Mass Spectrometry Data Center

National Institute of Standards and Technology
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Unexpected EI Fragmentations: Loss of Tetramethylsilane in Vicinal TMS diols

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Overview

- In the building of the NIST Mass Spectral Library, the overall goal is to measure and confirm the accuracy of mass spectral data (MSD). Several steps have to be followed. MSD obtained are evaluated using the NIST Mass Interpreter software system and the established ion fragmentation rules, besides library searches.

Introduction

- Unexpected fragmentations arising from complex rearrangements were commonly observed during the building of the 2020 NIST Library. Reported here is a related example: Isomers of the TMS derivatives of aromatic diols and triols have very different spectra depending on the TMSO positions. The derivatives with TMSO in *ortho*-position lose tetramethylsilane if a stable cation is formed in another part of the molecule. More than a dozen compounds have been studied.
- We will provide an interpretation of the fragmentations and support the putative mechanisms with the analysis of a series of similar compounds that have similar or very different mass spectra.

Methods

- Spectra from over 20,000 pure compounds purchased from different companies were added to the NIST 2017 Library to build the NIST 2020 Library. The underivatized and derivatized small molecule compounds were analyzed using GC-MS in the EI mode.
- Mass spectra were acquired at 70eV on an Agilent 7000 triple quadrupole. All the GC-MS data files were processed using NIST's Automated Mass Spectral Deconvolution and Identification System (AMDIS) software.
- Each spectrum was evaluated using the following steps: 1) Use of MS Interpreter, a program that links product ions to chemical structure. 2) Application of established MS fragmentation rules. 3) Use of library searches.
- After evaluation, a spectrum was accepted, put on hold for further experiments, or rejected. Unexpected fragmentations were always the subject of more attention.

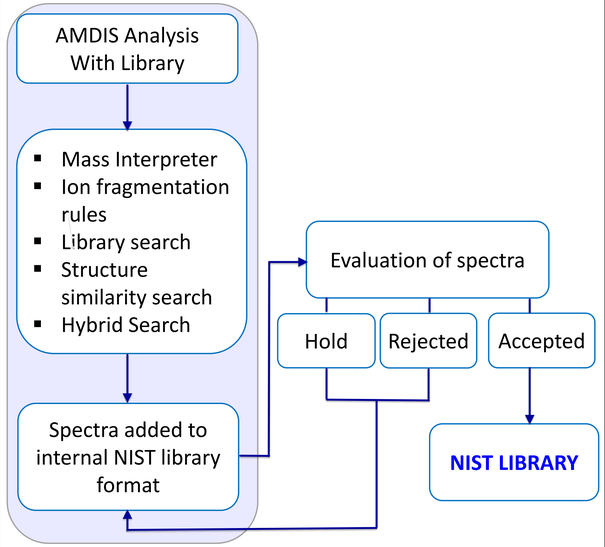
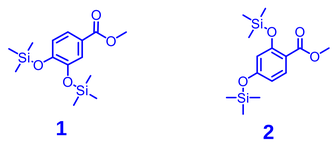


Figure 1. General process for building NIST MS library

Results

- The isomers Methyl 3,4-dihydroxybenzoate, 2TMS (1) and Methyl 2,4-dihydroxybenzoate, 2TMS (2), have very different spectra.
- Isomer 1 yields m/z 193 as base peak, which is very weak in isomer 2. In our study, all benzoic acid esters homologous with any vicinal TMS diols have this peak as major one. Similarly, TMS triols, like Methyl-trihydroxybenzoates with vicinal TMS diols showed m/z 281 as base peak.
- Isomer 2 shows $(M-15)^+$ as base peak, which is common in TMS derivatives. However, in isomer 1 $(M-15)^+$ is relatively weak (33%). Compounds with a trimethylsilyloxy group in *ortho*-position with the acid show $(M-15)^+$ as base peak.



