

# Identification of 4-oxoheptanedioic acid in the marine atmosphere by capillary gas chromatography–mass spectrometry

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First received 26 May 1994; revised manuscript received 16 August 1994

## Abstract

A capillary gas chromatographic (GC) analysis of the water-soluble fraction isolated from marine aerosols after  $\text{BF}_3$ -*n*-butanol derivatization showed the presence of several unknown carboxylic acids. Based on the characteristic mass fragment ions and molecular ion, and also the chemical composition calculated from accurate mass measurements, it is hypothesized that one of the unknown compounds is 4-oxoheptanedioic acid dibutyl ester. A comparison of its GC retention time and mass spectra with those of the dibutyl ester of an authentic standard confirmed that 4-oxoheptanedioic acid is present in the marine aerosols. This paper reports, for the first time, the identification of 4-oxoheptanedioic acid (4-ketopimelic acid) in marine atmospheric samples.

## 1. Introduction

Previous studies of water-soluble organic compounds including dicarboxylic acids in aerosol samples have provided important information for the photochemical oxidation mechanisms of organic matter in atmospheric environments [1–3]. Photochemical chamber experiments have also indicated the production of low-molecular-mass polar organic compounds from unsaturated hydrocarbons [4,5]. During the course of a capillary gas chromatographic (GC) study on short-chain  $\alpha,\omega$ -dicarboxylic acids, we detected many

unknown peaks in the diacid fraction isolated from remote marine aerosols. Some of them were identified as  $\omega$ -oxocarboxylic acids [6]. Identification of these unknown compounds is generally important because their chemical structures sometimes provide information on the origin, transformation mechanisms and fate of organic aerosols in the atmosphere. We have successfully identified one of the unknown compounds as an  $\alpha,\omega$ -dicarboxylic acid ( $\text{C}_7$ ) containing an additional keto group at the C-4 position (4-oxoheptanedioic acid).

In this paper we present electron impact mass spectra for 4-oxoheptanedioic acid dibutyl ester, identified in the  $\text{BF}_3$ -*n*-butanol derivatives of the water-soluble fraction isolated from remote marine aerosols using GC combined with low- and high-resolution mass spectrometry. Mass

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fragmentation mechanisms are described, based on the chemical compositions obtained from accurate mass measurements of the molecular ion and of characteristic mass fragment ions.

## 2. Experimental

### 2.1. Reagents and chemicals

All organic solvents were purchased from Wako. They were redistilled in the laboratory and checked for purity by GC prior to use. Organic-free pure water was prepared in the laboratory as follows. Water obtained from a Milli-Q system (Millipore) was boiled with potassium permanganate and then redistilled in all-glass apparatus. The redistilled organic solvents and pure water were stored in brown glass bottles with a Teflon-lined screw-cap. A solution of 14% boron trifluoride in *n*-butanol was purchased from Alltech/Applied Science. Authentic 4-oxoheptanedioic acid (4-ketopimelic acid) was purchased from Aldrich. The standard was derivatized to the dibutyl ester by the procedure described above.

### 2.2. Aerosol samples

Remote marine aerosol samples were collected on pre-combusted (450°C) quartz-fibre filters (Pallflex, 20 × 25 cm) using a high-volume air sampler (Shibata, HVC-1000), in the western equatorial and western North Pacific Ocean during a cruise of R/V Hakuho Maru (KH 90-2 and 90-3). The air sampler was operated with a wind speed and wind sector system to avoid potential contamination from the ship engine exhausts [7]. Thirty-three marine aerosol samples were collected in 13°S–34°N, 140°E–150°W during the period 3 September to 13 December 1990. Blank filters were set in the sampler cartridge, exposed to the air for a few seconds and then recovered. Filter samples and blank filters were placed in precleaned glass bottles (150 ml) with a Teflon-lined screw-cap and stored at –20°C until analysis.

