

Rearrangement of the TMS ester of 4-Oxo-4H-chromene-2-carboxylic acid and analogs in EI mass spectra

Quan-Long Pu; H. Martin Garraffo; Yufang Zheng; N. Rabe Andriamaharavo; Stephen E. Stein

National Institute of Standards and Technology, Gaithersburg, MD 20899



Overview

During the interpretation of the EI mass spectra of the TMS ester of 4-Oxo-4H-chromene-2-carboxylic acid and analogs, we observed an interesting ion formed by the rearrangement of the TMS group and intramolecular reaction with simultaneous loss of a C_3O (:C=C=C=O) molecule. This fragmentation path does not appear to have been previously reported.

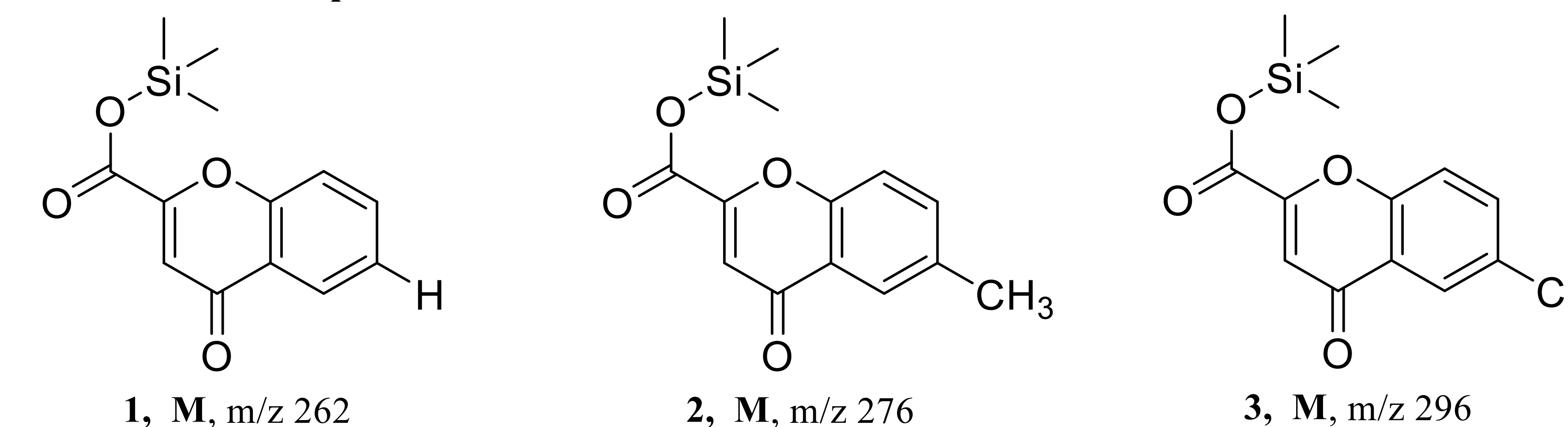
Introduction

In the course of adding spectra to the NIST/EPA/NIH Mass Spectral Library we investigated, and report here, the unusual migration of a dimethylsilyloxy group and elimination of C_3O in a TMS ester of 4-Oxo-4H-chromene-2-carboxylic acid and analogs. Specifically, we report a mechanism of formation of an ion 2,2-Dimethyl-4-oxo-1,4-dihydro-2H-benzo[d][1,3,2]dioxasilin-1-ium from rearrangement and intramolecular reaction of the TMS ester in three analogs by GC/MS and GC/MS/MS. This ion arises from an $[M-CH_3]^+$ in the EI mass spectra of the TMS ester of 4-Oxo-4H-chromene-2-carboxylic acid and analogs.

