Low-Resolution Mass Spectrometry study on *ortho*-menthane irregular monoterpenes as an initial step to build-up a library

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Introduction

ortho-Methane irregular monoterpenes (*o*-menthanes) represent a small group of natural products found concentrated in the essential oil of *Baccharis trimera* (Less.) DC (Asteraceae) (BTEO) [1,2]. Except for the well-known *o*-cymene, carquejyl acetate (I.) and carquejol (II.) (Fig. 1), commercial libraries usually do not contain mass spectra of other *o*-menthane derivatives. Following our work on this group of monoterpenes [1,2], we present here some related low-resolution mass spectra and their theoretical interpretation schemes, as an initial step to build-up a mass library of this structurally interesting group.

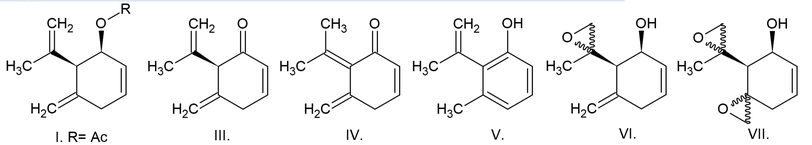
Experimental

Natural and semi-synthetic *o*-menthanes with different chemical functionalities (Fig. 1: I. to VII.) were obtained starting from BTEO, following original protocols [2]. ^{1}H- and ^{13}C-NMR allowed to confirm their structures [2]. Their low resolution-mass spectra were acquired with GC-MS instruments, using EI ionization (20/70 eV) using two different analyzers: 1) quadrupole (qMS: HP6890/HP-5973), and 2) ion trap (ITMS: Trace 1300/ITQ-900). Chromatographic separation was performed using (5%-diphenyl)-dimethylpolysiloxane as stationary phase for the capillary columns employed. Scan range: 50-350 amu. Theoretical interpretation of the spectra were according to the literature [3], with the aid of the Mass Frontier software. MS/MS^{n} experiments are currently under study (data not shown), in order to confirm the proposed fragmentation paths.

Results

The mass spectra recorded for each one of the seven *o*-menthanes studied (Fig. 1: I.-VII.) were distinctive, showing typical fragmentation patterns derived from their structures: *i.e.*, McLafferty (McL) and other hydrogen rearrangements (rH), as well as *i*- (inductive) and α-cleavages (Fig. 2 to 4).

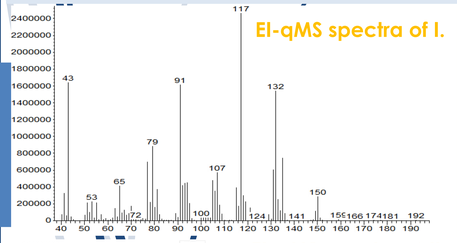
Figure 1: Chemical structures of the *o*-menthanes studied

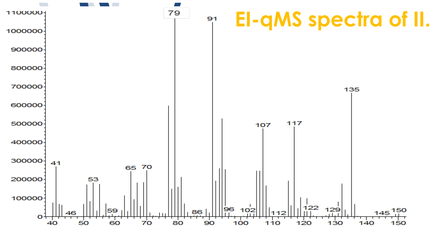


I. R= Ac
II. R= H

III. IV. V. VI. VII.

1. Natural *o*-menthanes





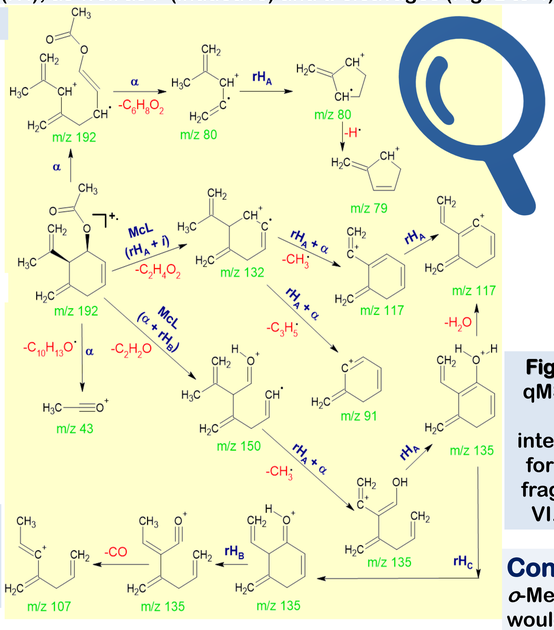
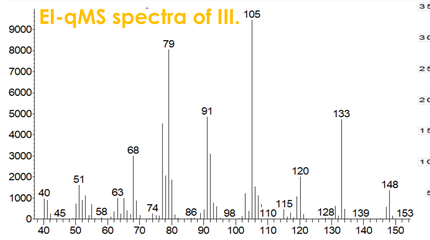
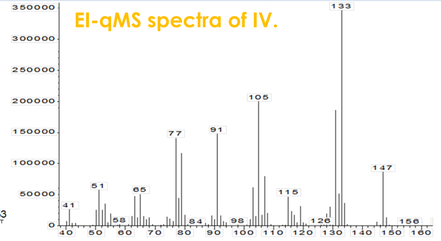


Figure 2: EI-qMS spectra and interpretation scheme for the main fragments of carquejyl acetate (I.) and carquejol (II.), the reported natural *o*-menthanes of BTEO.