### 2.3. Isolation

Water-soluble fractions were isolated and analysed by the methods reported previously [7]. Briefly, one eighth of each filter sample, which was cut into pieces of ca. 1 cm<sup>2</sup>, was extracted with organic-free water under ultrasonication. The water extracts, containing short-chain  $\alpha$ ,  $\omega$ -dicarboxylic acids and related compounds, were concentrated to ca. 1 ml by rotary evaporation under vacuum. To remove suspended particles, the concentrates were passed through a glass column (Pasteur pipette) packed with quartz-fibre wool and transferred to a 10-ml test-tube with a ground-glass stopper. The extracts were concentrated using a rotary evaporator under vacuum and then dried in a nitrogen stream. A 0.2-ml aliquot of 14% boron trifluoride in *n*-butanol was immediately added to the test-tube and the carboxyl groups were derivatized to dibutyl esters at 100°C for 30 min. To the test-tube were added *n*-hexane (5 ml), pure water (3 ml) and acetonitrile (0.2 ml), and the esters were extracted into the *n*-hexane layer. The hexane extracts were washed twice with pure water (3 ml). The extract containing the diacid dibutyl esters and unknown compounds was concentrated using a rotary evaporator and a nitrogen stream. The esters were dissolved in 50  $\mu$ l of hexane and then analysed by GC and GC–mass spectrometry (GC–MS).

The water-bath temperature during rotary evaporation was maintained at less than 50°C for water extracts and less than 30°C for esters. Recoveries of oxalic acid and succinic acid were 70% and 90%, respectively [7].

### 2.4. GC, GC–MS and GC–high resolution (HR) MS analysis

Dibutyl esters of carboxylic acids were determined using a capillary gas chromatograph (Hewlett-Packard HP-5890) equipped with a split–splitless injector, a Hewlett-Packard fused-silica capillary column (HP-5, 25 m × 0.32 mm I.D., 0.52- $\mu$ m film thickness) and a flame ioniza-

tion detector. Helium was used as the carrier gas. The column oven temperature was programmed from 50°C (held for 2 min) to 120°C at 30°C/min, and then to 310°C (held for 10 min) at 8°C/min. The temperatures of the injection port and the detector were maintained at 300 and 320°C, respectively. The data were processed using a Hewlett-Packard 3396A integrator or a Shimadzu C-R7A Chromatopac integrator. Conventional GC–MS analysis was conducted using an ion-trap mass spectrometer (Finnigan MAT ITS-40) interfaced to a capillary gas chromatograph (Varian GC 3400). The GC–MS data were processed using the ITS 40 data system with a NIST library. High-resolution mass spectra were obtained using a double-focusing mass spectrometer (JEOL SX-102) interfaced to a capillary gas chromatograph (HP 5890 Series II). The SX-102 mass spectrometer was operated at a resolution of 10 000. The GC column conditions for the GC–MS measurements were similar to those described above.

### 3. Results and discussion

Fig. 1 shows a reconstructed ion chromatogram of the butyl esters of a fraction isolated from the equatorial Pacific aerosol sample. Homologous series of straight-chain saturated  $\alpha,\omega$ -dicarboxylic acids and of  $\omega$ -oxocarboxylic acids were detected in the range  $C_2$ – $C_9$  in the marine aerosol samples studied [6,7]. In the samples studied, oxalic ( $C_2^{di}$ ), malonic ( $C_3^{di}$ ), succinic ( $C_4^{di}$ ), glyoxylic ( $\omega$ -oxocarboxylic acid,  $C_2^{\omega}$ ) and malic acid (hydroxysuccinic acid,  $C_4^{di}$ ) were detected as major species. These low-molecular-mass dicarboxylic acids and related compounds have been reported in continental [8–10] and marine [1,2,7] aerosols, and are considered for the most part to be derived from the photochemical oxidation of anthropogenic unsaturated hydrocarbons [10] and biogenic unsaturated fatty acids [1,3,8].