Materials and Methods

7-Chloro-4-oxo-4H-chromene-2-carboxylic acid was purchased from a commercial source and dissolved in acetonitrile at concentrations of about 1mg/ml, and the TMS derivative was prepared by adding 30 μ l of BSTFA to 95 μ l of sample solution at 50 $^\circ$ C for 5 hrs. The mass spectrum was acquired at 70eV on a triple quadrupole GC/MS instrument, in the EI mode, and also in tandem EI mode. The collision gas for GC/MS/MS was N_2 and the collision energies were 5V, 10V, 20V, and 40V. The mass spectra of the other two analogs were from the NIST/EPA/NIH Mass Spectral Library.

The studied compounds are listed below:



Results

GC/MS

Mass spectrum of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS has characteristic ions **a** (m/z 281/283), **b** (m/z 229/231) and **c** (m/z 53).

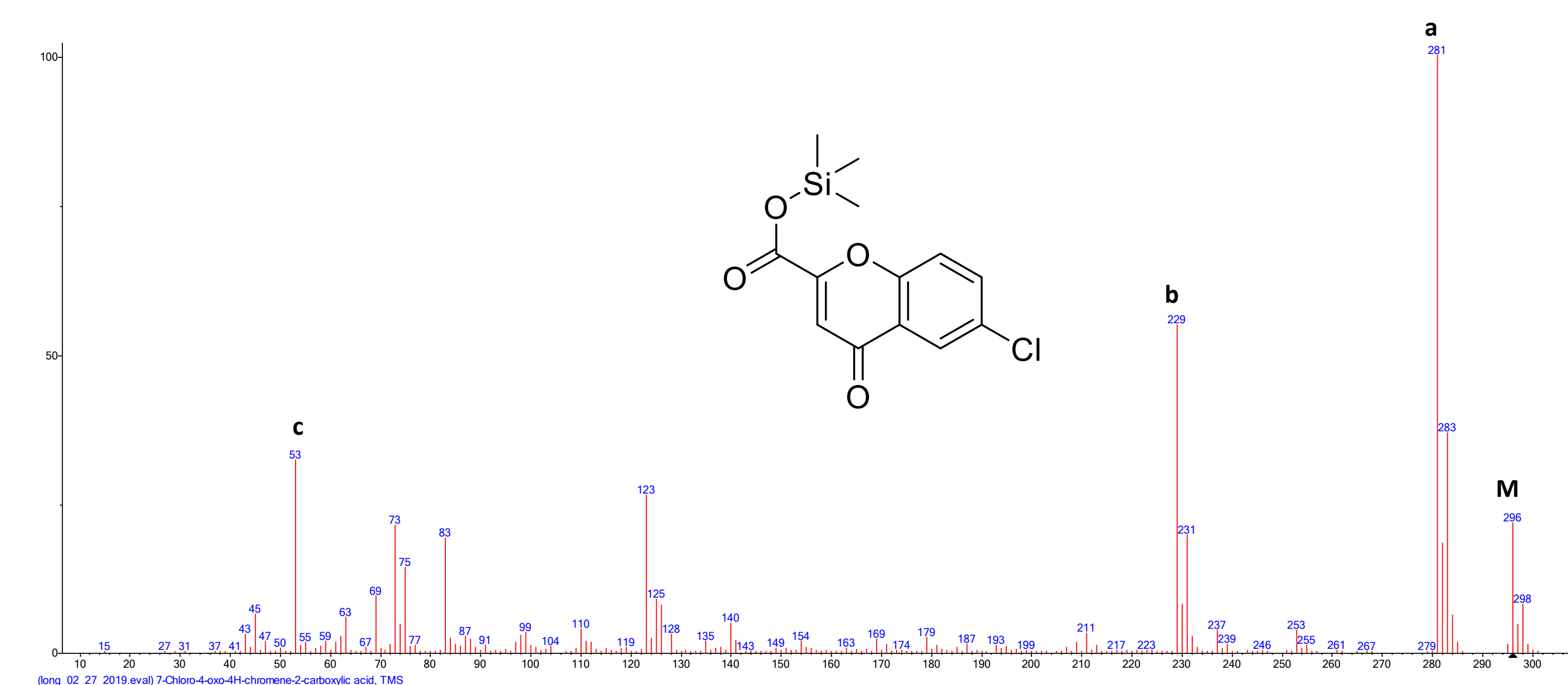


Figure 1. EI Mass spectrum of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS [compound 3]

The mass spectrum of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS (Figure 1) shows a base peak at m/z 281/283 (ion **a**), a second intense peak at m/z 229/231 (ion **b**) and a third at m/z 53 (ion **c**). Ion **b** is not recognized by the MS interpreter software tool and cannot be explained by a simple reaction.

