

Supplement of “Bromine Speciation in Volcanic Plumes: New in-situ Method for the Determination of Gaseous Hydrogen Bromide by Gas Diffusion Denuder Sampling”

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1 Reagents and material

1.1 Chemicals

5,6-Epoxy-5,6-dihydro-[1,10]-phenanthroline (EP), *trans*-cinnamic acid and 2,4,5-tribromanisol were purchased from Aldrich (Steinheim, Germany). Neocuproine (NC), *trans*-oxirane-2,3-dicarbon acid and pyridine were purchased from Sigma-Aldrich
15 (Steinheim, Germany). Oleic acid, (-)- α -pinene and ethylenediaminetetraacetic acid disodium salt were purchased from Fluka (Steinheim, Germany). 1,2-Epoxyoctane, sodium hydrogen carbonate and silica gel 60 (F254) were purchased at Merck. 2,4,6-Tribromanilin (98% purity), sodium carbonate and phosphorpentoxide were obtained from Acros Organics (Geel, Belgium). Hydrobromic acid (48%) and *cis*-stilbene were purchased from Alfa Aesar (Karlsruhe, Germany). *Trans*-stilbene was obtained from TCI. All other chemicals were of analytical reagent grade. Deionized water (18 M Ω cm) was used for aqueous solutions.

20 1.2 Preparation of standards

2-bromocyclooctanol, 2,3-epoxy-3-phenylpropanoic acid, 9,10-epoxystearic acid, 10-bromo-9-hydroxystearic acid and 5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr) were not commercially available and have been synthesized.

1.2.1 2-Bromocyclooctanol

The synthesis followed Haufe et al. (1977). 20 mmol 1,2-epoxycyclooctane were solved in 5 mL chloroform. While vigorous stirring
25 10 mL hydrobromic acid (48%) were added. After 30 min stirring the organic phase was separated and washed with water, saturated NaHCO₃-solution and again water. A yield of 85-90% of an oily colourless liquid was obtained.

1.2.2 3-Phenyloxirane-2-carboxylic acid

Following the synthesis of Corey and Ward (1986) and Shee et al. (2019) to 0.75 mmol trans-cinnamic acid in 500 μ L acetone 3.3 mmol NaHCO_3 in 500 μ L in water was added dropwise. A solution of Oxone (1.4 mmol, 1.8 equiv. KHSO_5) in 1.6 mL 0.4 mM ethylenediaminetetraacetic acid disodium salt was added dropwise over an hour while the temperature was kept approximately at 25 $^\circ\text{C}$ and pH 7.5. After another hour of stirring the mixture was cooled to 0 $^\circ\text{C}$ and acidified with 12 M HCl to pH 2. After adding 5 mL ethyl acetate with rapid stirring the mixture was filtered and extracted with 3 times 50 mL ethyl acetate. The combined organic fractions were washed with NaCl and dried over MgSO_4 , filtered and dried under vacuum. 1 mL ethanol was added to the resulting oil and cooled in ice. After adding 3.6 mmol KOH in another 1 mL ethanol the mixture was filtered, washed with ethanol and dried under vacuum. Approximately 75 % of the total yield of the potassium salt was obtained. The crude product was used as a coating material.

1.2.3 9,10-Epoxy stearic acid

The synthesis of 9,10-epoxy stearic acid followed Findley et al. (1945) with optimization of Milchert and Smagowicz (2009) and Milchert et al. (2010). 0.22 g acetic acid and 0.07 g sulfuric acid were added to 3.00 g oleic acid. While stirring for 15 min the solution was heated to 40 $^\circ\text{C}$ in a water bath. 1.08 g H_2O_2 were added with continued stirring to the black solution. The solution turned colourless. After 4 hours stirring the phases were separated and 5 mL water was added to the organic phase and stored at 4 $^\circ\text{C}$ for 15 min. The colourless precipitation was filtered. And washed with water until the filtrate was pH 7. 6 mL hexane and 2 mL cyclohexane were added to 3.0 g raw product and heated to 50 $^\circ\text{C}$. The product separated as a liquid phase underneath the solvents. After 16 h at 4 $^\circ\text{C}$, colourless precipitation was obtained, filtered and dried. Pure products were isolated by SiO_2 column chromatography with 1:1 of hexane and ethyl acetate as a mobile phase. 1.07-2.11 g product was obtained (37.5-73.9% yield).