In addition to the small diacids and  $\omega$ -oxo acids identified in the aerosol samples, many

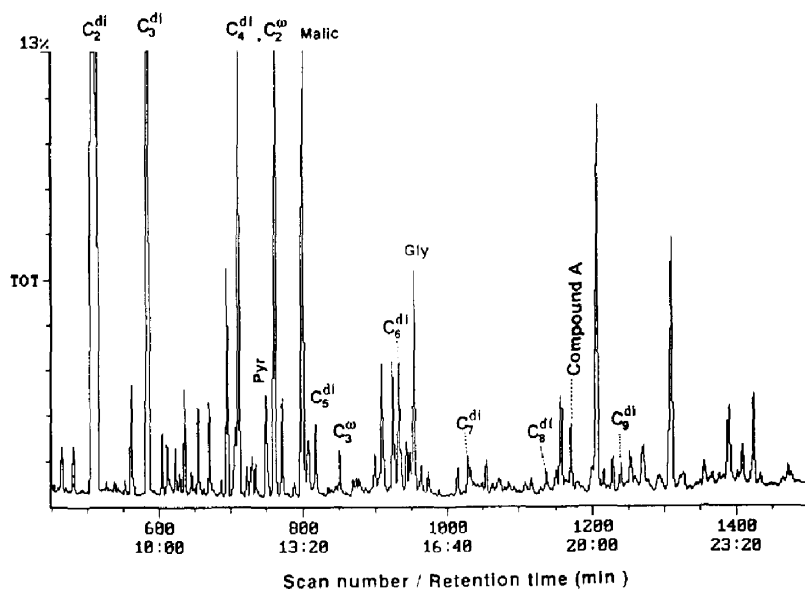


Fig. 1. Reconstructed ion chromatogram of the dicarboxylic acid dibutyl ester fraction isolated from the remote marine aerosol sample (QFF 276) collected from the western equatorial Pacific (2.39°N, 154.81°E).  $C_n^{di}$  and  $C_n^{\omega}$  denote  $\alpha,\omega$ -dicarboxylic acid and  $\omega$ -oxocarboxylic acid with  $n$  carbon atoms, respectively. Pyr, Malic and Gly denote pyruvic acid, malic acid and glyoxal, respectively.

unknown peaks were detected in the gas chromatogram of the  $\text{BF}_3$ -*n*-butanol derivatized ester fraction. Among them, we have successfully identified one peak (hereafter referred to as compound A; see Fig. 1) as a ketodicarboxylic acid dibutyl ester. Compound A elutes between suberic acid ( $\text{C}_8$ ) dibutyl ester ( $M_r = 286$ ) and azelaic acid ( $\text{C}_9$ ) dibutyl ester ( $M_r = 300$ ), suggesting that its molecular mass is close to those of  $\text{C}_8$  or  $\text{C}_9$  dicarboxylic acid dibutyl esters. The results showed that compound A was not detected in the blanks, indicating that it was not the result of contamination during either sample collection, transportation, storage or analytical procedures in the laboratory.

Fig. 2 shows an electron impact mass spectrum (low resolution) for compound A, together with its possible structure. The mass spectrum gives a base peak at  $m/z$  101 and other characteristic fragments at  $m/z$  41, 55, 73, 111, 129, 157, 185, 213 and 286. Unfortunately, the NIST library search did not provide any matching spectrum. The  $m/z$  286 ion was interpreted as the molecular ion ( $M^+$ ). The  $m/z$  213 ( $M - 73$ ) ion suggested the presence of a butyl ester group in the structure of compound A. It probably arises by elimination of a butoxy group ( $\text{C}_4\text{H}_9\text{O}$ ) from a

butyl ester moiety, and further decomposes by loss of  $\text{C}_4\text{H}_8$  [8,11] to result in the  $m/z$  157 ion. The  $M^+$  ion probably decomposes via  $\alpha$ -cleavage at the carbonyl group of a butyl ester to give the base peak at  $m/z$  101 ( $\text{COOC}_4\text{H}_9$ ) and the complementary  $M - 101$  ion ( $m/z$  185). The latter further decomposes to give the  $m/z$  111 ion by loss of butanol. Because of an absence of an even-mass number fragment ion, the structure of compound A is suggested to have no  $\gamma$ -hydrogen that can produce such a fragment ion through a McLafferty rearrangement. These considerations suggested that compound A contains an additional functional group in the carboxylic acid skeleton.