GC/MS/MS

1. GC/MS/MS Product ion scan of ion **M**⁺ (m/z 296) using collision energy of 5V. Ion **a** ($M-CH_3$, m/z 281) is a product ion of **M**⁺.

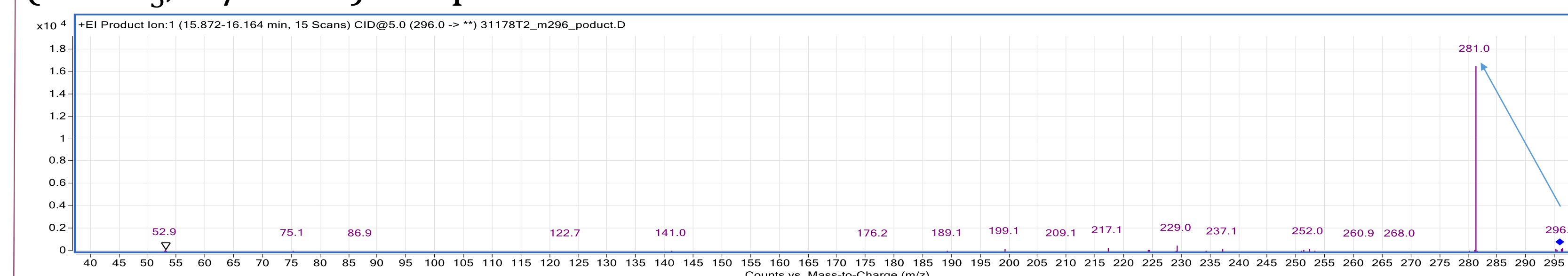


Figure 2. MS/MS Product ion scan of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS; precursor ion **M**⁺.

2. GC/MS/MS Product ion scan of ion **a** ($M-CH_3$, m/z 281) using a collision energy of 20V. Ions **b** (m/z 229) and **c** (m/z 53) are product ions of **a** ($M-CH_3$)⁺.

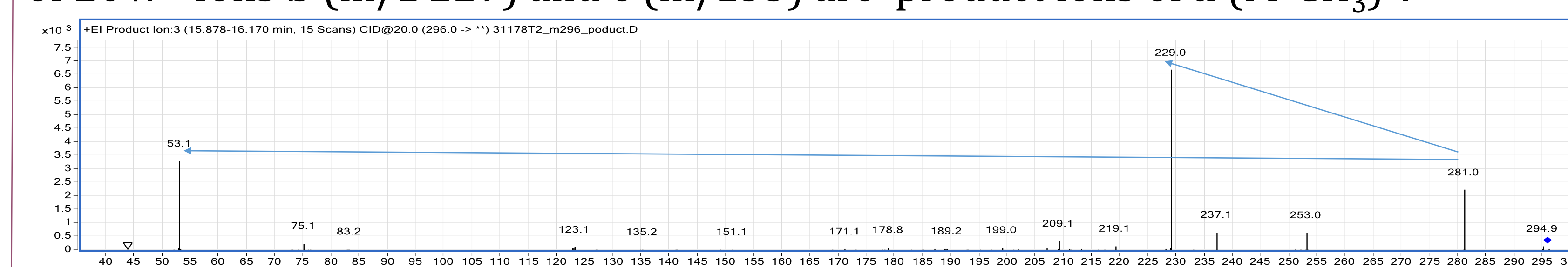


Figure 3. MS/MS Product ion scan of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS; precursor ion $[M-CH_3]^+$.