1.2.4 10-Bromo-9-hydroxystearic acid

10-Bromo-9-hydroxystearic acid was synthesized following King (1949). 3.0 g diethyl ether and 3.0 mL hydrobromic acid (48%) were added to 0.3 g of 9,10-epoxy stearic acid. After stirring for 1 h the organic phase was washed with conc. sodium carbonate and water. The dried product resulted in 81 % yield. SiO_2 column chromatography with 1:1 of hexane and ethyl acetate as a mobile phase resulted in 70 % purity for 10-Bromo-9-hydroxystearic acid (GC/MS determinations).

1.2.5 5-Bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr)

A solution of 1 mmol EP in 1 mL 48% aqueous HBr was stirred for 1 hour at room temperature. When neutralizing the solution with 8 mL aqueous saturated NaHCO_3 -solution the EPBr precipitated. The colourless solid has been extracted, washed twice with 2 mL saturated NaHCO_3 -solution and three times with 3 mL water. The product has been dried under vacuum at room temperature

resulting in 72% of the theoretical yield. This is a revised prescription of the principal reported in Chini et al. (1992) and Haufe et al. (1977). Synthesis of EPBr after Porter et al. (1995) did not succeed.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ = 8.83 – 8.64 (m, 2H), 8.04 (dd, $J=7.8, 1.7, 1\text{H}$), 7.95 (dd, $J=7.7, 1.7, 1\text{H}$), 7.58 – 7.42 (m, 2H), 6.20 (d, $J=4.9, 1\text{H}$), 5.64 (d, $J=2.8, 1\text{H}$), 5.05 – 4.99 (m, 1H). The spectrum is shown in Figure S1.