According to the above mass spectral information and interpretation, we considered compound A to be a dibutyl ester of a straight chain  $\alpha,\omega$ -dicarboxylic acid containing an additional keto group at a  $\gamma$ -position. We hypothesized, from the molecular mass ( $M_r = 286$ ), that compound A is the dibutyl ester of 4-oxoheptanedioic acid ( $\text{C}_{15}\text{H}_{26}\text{O}_5$ ) (see Fig. 2). By assuming this structure, the  $m/z$  157 and 129 ions can be explained as being formed by a cleavage of a C-C bond adjacent to the keto group. The  $m/z$  129 ion may also occur by loss of CO from

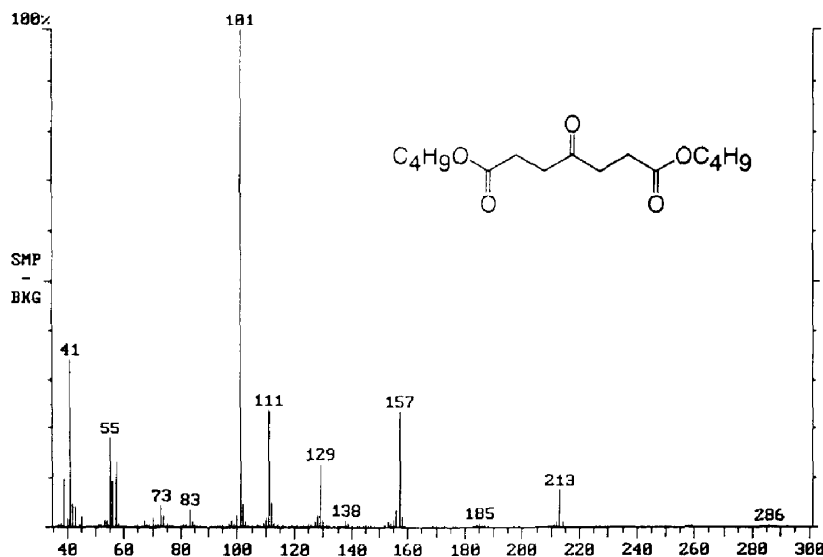


Fig. 2. Electron impact mass spectrum obtained for the unknown compound A and its hypothesized structure.

Table 1

Accurate mass measurements by HRMS for the molecular ion and major fragment ions of the compound A and their calculated chemical composition

Mass ( $m/z$ )	Error (mu)	Unsaturation	Composition
286.1746	-3.4	3.0	$C_{15}H_{26}O_6$
213.1134	0.7	3.5	$C_{11}H_{17}O_4$
157.0872	0.7	2.5	$C_8H_{13}O_3$
157.0501	0.0	3.5	$C_7H_9O_4$
129.0580	2.8	2.5	$C_6H_9O_3$
111.0436	-1.0	3.5	$C_6H_7O_2$
101.0230	0.8	2.5	$C_4H_5O_3$
73.0285	-0.5	1.5	$C_3H_5O_2$

the  $m/z$  157 ion, and decomposes to the  $m/z$  55 ion ( $CH_2CHCO$ ) by loss of butanol. These considerations are consistent with the hypothesized structure of compound A (4-oxoheptanedioic acid).

To confirm the structure, the mass spectrum of compound A was measured with a high-resolution mass spectrometer interfaced to a capillary gas chromatograph. Table 1 summarizes the measured accurate masses for the molecular ion ( $M_r = 286$ ) and major mass fragment ions and their postulated elemental compositions. Differences between the measured and calculated masses are within  $\pm 5$  mu as seen in Table 1. The accurate mass measurement of the molecular ion ( $M^+$ ;  $m/z$  286.1746) indicates that the elemental

composition of compound A is  $C_{15}H_{26}O_6$ , consistent with the structure of 4-oxoheptanedioic acid dibutyl ester as hypothesized above. The fragment ion of  $m/z$  213.1134 corresponds to  $C_{11}H_{17}O_4$ , a fragment ion ( $M - 73$ )<sup>+</sup> derived by a loss of a butoxy group ( $C_4H_9O$ ). These considerations indicate that the hypothesized structure of 4-oxoheptanedioic acid dibutyl ester is correct. Based on the HRMS results, this structure was further examined by considering mass fragmentation mechanisms, as shown in Fig. 3.