3. GC/MS/MS Precursor ion scan of **b** (m/z 229) using a collision energy of 10V. The ion **a** (m/z 281) is a precursor ion of **b** (m/z 229).

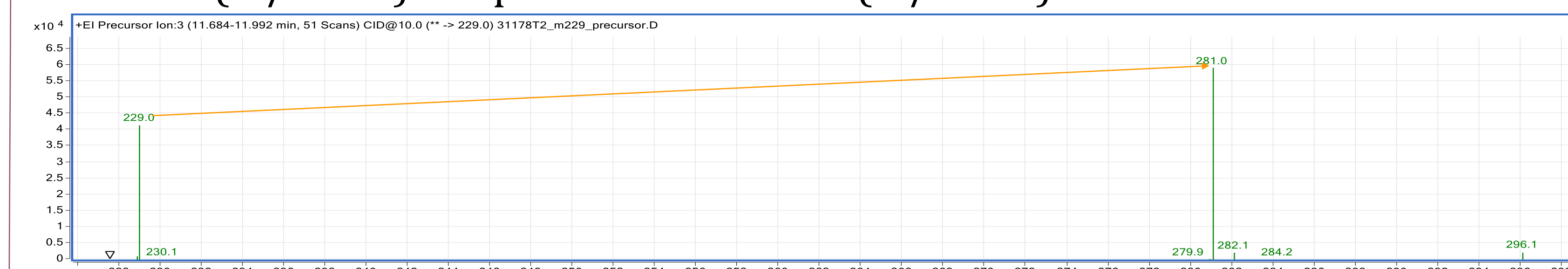
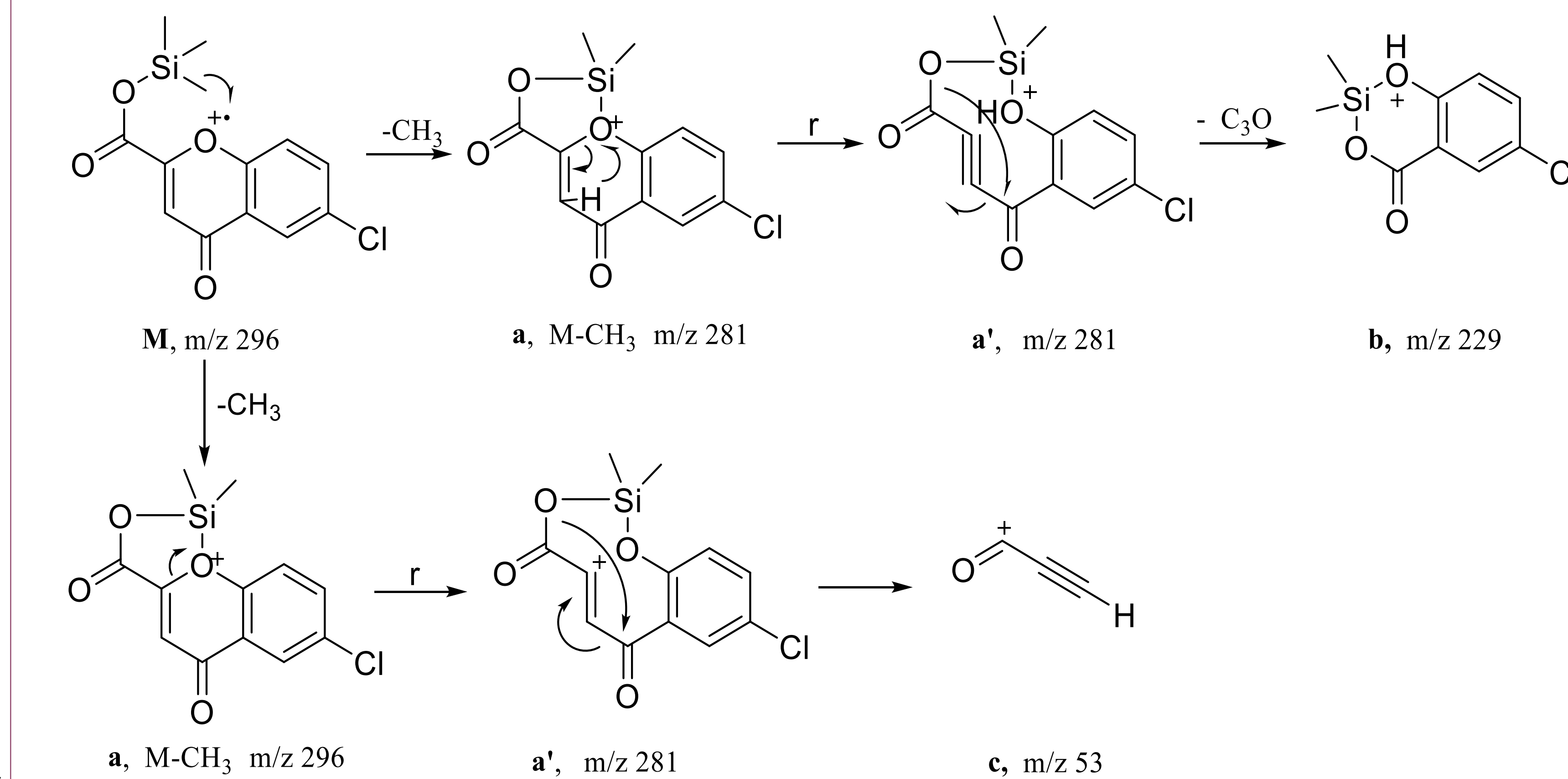


