

Measurement and Evaluation of Plant Derived Compounds for a Comprehensive Electron Ionization MS Library

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Overview

- Plant derived compounds are of great commercial and societal importance. They are hugely diverse in structure, many with attached glucose units. Some are found only in specific plant species.

Introduction

- Identification of volatile chemical components has long been done by GC-MS, using spectrum matching and retention index against comprehensive libraries of electron ionization mass spectra. However, the range of compounds capable of analysis by this method can be greatly expanded by derivatization of otherwise thermally sensitive plant metabolites.
- In this work we describe efforts to significantly increase the coverage of such materials in a widely used EI library.

Methods

A wide range of sources of plant derived compounds and mixtures were purchased from a diverse range of sources. In some cases, specific spectra were derived from plant materials, guided by published determinations of chemical structures in those materials to confidently determine their spectra. Over one thousand plant metabolites identified by NMR and other methods were purchased directly from a major supplier of such chemicals. Multiple derivatives were attempted for all, including TMS, methylation, acetylation and TFA. Electrospray MSMS was done for all underivatized compounds to confirm their identity and add to a separate tandem spectrum library. Spectra were extracted using NIST AMDIS software and evaluated with the help of NIST Mass Spectrum Interpreter using hybrid and similarity searches against the full library. Besides the Mass Spectrum data, retention index data were added using AMDIS software for each spectrum. Recently, AIRI (Artificial Intelligence Retention Index) was added as another tool for compound validation.



