SYNTHESIS OF 2-NAPHTHALENE-$\underline{d}_7$-SULFONIC ACID

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SUMMARY

2-Naphthalene-$\underline{d}_7$-sulfonic acid, required as an internal standard for the analysis of organic compounds in water by gas chromatography/mass spectrometry, was synthesized in one step from commercially available naphthalene-$\underline{d}_8$ and sulfuric acid-$\underline{d}_2$. A high-performance liquid chromatographic method was developed to separate 1- and 2-naphthalene-$\underline{d}_7$-sulfonic acids. The electron impact mass spectrum and isotopic purity of the 2-naphthalene-$\underline{d}_7$-sulfonic acid were determined.

Key Words: 2-napthalene-$\underline{d}_7$-sulfonic acid, deuterium labeling, mass spectra, liquid chromatography

INTRODUCTION

The Environmental Protection Agency is developing a "Master Analytical Scheme" which is an intended protocol for qualitative and quantitative analysis of organic chemicals in water by means of gas chromatography/mass spectrometry (1). For these analyses, materials labeled with the stable isotope deuterium are needed as internal standards. Many of the required deuterium-labeled materials were commercially available. However, 2-naphthalene-$\underline{d}_7$-sulfonic acid was not, and was synthesized.

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0362-4803/82/091081-07$01.00

Received February 19, 1982
Revised May 12, 1982

The sulfonation of naphthalene with concentrated sulfuric acid can lead to two isomers, with the sulfonic acid group being in the one or two position. The amount of each isomer obtained is temperature-dependent. At low or moderate temperatures, 1-naphthalenesulfonic acid is formed (2); at a temperature of 160 °C, largely the 2-naphthalenesulfonic acid is formed (3). Small amounts of 2,2'-naphthylsulfone and of naphthalene-1,6-disulfonic acid may also be formed (3).

A method for the determination of the chemical purity of the 2-naphthalene-$\underline{d}_7$-sulfonic acid was required, since 1-naphthalenesulfonic acid can be produced along with 2-naphthalenesulfonic acid. Various paper chromatographic (4) and thin-layer chromatographic (5) techniques have been reported, but separation and quantitation are difficult. A high performance liquid chromatographic method which provided separation was developed.

The mass spectra of labeled and unlabeled 2-naphthalenesulfonic acids and the isotopic purity of the 2-naphthalene-$\underline{d}_7$-sulfonic acid were determined.

RESULTS AND DISCUSSION

A convenient method for the preparation of 2-naphthalene-$\underline{d}_7$-sulfonic acid by the sulfonation of deuterated naphthalene with deuterated sulfuric acid has been developed. The method gives a 68 percent yield with 98.5 percent chemical purity as determined by liquid chromatography and an atom percent deuterium of 98.2 percent.

For the determination of the purity of the product, a reverse phase ion-pairing liquid chromatographic method gives baseline separation of 1- and 2-naphthalenesulfonic acids, as shown in Fig. 1, and permits quantitative analysis.

Commercial samples of 1- and 2-naphthalenesulfonic acids as well as the 2-naphthalene-$\underline{d}_7$-sulfonic acid were analyzed. The 2-naphthalene-$\underline{d}_7$-sulfonic acid had a retention time of 26.1 and

