

Structure Validation:

Automated MRR Library Building for Confident Molecular Identification

Introduction

Terpenes are a structurally diverse and commercially important class of natural products used in flavors & fragrances, pharmaceuticals, and botanical authentication. Subtle differences in stereochemistry or functional group orientation can significantly influence aroma, biological activity, and regulatory classification. Accurate structural characterization is essential for compound identification. Despite this significance, closely related terpenes remain difficult to distinguish using conventional analytical techniques. These methods often rely on chromatographic retention behavior or fragmentation-based spectral libraries that may fail to resolve stereoisomers or structurally similar compounds within complex mixtures. This application note presents an automated structure-validation workflow for generating experimentally confirmed MRR spectral libraries that enable unambiguous molecular identification in complex samples.



Figure 1. Terpene chemical space linking molecular structure to natural sources across hydrocarbons, alcohols, and sesquiterpenes. Closely related terpenes and stereoisomers cluster despite subtle differences in functional groups, highlighting the analytical challenge of terpene-rich mixtures and the need for structure-specific rotational spectroscopy.

MRR as a Structure-Specific Solution

Molecular rotational resonance (MRR) spectroscopy provides direct structural information by measuring gas-phase rotational transitions that are uniquely determined by a molecule's three-dimensional geometry. Each molecule produces a distinct rotational spectrum that functions as a structural fingerprint. This enables the differentiation of isomers (as well as other closely related species) without reliance on chromatographic separation or inference from fragmentation.

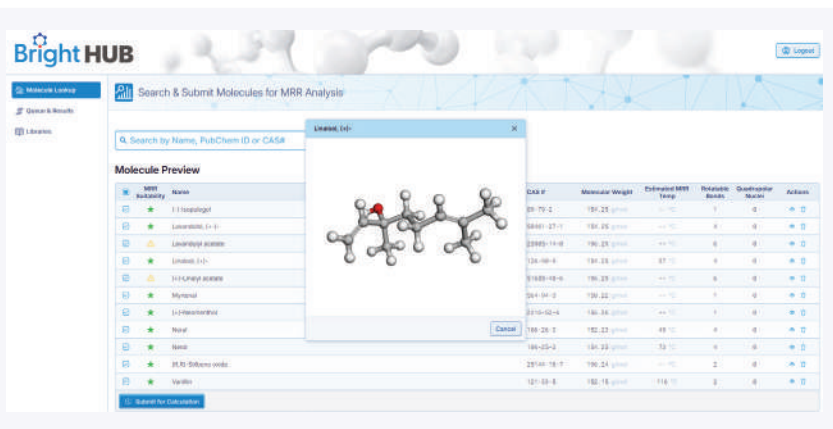
When combined with the simulated rotational spectra of proposed molecular structures, MRR enables a structure-validation workflow in which theoretical predictions are directly validated against experimental data. The agreement between predicted and measured spectra provides definitive confirmation of molecular identity.

Workflow for Structure Validation and Experimental Library Creation

The same validation process used for individual structure confirmation can be repeated across related molecules to generate experimentally confirmed spectral references. In this way, MRR enables scalable construction of spectral libraries that support rapid future identification within defined chemical classes. The practical operation of this workflow is illustrated here using an automated measurement of a representative terpene.

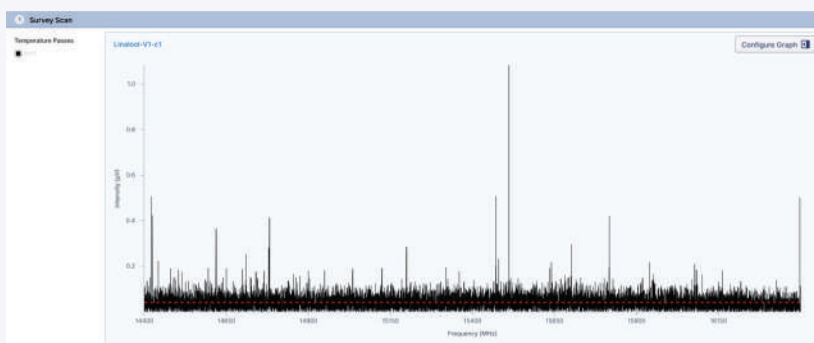
Step 1: Define the candidate structures

Candidate molecular structures are defined and submitted to BrightHub to generate predicted rotational spectra, which form the theoretical reference library used for subsequent spectral matching. These calculations also dictate the parameters to be used for experimental data collection.



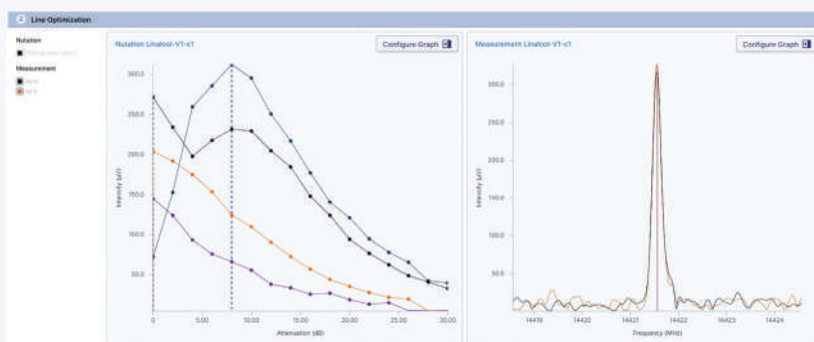
Step 2: Acquire the experimental spectrum

The sample is introduced for automated MRR measurement to acquire the experimental rotational spectrum for subsequent comparison with the predicted reference library.