Figure 1. Examples of purchased materials

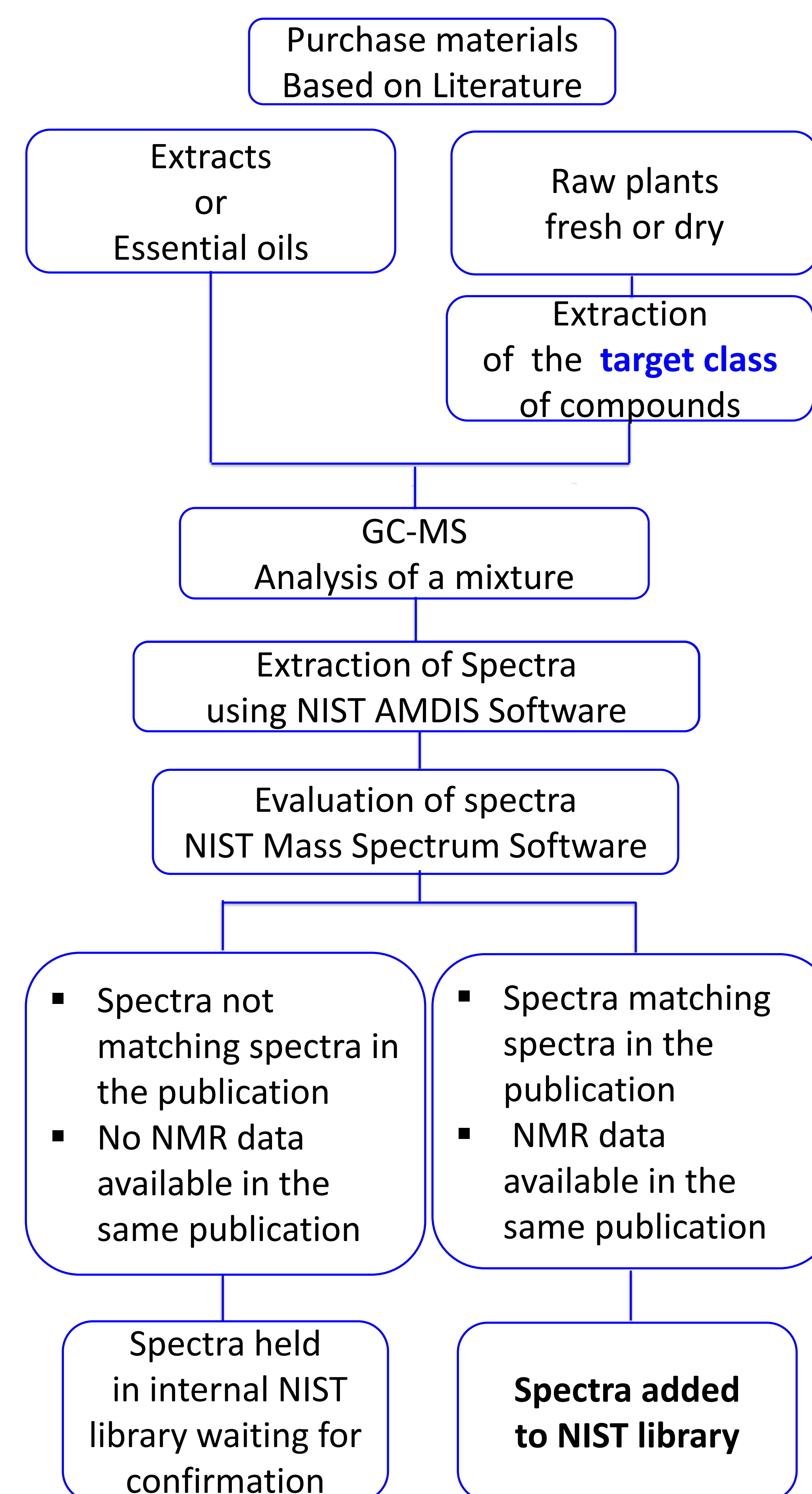


Figure 2. Different processes for building NIST MS from selected plant-derived spectra

Results

Spectra derived from plant materials

Example 1. Alkaloids from *Sophora tokinensis*

- Cytisine and derivatives, and Matrine-Type Alkaloids are reported occurring in the genus *Sophora* (1,2)
- An alkaloid extract of the roots of *Sophora tokinensis* allowed the identification of 4 alkaloids.

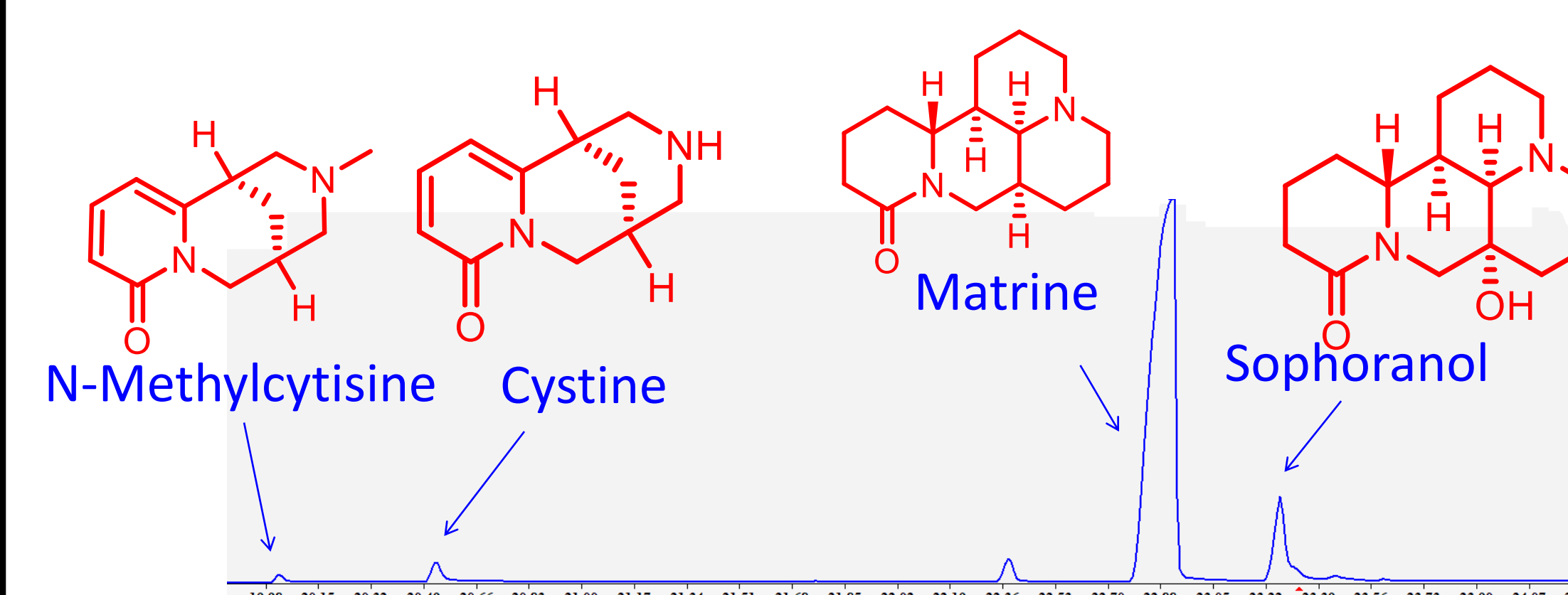


Figure 3. TIC of an alkaloids extract of *Sophora tokinensis*

Example 2. Essential oil of vetiver

Identification of some compounds were performed using the work of Peter Weyerstahl (3)

