Structure analysis of unknown compound in oyster using HS-SPME-GC-TOFMS

Product used: Mass Spectrometer (MS)

Introduction

Oysters are a shellfish that are eaten all over the world because of their rich flavor and delicious texture. Oysters have a unique odor, and previous study has revealed that this odor comes from (Z)-1,5-Octadien-3-ol (Oyster Alcohol, Figure 1)[1]. In this previous study, oyster extracts were analyzed using a nuclear magnetic resonance spectrometer (NMR) and aroma components were analyzed using a gas chromatograph mass spectrometer (GC-MS) , and (Z)-1,5-Octadien-3-ol was synthesized for final confirmation and identification.

GC-MS is often used to analyze aroma components. In qualitative analysis using GC-MS, compound identification is commonly performed by library search using commercially available electron ionization (EI) mass spectral database (DB) like NIST DB. However, 1,5-Octadien-3-ol is an “unknown compound” that is not registered in the NIST DB. In this case, the molecular formula of even an unknown compounds can be determined by using a time-of-flight mass spectrometer (TOFMS) as a mass spectrometer and performing an "integrated analysis" that combines electron ionization and soft ionization[2]. Furthermore, by using automated structure analysis software named “msFineAnalysis AI” which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures, it is possible to estimate the structural formula[3].

Therefore, in this MSTips, we used msFineAnalysis AI to analyze the unregistered compound "1,5-Octadien-3-ol" in the DB, and confirmed the accuracy with which the corresponding structure could be obtained.

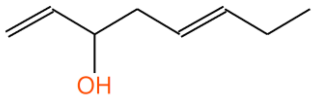

Figure 1 1,5-Octadien-3-ol

Experimental

Sample and measurement

Commercially available raw oysters were used as samples. Finely chopped raw oyster 2.5 mg was sealed in a 20 mL vial (Figure 2). The SPME mode of the HT2850T autosampler (HTA S.R.L.) was used as the sample preparation device, and volatile components in the headspace area of the vials were targeted for the measurement. A GC-TOFMS (JMS-T2000GC AccuTOF™ GC-Alpha, JEOL Ltd., Figure 3) was used for the measurement. We performed HS-SPME-GC-TOFMS measurements using both EI and field ionization (FI) modes with a combination EI/FI ion source. The qualitative data processing was performed with msFineAnalysis AI (JEOL Ltd.). Measurement conditions are shown in Table 1.

Figure 2 Oyster sample in a vial

Figure 3 JMS-T2000GC with HT2850T autosampler

Table 1 Measurement condition

SPME	
SPME Fiber	50/30 µm DVB/CAR/PDMS 2mm (Merck)
Sample amount	2.5 mg
Extraction temp.	50 °C
Extraction time	30 min
Desorption time	3 min

GC	
Column	ZB-WAX (Phenomenex) 30 m×0.25 mm I.D., df=0.25 µm
Inlet	230 °C, Splitless
Oven	50 °C (2 min) →10 °C/min→240 °C/min (10 min)
Carrier flow	He, 1.0 mL/min (Constant Flow)

MS	
Ion Source	EI/FI combination ion source
Ionization	EI+:70 eV, 300 µA, FI+:-10 kV
m/z Range	*m/z* 33 - 800

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Data analysis

Data analysis was performed by msFineAnalysis AI version 2 (JEOL Ltd.). For searching 1,5-Octadien-3-ol, target analysis function of msFineAnalysis AI was used. Target analysis is a function that searches for compounds based on the molecular formula, *m/z* value, and CAS# if registered in NIST database that are pre-registered in the target list (Figure 4). Although 1,5-Octadien-3-ol, the target of this analysis, is an unregistered component in the DB, this function was used in the analysis because a rapid search for 1,5-octadien-3-ol can be expected by registering its molecular formula.