The HRMS measurements indicate that the  $m/z$  157 ion obtained by the low-resolution mass spectrometer (Fig. 2) is composed of two different ions, of  $m/z$  157.0501 and 157.0872 (see Table 1). As seen in Fig. 4, a high-resolution mass spectrum clearly shows two fragment ions in the mass range 156.8–157.3. The elemental composition of the  $m/z$  157.0872 ion is calculated as  $C_8H_{13}O_3$ . This formula is consistent with the mass fragment ( $C_8H_{13}O_3$ ) predicted from  $\alpha$ -cleavage at the C–C bond adjacent to the keto group as shown in Fig. 3. In contrast, the elemental composition of the  $m/z$  157.0501 ion is calculated as  $C_7H_9O_4$ . This fragment should be produced from the  $m/z$  213 ion ( $C_{11}H_{17}O_4$ ) by loss of  $C_4H_8$  ( $M_r = 56$ ) (see Fig. 3). The elemental composition of the  $m/z$  129.0580 ion is calculated to be  $C_6H_9O_3$ , which is probably produced by loss of CO from the  $m/z$  157.0501 ion ( $C_7H_9O_4$ ). The composition for  $m/z$  111.0436 is calculated as  $C_6H_7O_2$ , which is produced by an elimination of  $H_2O$  from the

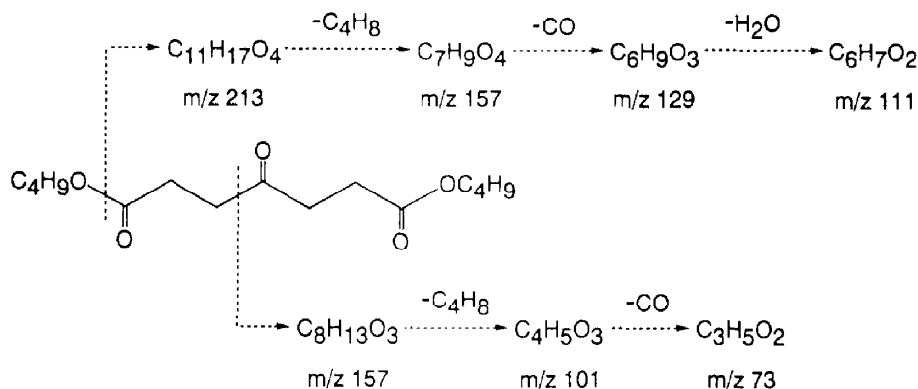


Fig. 3. Proposed schemes for mass fragmentation mechanisms of 4-oxoheptanedioic acid dibutyl ester.

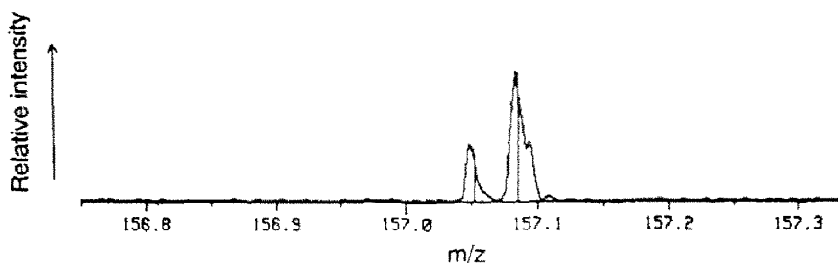


Fig. 4. High-resolution mass spectrum obtained for the unknown compound A in the mass range from  $m/z$  156.75 to 157.35.

$m/z$  129.0580 ion ( $C_6H_9O_3$ ). Elimination of  $C_4H_8$  from the  $m/z$  157.0872 ion ( $C_8H_{13}O_3$ ) produces the base peak at  $m/z$  101.0230 ( $C_4H_5O_3$ ).