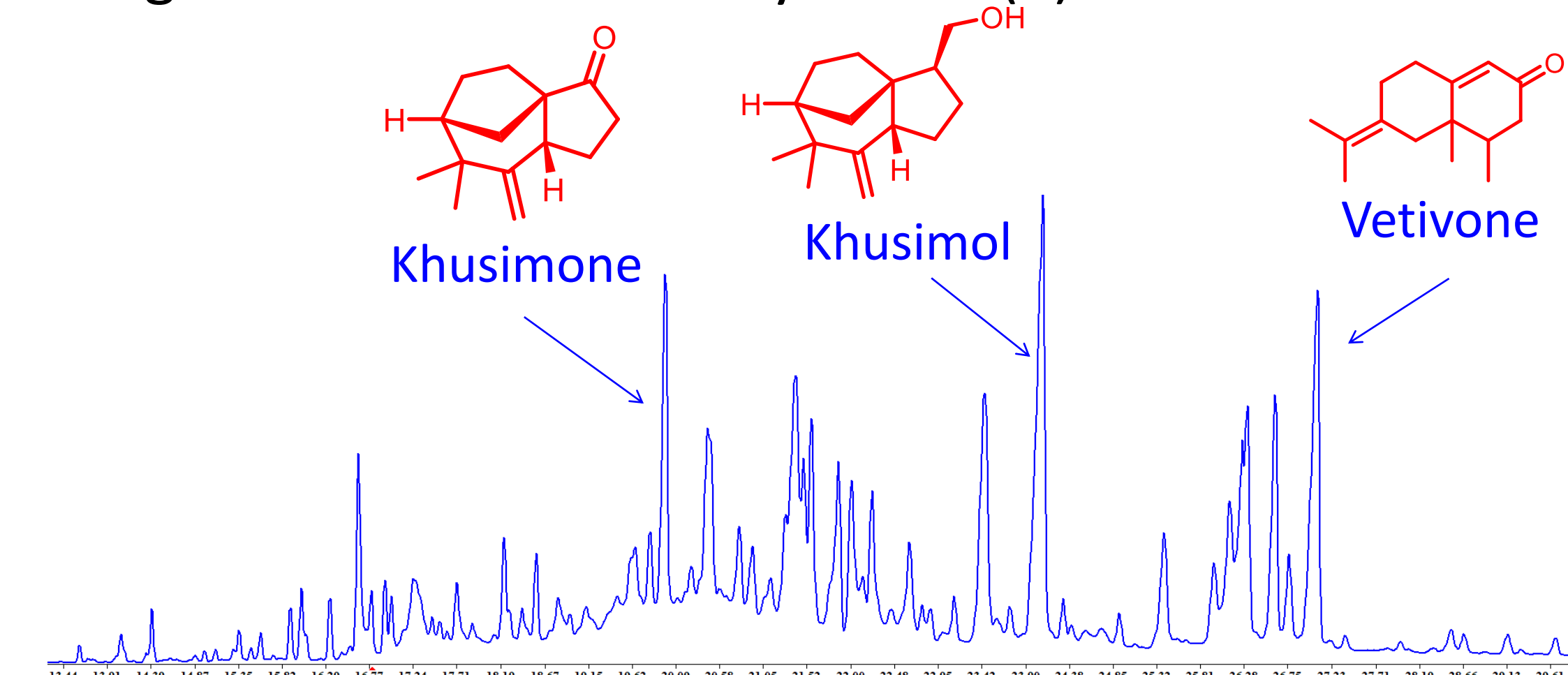


Figure 4. TIC of an Essential oil of a Vetiver

Spectra from extracted plant metabolites

- Plant metabolites were purchased directly from a major supplier. The list of compounds to be ordered was selected by software in order to avoid redundancy.
- In plants, many compound are present as glycosides. Those compounds are not directly suitable with GC-MS analysis. Multiple derivatives were attempted for all, including TMS, methylation, acetylation and TFA.

(1) *Planta Medica* (2006), 72(9), 854-856
(2) *Journal of Natural Products*, 2015, 78(7), 1683-1688
(3) *Flavour and Fragrance Journal* 2000, 15, 395-412

Example: TMS and TFA derivatives of Icarin II and Urceolide

- Icarin II is a flavonol glycoside found in the genus *Epimedium* (4). Icarin II was reported to have anticancer activity (5)
- Urceolide is a monoterpene diglycoside, isolated from the roots of *Triosteum pinnatifidum* (6)