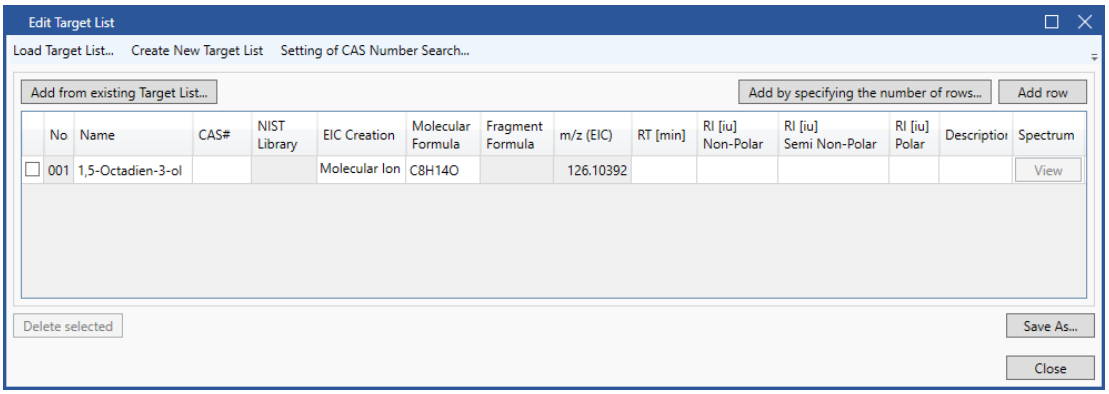

Figure 4 Target list

Results and Discussion

Search for 1,5-Octadien-3-ol using target analysis function

Figure 5 shows TICC and extracted ion chromatogram (EIC) of 1,5-Octadien-3-ol molecular ion. The most intense peak in TICC (RT 9.91 min) was also detected in EIC, and therefore this compound was analyzed in detail. Figure 6 show target analysis result of this peak. In target analysis, the presence of target compounds are confirmed by a combination of several judgments. In this measurement, three types of judgements were used: accurate mass analysis of molecular ions, isotope pattern matching, and EI fragment ion coverage. As a result, all judgements were "OK," and it was estimated that this compound was 1,5-octadien-3-ol. Therefore, AI structure analysis of this compound was carried out.

AI structure analysis result for 1,5-Octadien-3-ol

Figure 7 shows AI structure analysis result of this compound. There were 2,622 candidates in AI structure analysis result for the molecular formula ($C_8H_{14}O$) that matched 1,5-Octadien-3-ol. Since 1,5-octadien-3-ol has a hydroxyl group, the “OH” substructure filter was used to narrow down the candidates to 1,056. Finally, the structural formula of 1,5-Octadien-3-ol was obtained as the No.1 candidate. In addition, msFineAnalysis AI calculates an AI score between the measured and predicted mass spectra, which was also high at 892 (Max 999).

As shown above, structural formula of 1,5-Octadien-3-ol was obtained good accuracy by AI structure analysis result of msFineAnalysis AI. Although this structural analysis result does not include stereoisomer information and therefore cannot allow complete identification, it has been shown that speedy structural estimation is possible without relying on the equipment or the skill of the analyst.