1-naphthalene-$\underline{d}_7$-sulfonic acid of 22.9 min with the experimental

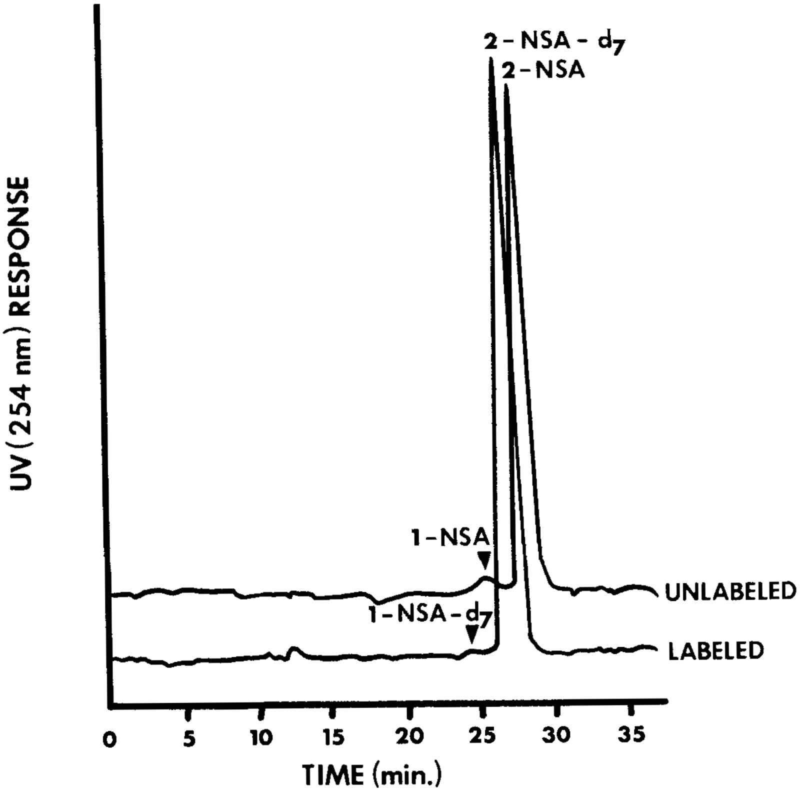

Fig. 1. Reverse Phase High Performance Liquid Chromatographic Separation of 1- and 2-Naphthalenesulfonic Acids (1-NSA and 2-NSA).

conditions used; baseline resolution was obtained. The 2-naphthalene-$\underline{d}_7$-sulfonic acid contained 0.6 percent 1-naphthalene-$\underline{d}_7$-sulfonic acid, plus low levels of unidentified impurities at retention times of 11 and 12.5 minutes. Retention times for the deuterated materials are 1 to 1.2 minutes less than for the corresponding non-deuterated compounds.

The mass spectrum of 2-naphthalenesulfonic acid is shown in Fig. 2. The molecular ion is observed at m/z 208, and the major fragments are m/z 144 resulting from the loss of SO_2, m/z 127 resulting from loss of $\cdot SO_3H$, and m/z 115 corresponding to

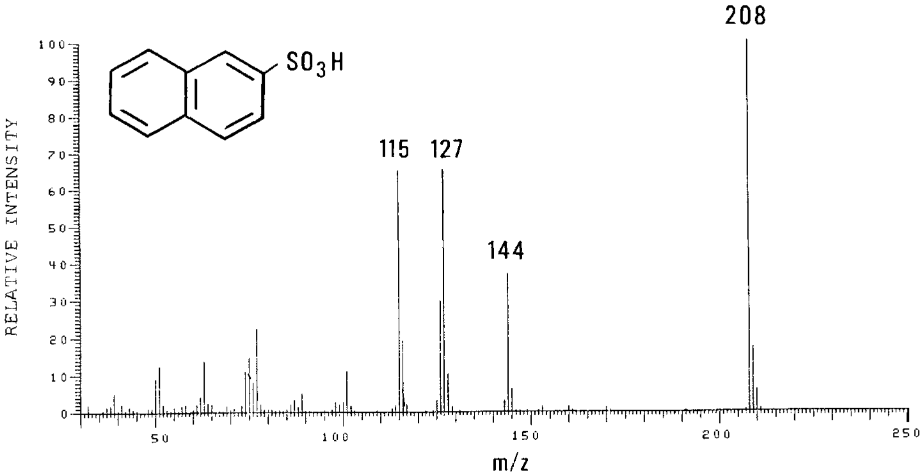

Fig. 2. Mass Spectrum of 2-Naphthalenesulfonic Acid.