2. Semi-synthetic *o*-menthanes: ketones and carquejiphenol





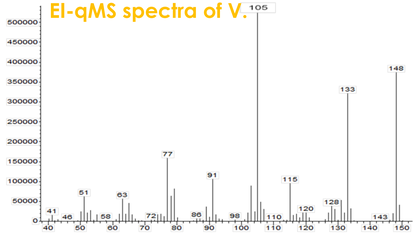
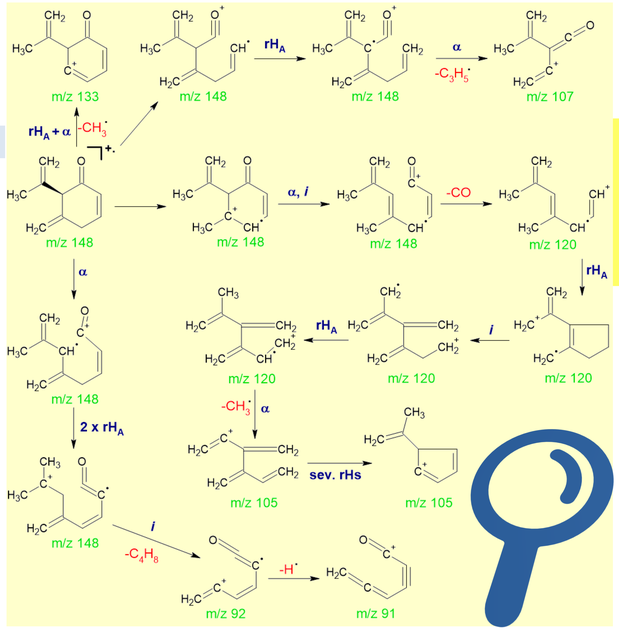
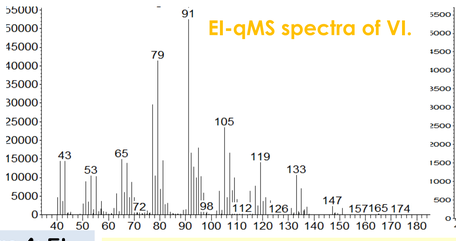


Figure 3: EI-MS spectra and interpretation scheme for the main fragments of III. to V.

The recorded mass spectra of the semi-synthetic compounds allowed, through a careful search in the GC-MS (TIC and SIM) chromatograms of BTEO to identify V. (carquejiphenol) as a natural product not previously reported.



3. Semi-synthetic *o*-menthanes: epoxides



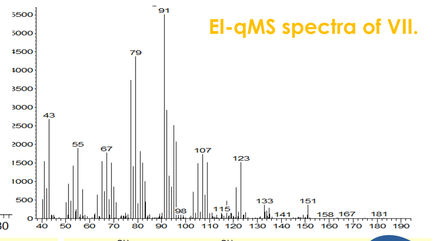
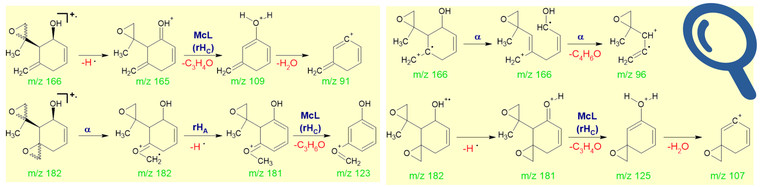
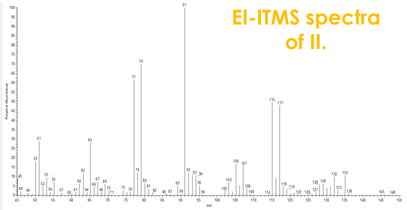


Figure 4: EI-qMS spectra and interpretation for the main fragments of VI. and VII.



4. Comparisons: quadrupole *vs.* ion trap

Spectra obtained from the two analyzers (qMS and ITMS), evidenced intensity differences in some fragments. A fact to be considered when automated searches are performed for comparisons.



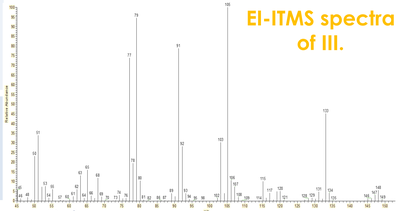


Figure 5: EI-ITMS spectra of II. and III. Compare with the Fig. 2 and 3.

Conclusion

o-Menthanes comprises an interesting group to build-up a new mass spectral library that would assist in the confident identification of them in complex compositions, like BTEO.

References:

1. M. Minteguiaga *et al.* in P. Balakrishnan, S. Gopi (eds.). Flavors and Fragrances in Food Processing: Preparation and Characterization Methods, ACS, Washington 2021, pp. 361-383 (and references therein).
2. M. Minteguiaga. PhD Thesis, Facultad de Química-UdelaR, Montevideo 2019, pp 390-481.
3. J.H. Gross. Mass Spectrometry- A Textbook, Third Edition, Springer, Cham 2017, pp. 325-428.