Figure 4. MS/MS Precursor ion scan of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid, TMS; daughter ion **b** (m/z 229).

Based on the GC/MS/MS results, the proposed mechanism begins with a CH_3 cleavage from the trimethylsilyl group and formation of an intermediate ring (ion **a'**, $M-CH_3$). The prominent peak at m/z 229/231 (ion **b**) in the spectrum is proposed to arise through a rearrangement with a C_3O (:C=C=C=O) loss. The GC/MS/MS analysis of product and precursor scanning shows that $M^+ \rightarrow$ ion **a** ($M-CH_3$) \rightarrow ion **b** ($M-15-52$). The driving force of this fragmentation process is probably the stability of the ion **b** produced.

The proposed fragmentation pathway of the TMS ester of 7-Chloro-4-oxo-4H-chromene-2-carboxylic acid is shown below:



The studied compounds and their resulting fragments ions **a**, **b**, and **c** in the EI mode are listed in table 1.

$(CH_3)_3Si-O-CO-(C_9H_8O)(=O)-R$

No	R	M (m/z)	Ion a , m/z (%)	Ion b , m/z (%)	Ion c , m/z (%)
1	H	262	247 (100)	195 (97)	53 (31)
2	CH_3	276	261 (100)	209 (96)	53 (25)
3	Cl	296	281 (100)	229 (55)	53 (32)

Table 1. Studied compounds and their characteristic ions **a**, **b** and **c**

Conclusion and discussion

Ions **b** [$C_9H_{10}O_3SiR$]⁺ and **c** [C_3HO]⁺ are the characteristic ions of the TMS ester of 4-Oxo-4H-chromene-2-carboxylic acid and analogs in EI mass spectra. Both result from $[M-CH_3]^+$ via an intermediate ring (ion **a'**). Ion **b** has a further loss of a C_3O (:C=C=C=O) molecule. Ion **c** arises also from **a'**, carrying the charge on the other side of the cleavage.

The driving force of this fragmentation process is probably the stability of the ion **b** produced.

The loss of C_3O does not appear to have been previously reported in the fragmentation progress of organic compounds in EI mass spectrometry. Tricarbon monoxide C_3O (Ref. 1) is a reactive radical oxocarbon molecule found in space, which can be made as a transient substance in the laboratory. It can be trapped in an inert gas matrix or made as a short lived gas. C_3O can be classified as a ketene.