Initially, we considered that the  $m/z$  185 ion was derived by loss of the butyl ester portion ( $COOC_4H_9$ ), and the  $m/z$  111 ion was produced by a subsequent loss of butanol from the  $m/z$  185 ion. However, the calculated composition ( $C_4H_5O_3$ ) for the  $m/z$  101.0230 ion does not support  $\alpha$ -cleavage at the butyl ester portion, but rather suggests the production of the  $m/z$  101 ion by elimination of  $C_4H_8$  from  $C_8H_{13}O_3$  ( $m/z$  157.0872, Table 1). These considerations led to the conclusion that the  $m/z$  101.0230 ( $C_4H_5O_3$ ) fragment ion is not  $COOC_4H_9$  but occurs by loss of  $C_4H_8$  from the  $m/z$  157.0872 ion ( $C_8H_{13}O_3$ ). The elemental composition of the  $m/z$  73.0285 ion is calculated as  $C_3H_5O_2$ , which probably arises from the  $m/z$  101.0230 ion ( $C_4H_5O_3$ ) by loss of CO. The lack of detection of the  $m/z$  73 ion derived from butyl ester moiety ( $OC_4H_9$ ) suggests that elimination of the butoxy group is insignificant. All the results and interpretations based on the high-resolution mass spectra support the hypothesis that compound A is 4-oxoheptanedioic acid dibutyl ester.

Authentic 4-oxoheptanedioic acid (4-oxopimelic acid) was purchased and esterified with 14%  $BF_3$ -*n*-butanol to the corresponding dibutyl ester, using the procedure described above for the samples. The ester was analysed by GC and GC-MS. The GC retention time of the esterified authentic compound showed excellent agreement with that of compound A. Further, the low-resolution mass spectrum of the esterified au-

thentic standard was confirmed to be identical with that of compound A (Fig. 2). The GC-HRMS analysis further supported the chemical composition for the molecular ion and mass fragment ions, as listed in Table 1. The data provide unequivocal evidence for identification of 4-oxoheptanedioic acid and indicate that the presumed mass fragmentation mechanism for the ester (Fig. 3) is reasonable. In the final stage of this study, we realized that this compound had been reported in continental aerosols as the dimethyl ester with no mass spectral information [8].

The concentrations of 4-oxoheptanedioic acid were found to be 0.03–2.5  $ng/m^3$  in the marine aerosol samples studied. Its concentrations were lower than those of dicarboxylic acids such as oxalic and malonic acid. However, this compound was detected in relatively high abundance in the marine aerosols collected over western equatorial Pacific. Although the source has not yet been identified, 4-oxoheptanedioic acid may be produced in the atmosphere by the photochemical oxidation of precursor compounds such as monocarboxylic acids having an additional keto group at the C-4 position. Interestingly, 4-ketocarboxylic acids ( $C_7$ – $C_{15}$ ) have been detected in the marine atmosphere [2,12]. They are probably produced by oxidation of monocarboxylic acids which are counterparts of the photochemical oxidation reactions of biogenic unsaturated fatty acids [1,2]. 4-Oxoheptanedioic acid may be further oxidized in the atmosphere to result in malonic and/or succinic acid, which have been abundantly detected in marine and continental aerosols [7,10].

#### 4. Conclusions

A dicarboxylic acid with an additional keto group (4-oxoheptanedioic acid) has been identified for the first time in marine aerosol samples, collected from the western Pacific, by using capillary GC–MS and GC–HRMS. The molecular structure was hypothesized based on the molecular ion and fragment ions obtained from low- and high-resolution mass spectra. The hypothesized structure was confirmed by comparing the GC retention time and mass spectra with those of the authentic standard. Based on the elemental compositions of the fragment ions obtained from high-resolution mass measurements, the formation mechanisms of the characteristic mass fragments of 4-oxoheptanedioic acid butyl ester were interpreted. 4-Oxoheptanedioic acid may be an intermediate in the formation of dicarboxylic acids such as succinic acid. This study demonstrated that capillary GC–HRMS is a powerful technique for identifying highly oxygenated organic compounds in atmospheric samples, which often retain information on the photochemical transformation of organic matter in the atmosphere.

#### Acknowledgement

This study was supported in part by the Ministry of Education, Science and Culture through Grant-in-Aid 03248104.

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