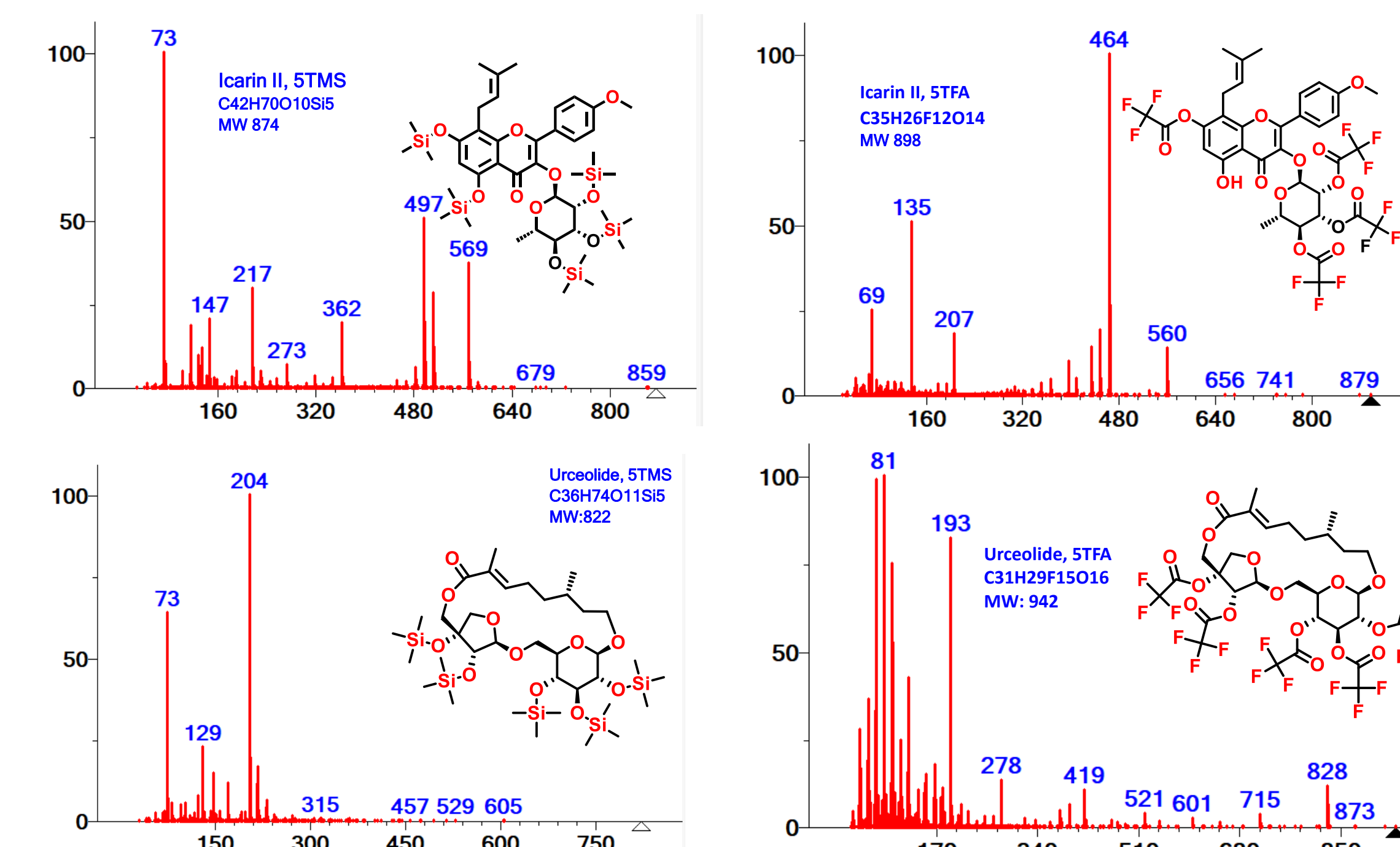


Figure 4. EI-MS of TMS and TFA derivatives of Icarin II and Urceolide

- 560 extracts of 187 species were studied
- 1366 spectra were identified after comparison with the literature
- 439 tentative structures have also been proposed and held in our repository for possible future use.
- Unidentified spectra found multiple times were added to our Recurrent Unknown Spectra (RUS) internal library.
- 1294 plant metabolites were purchased of which 1076 were possibly amenable to GC/MS analysis, with or without derivatization.
- 1877 EI natural products spectra were added to 2023 EI Library.

Conclusion

We described our procedures for generating EI Mass spectra and GC retention indexes (RI) of plant metabolites. The use of derivatization methods has allowed us to identify a greater range of compounds occurring in plants, in particular glycosides which play an essential role in the biological activity of the plant.

(4) *Journal of Chromatography A* (2005), 1064(1), 53-57
(5) *Cancer Letters* (2010), 298(2), 222-230
(6) *Phytochemistry Letters* (2014) 7, 30-34