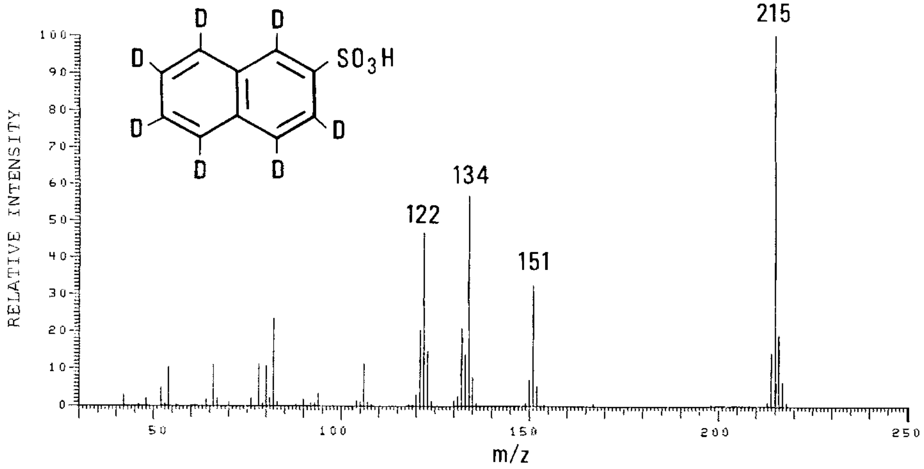

Fig. 3. Mass Spectrum of 2-Naphthalene-$\underline{d}_7$-sulfonic Acid

successive losses of SO_2 and ·HCO. The fragmentation closely resembles that reported for benzenesulfonic acid (6). 2-Naphthalene-$\underline{d}_7$-sulfonic acid gave a molecular ion at m/z 215 (Fig. 3), and the elemental composition of this ion was confirmed by high resolution mass spectrometry. The three major fragments resulted from the same losses observed for the unlabeled compound.

EXPERIMENTAL

The deuterium labeled starting materials were obtained from commercial sources and were used as received. The naphthalene-$\underline{d}_8$ was 98+ atom percent deuterium; the sulfuric acid-$\underline{d}_2$, a 98 percent solution in deuterium oxide, was 99.5+ atom percent deuterium.

Naphthalene-$\underline{d}_8$ (4.83 g, 0.0355 moles) was placed in a 25-mL round-bottom flask which had been pre-dried and flushed with nitrogen. A magnetic stirring bar was added to the flask, and the flask was placed in a silicone oil bath at 160 °C. The naphthalene was melted, and 4.5 mL (0.081 mol) sulfuric acid-$\underline{d}_2$ was added dropwise from a separatory funnel over a period of several minutes with stirring. The mixture was stirred an additional ten minutes, and poured into a beaker containing 40 mL water in an ice bath. The precipitate (0.048 g) of unreacted naphthalene-$\underline{d}_8$ and 2,2'-naphthyl-$\underline{d}_7$-sulfone (7) was removed by filtration through a sintered glass funnel. The filtrate was extracted with two 50-mL portions of toluene to remove the last traces of these compounds. The aqueous layer containing the 2-naphthalene-$\underline{d}_7$-sulfonic acid was concentrated to about 15 mL under reduced pressure on a rotary evaporator and allowed to crystallize. After the mixture was cooled overnight at 4 °C, the crystals were collected by filtration on a sintered glass filter, and washed several times with small amounts (less than 1 mL each time) of ice-cold 3 mol/L hydrochloric acid. The material was then transferred to a 30-mL centrifuge tube, dissolved in warm (70 °C) 3 mol/L hydrochloric acid, and allowed to crystallize, first at room temperature, then at 4 °C. The material was centrifuged, the mother liquor was removed with a Pasteur pipette, and the crystals rinsed with cold 3 mol/L hydrochloric acid. A second recrystallization was done in the same way. The crystals were dried in a vacuum desiccator over sodium hydroxide pellets. The yield of white crystals of

2-naphthalene-$\underline{d}_7$-sulfonic acid monohydrate was 5.61 g (68%), mp 121-3 °C (lit mp for unlabeled 2-naphthalenesulfonic acid monohydrate 124-125 °C). Anal. Calcd for $C_{10}HD_7SO_3 \cdot H_2O$: C, 51.51; apparent H, 4.66; S, 13.75. Found: C, 51.45; apparent H, 4.72; S, 13.64.

For high performance liquid chromatography, a 20-μL sample loop and a 25 x 0.46 cm column packed with a microparticulate octadecylsilane of 6-8 μm particle diameter operated at a flow rate of 1 or 2 mL/min with ultraviolet absorption detection at 254 nm were used. The mobile phase was 20 percent acetonitrile in aqueous 0.005 mol/L tetrabutylammonium phosphate. Under these conditions, the retention time for 2-naphthalene-$\underline{d}_7$-sulfonic acid was 26.1 min, for 1-naphthalene-$\underline{d}_7$-sulfonic acid, 22.9 min.

Electron impact mass spectra were recorded at 70 eV and an ion source temperature of 150 °C. The samples were introduced by direct probe at 73-77 °C. The isotopic purity was calculated from an average of six scans of the molecular ion cluster obtained under the same conditions as the complete spectrum. The atom percent deuterium for the labeled positions was 98.2 with an uncertainty estimated not to exceed ±0.3. The high resolution mass spectrum was recorded photographically at a resolution of 15,000. The exact mass of the molecular ion was measured. Calcd. for $C_{10}HD_7SO_3$: 215.0634. Found 215.0626.

ACKNOWLEDGMENT

Partial financial support from the U. S. Environmental Protection Agency under Interagency Agreement No. EPA-IAG05-E684 is gratefully acknowledged.

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