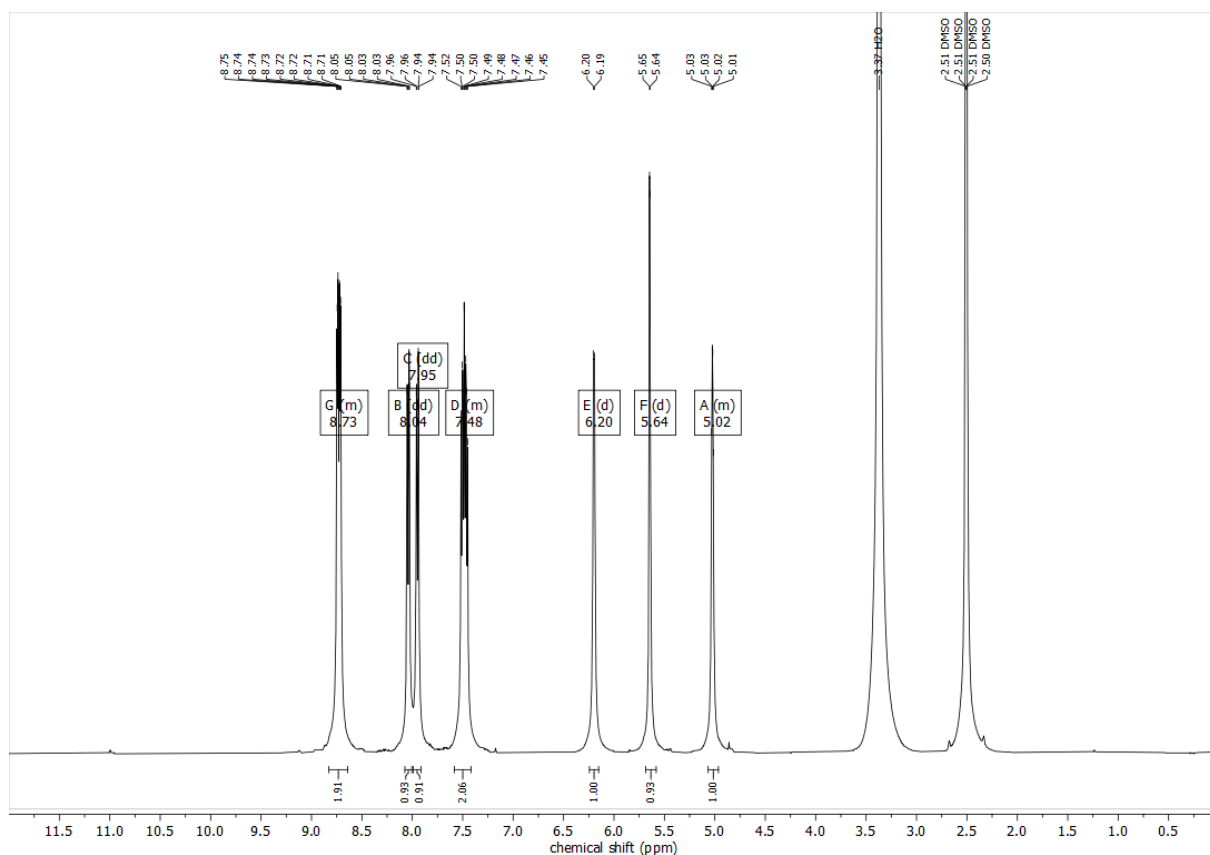


Figure S1: ^1H -NMR for 5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline

2 Gas Chromatography oven temperature programs

Table S2: GC-temperature program A, analysis of 1,2-epoxycyclooctane coated denuders

Heating rate [$^{\circ}\text{C min}^{-1}$]	End temperature [$^{\circ}\text{C}$]	Holding [min]	Duration [min]
	90	3.00	3.00
38	210	0.00	6.16
9.5	235	0.00	8.79
30	250	min. 2	min. 11.29

65 **Table S2: GC-temperature program B, analysis of 9,10-epoxystearic acid-coated denuders**

Heating rate [°C min ⁻¹]	End temperature [°C]	Holding [min]	Duration [min]
	120	0.50	0.50
38	250	0.00	3.92
10	300	0.00	8.92

Table S3: GC-temperature program C, analysis of trans-oxirane-2,3-dicarboxylic acid and 3-Phenyloxirane-2-carboxylic acid coated denuders.

Heating rate [°C min ⁻¹]	End temperature [°C]	Holding [min]	Duration [min]
	90	3.00	3.00
18	150	3.00	9.33
25	250	17.00	30.33

70

Table S4: Overview on applied temperature programs, resulting retention times and considered m/z-ratios of analytes obtained by gas chromatography coupled to electron impact ionization and quadrupole mass spectrometry, BSTFA = *N,O*-bis(trimethylsilyl)trifluoroacetamide.

compound	GC-temperature program	Retention Time [min]	m/z used for Quantification	Retention time TBA [min]
1,2-epoxycyclooctane	A	4.93	55	7.57
2-bromocyclooctanol	A	6.45	109	7.57
9,10-epoxystearic acid	B	6.86	75, BSTFA derivatized	4.13
10-bromo-9-hydroxystearic acid	B	8.09	317, BSTFA derivatized	4.13
9,10-dihydroxystearic acid	B	7.43	317, BSTFA derivatized	4.13
trans-oxirane-2,3-dicarboxylic acid	C	9.51	147, BSTFA derivatized	11.82
3-phenyloxirane-2-carboxylic acid	C	7.19	147, BSTFA derivatized	11.82

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