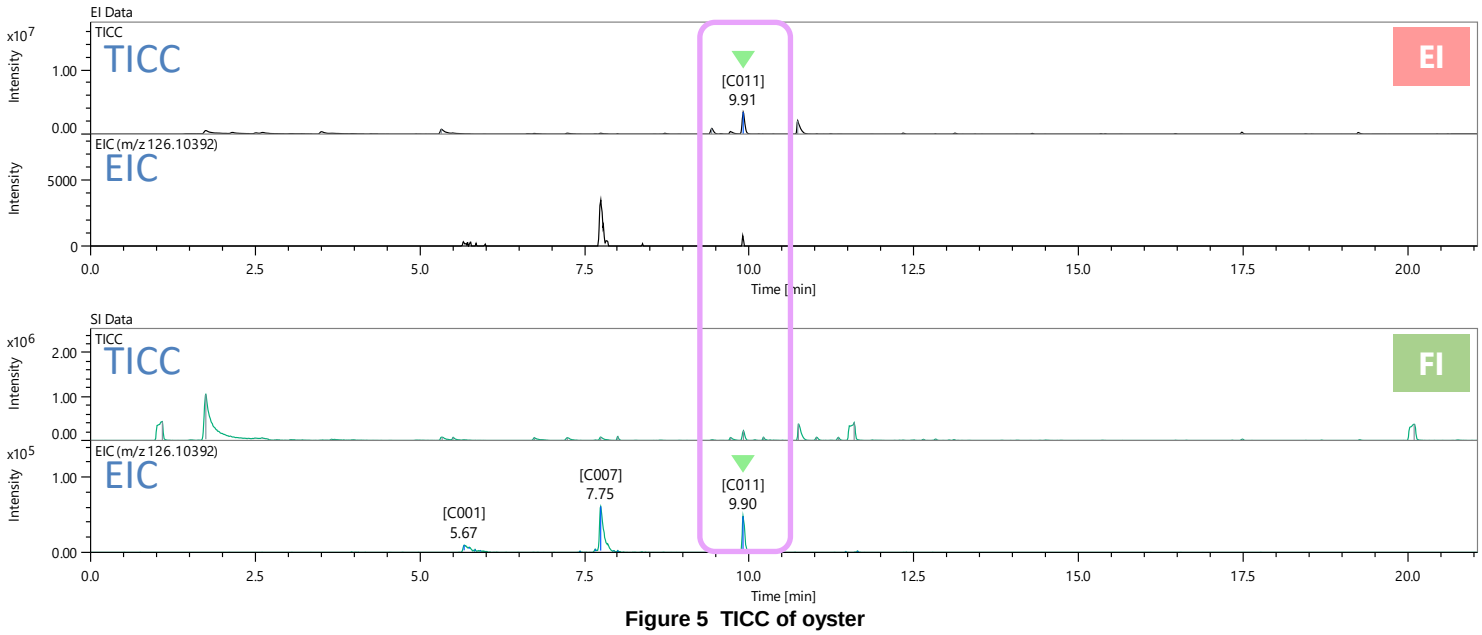

Figure 5 TICC of oyster

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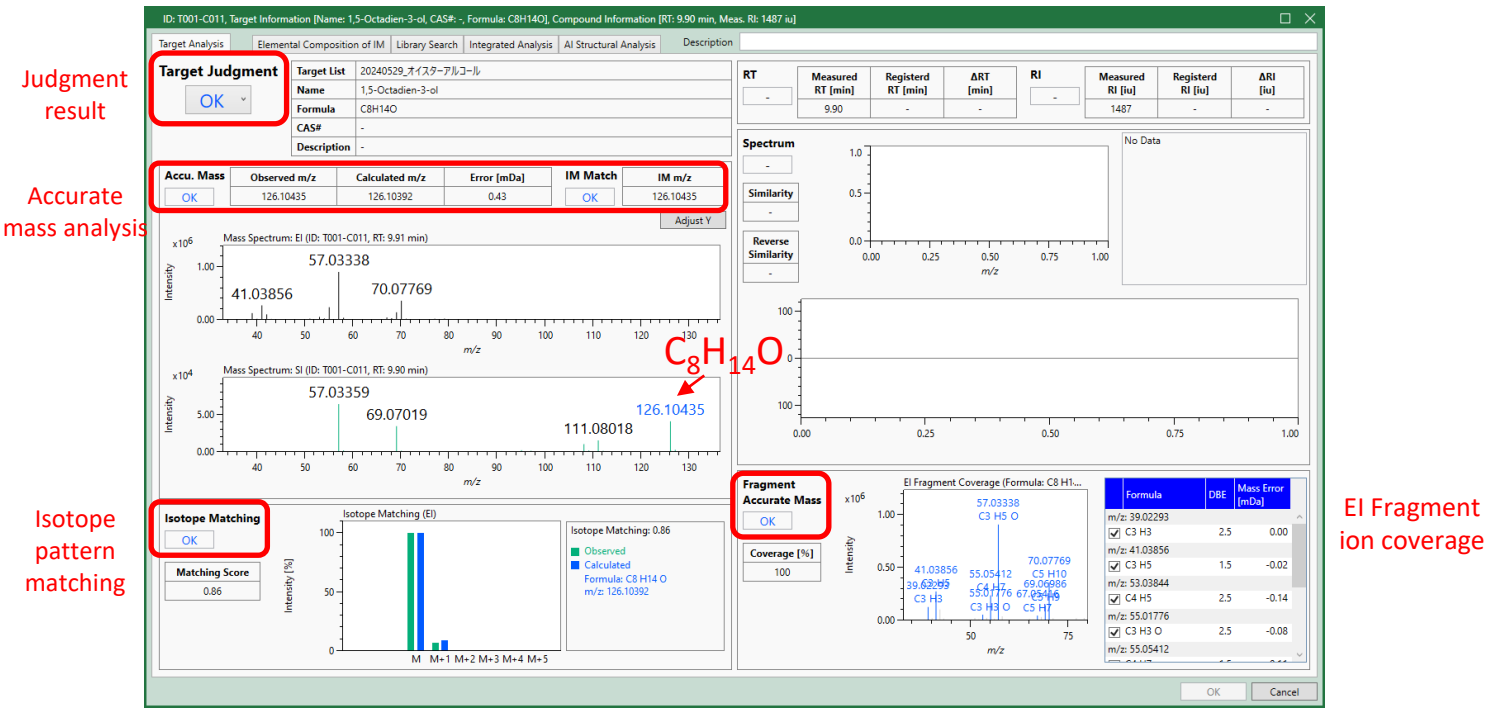