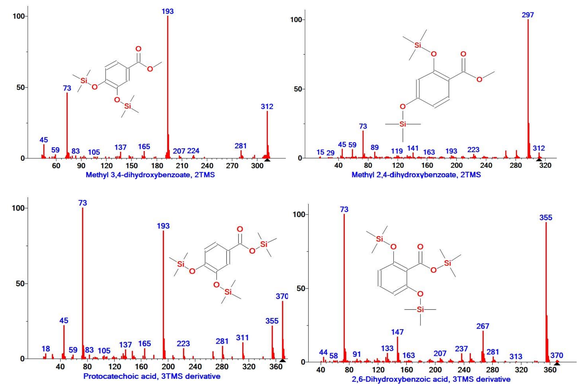


Figure 2. GC-MS spectra of dihydroxybenzoates, TMS derivatives

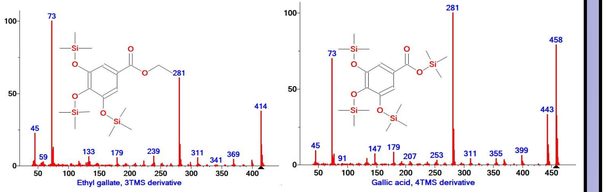
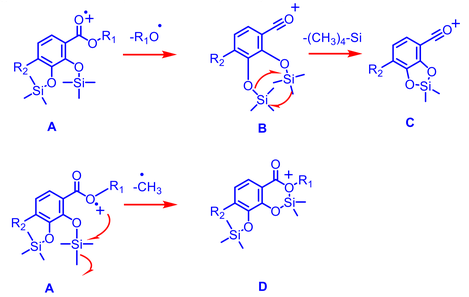


Figure 3. GC-MS spectra of trihydroxybenzoates, TMS derivatives



Ion B results from the loss of a radical $R_1O^{\bullet}$
Ion C appears to result from a cyclisation with the transfer of a methyl and the loss of the neutral compound tetramethylsilane. Ion B has to have a positive charge very stable and two TMSO groups in an *ortho*-position.
A competing reaction is the loss of a CH_3 group from any TMS group. This reaction will give a six-membered stable ring when the TMSO group is in an *ortho*-position with the acid. This would explain why $(M-15)^+$ is the base peak in those compounds. Otherwise $(M-15)^+$ is relatively weak (see Table 1).

Table 1. Some examples of compounds and their characteristic ions

Compound	$M^{+\cdot}$(m/z)	$(M-15)^+$	Ion B	Ion C
Methyl 3,4-dihydroxybenzoate, 2TMS	312 (33)	297 (2)	281 (5)	193 (100)
Methyl 2,4-dihydroxybenzoate, 2TMS	312 (4)	297 (100)	281 (6)	193 (2)
Protocatechoic acid, 3TMS	370 (38)	355 (22)	281 (8)	193 (85)
2,6-Dihydroxybenzoic, 3TMS	370 (1)	355 (94)	281 (4)	193 (2)
Ethyl gallate, 3TMS	414 (38)	399 (4)	369 (5)	281 (61)
Gallic acid, 4TMS	458 (79)	443 (33)	369 (3)	281 (100)

This reaction of cyclisation with loss of a neutral molecule was also seen in *tert*-Butyldimethylsilyl derivatives (TBDMS derivatives), with the transfer of *tert*-butyl and loss of di-*tert*-Butyldimethylsilane.

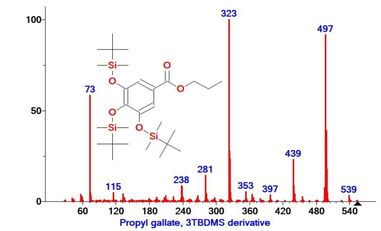
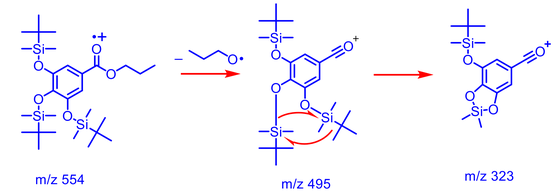


Figure 4. GC-MS spectrum of Propyl gallate, 3TBDMS derivative



Conclusion

To our knowledge, this is a new type of fragmentation involving the elimination of tetramethylsilane and formation of a siloxane ring from a stable cation with two vicinal TMSO groups. The reaction was also observed with the elimination of di-*tert*-Butyldimethylsilane in TBDMS derivatives.