0859. Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Bruker CCD Area Detector diffractometer by using the ω/φ scan technique with Mo–Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by using multiscan techniques.[17] The structure was solved by direct methods with SHELXS-97[18] and refined by full-matrix least squares with SHELXL-97[19] within WINGX.[20] All nonhydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups.

CCDC No620429 (for **1**) and No. 620428 for **2** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

Antibacterial tests of the compounds (**1**) and (**2**): Broth culture medium was prepared by mixing 10 g of albumen, 3 g of beef cream, 5 g of sodium chloride and 1000 ml distilled water at ca 37°C. 5 ml of broth culture medium was poured into the Petri-dishes and allowed to solidify. 0.2 ml of broth culture medium containing approximately 10^6 CFU/ml of Colon or Hay bacillus was uniformly plated on the surface of the sterile Petri-dishes prepared before. Then three holes of 6 mm diameter were made carefully and these were completely filled with the test solution (concentration is 200 μg/ml in ethanol solution). After the bacterium was incubated for 24 h at ca 37°C, the diameter of the inhibiting area around each hole was estimated, which is described as the inhibiting effect against bacteria.[13] The average of three diameters was calculated for each sample.

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