Figure 6 Target analysis result of "1,5-Octadien-3-ol "

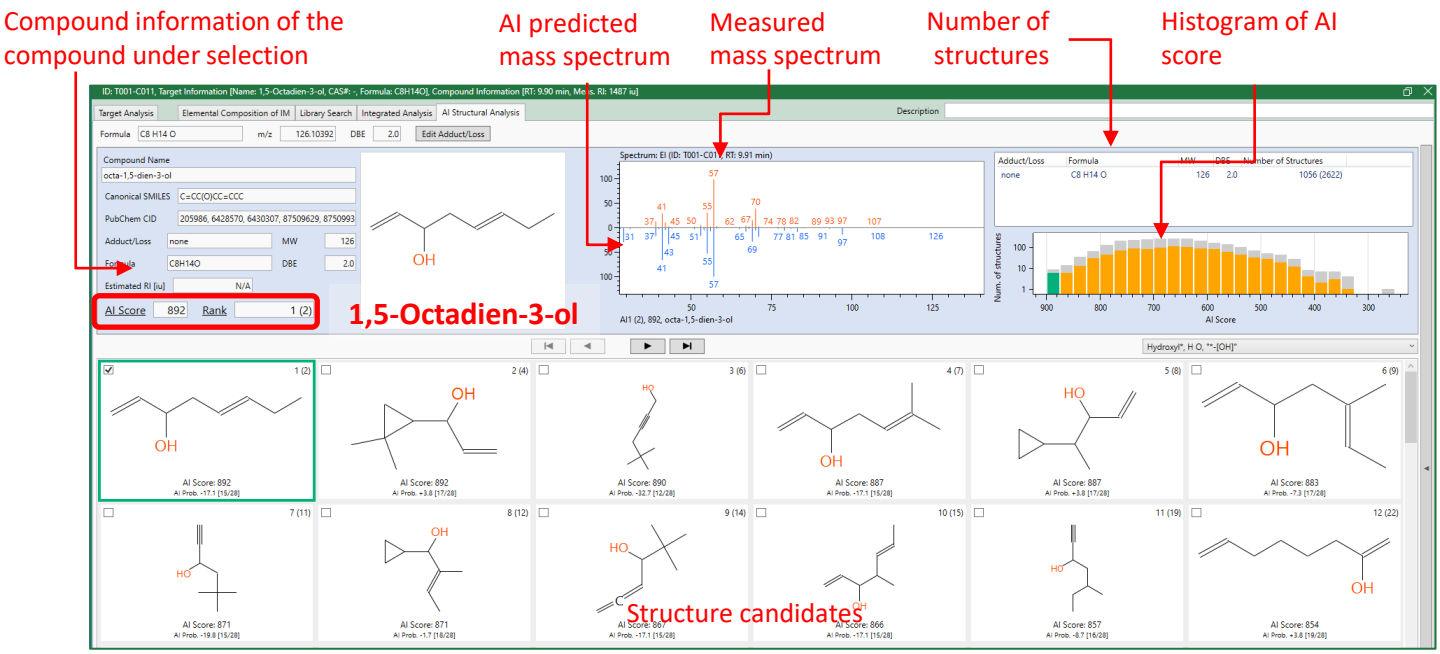

Figure 7 AI structure analysis result

Conclusions

In this MSTips, we used msFineAnalysis AI to analyze the unregistered compound "1,5-Octadien-3-ol" in the DB, and confirmed the accuracy with which the corresponding structure could be obtained. By AI structure analysis, the structural formula of 1,5-Octadien-3-ol was obtained as No.1 candidate. In addition, the AI score was high at 892, resulting in high accurate result. GC-TOFMS and msFineAnalysis AI are effective for analyzing aroma components in foods by using GC-MS.

Reference

1) K. Ueda et al, J. Oleo Sci. 72, (7) 725-732 (2023).
2) M. Ubukata et al, Rapid Commun Mass Spectrom. 2020; 34:e8820.
3) A. kubo et al, *Mass Spectrometry*, **2023**, *12*, A0120.

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