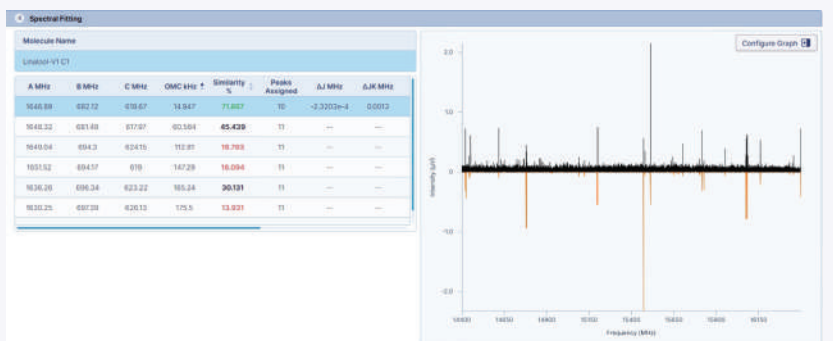
Step 3: Optimize and measure

Acquisition conditions are refined to obtain a high-quality experimental spectrum suitable for matching to the predicted spectrum.



Step 4: Match theory and experiment

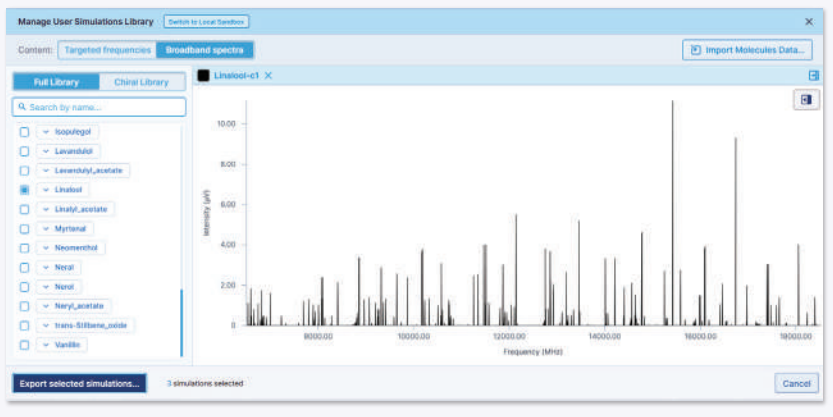
The experimental rotational spectrum is compared with the predicted spectra for the candidate structures. Spectral agreement identifies a single matching structure and provides definitive confirmation of molecular identity.



Step 5: Capture the validated reference

The validated spectrum, confirmed through Edgar analysis, is established and incorporated into an experimental spectral library for confident future identification.

Because the spectra are a unique molecular-structure-dependent fingerprint, they can now be used for matching across all MRR instruments without the need for repeat calibration runs in the future.



From Single Confirmation to Scalable Libraries

Repeating this automated structure validation workflow across multiple terpenes enables systematic accumulation of experimentally confirmed spectra, producing a class-specific library for confident future identification. Because each entry is grounded in direct experimental structural confirmation, these libraries support high-confidence screening, authentication, and quality control for terpene-containing samples.

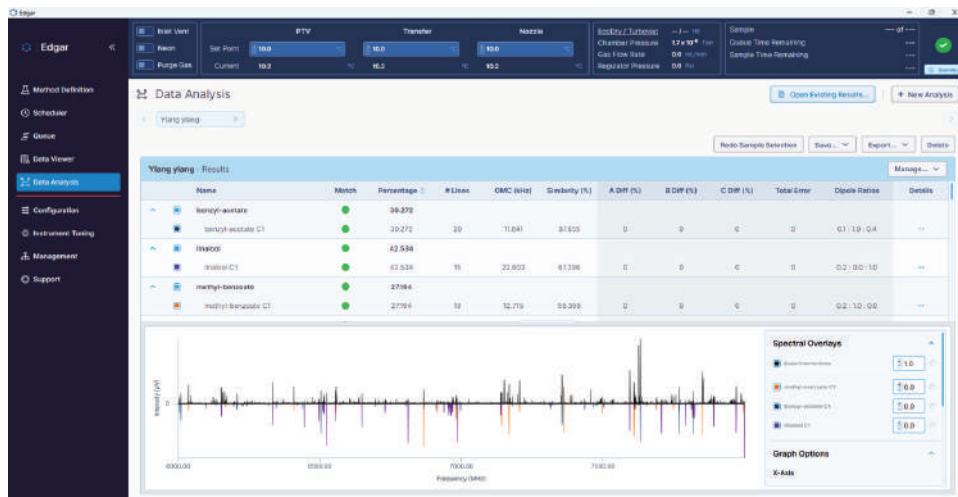


Figure 2. Direct identification of linalool and related terpenes in ylang-ylang oil.

Identification is enabled by a structurally specific, experimentally confirmed spectral library that supports confident screening, authentication, and quality control.

Conclusion

MRR enables a direct path from proposed molecular structure to definitive experimental confirmation. When combined with automated spectral acquisition and repeated across related molecules, this workflow extends beyond single-compound validation to create scalable spectral libraries that support confident molecular identification across diverse chemical classes and analytical applications.