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ANNOUNCEMENT

MACE – An Open Access Data Repository of Mass Spectra for Chemical Ecology

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Abstract

MACE is an open access collection of electron impact (EI) mass spectra for coupled gas chromatography-mass spectrometry (GC/MS) that serves as an add-on database, comprising curated spectra not present in widely available commercial mass spectral libraries, such as the NIST or WILEY databases. The spectra are stored as text files that allow easy integration into individual GC/MS systems. The article describes the concept of MACE, the data structure, how to contribute, and its usage. MACE is designed as a community effort and will require contributions from the community to be successful.

Keywords Mass spectrometry · GC/MS · Pheromones · Database · Open data · Semiochemicals

Introduction

Chemical Ecology deciphers the influence of naturally produced compounds on other organisms occurring within the same habitat. A fundamental prerequisite for research in Chemical Ecology is knowing the exact structures of the compounds involved. Gas chromatography/mass spectrometry (GC/MS) has proven to be a highly effective tool in this respect, playing a crucial role in the identification of many volatile, semi-volatile, apolar, or polar small compounds. GC/MS combines high sensitivity, high separation power, and affordable equipment costs with the generation of key pieces of information about the structure of an unknown compound. Mass spectra taken at 70 eV in electron impact (EI)-mode are highly reproducible and relatively independent of the instrument manufacturer, as well as local settings. Furthermore, their information content is high due to the many C–C bond cleavages observed in the spectra, allowing users to postulate structural elements, while the fingerprint character of the spectra allows differentiation between compounds, an advantage which is not found in other, mostly soft, ionization modes such as ESI (electrospray ionization) or CI (chemical ionization), which usually produce much less fragmentation, and consequently less structural information. Both ESI and CI preferentially induce the formation of molecular ions and loss of heteroatoms, often leaving C–C bonds intact. Finally, extensive databases of EI-mass spectra with several hundred thousand entries, such as the National Institute of Standards (NIST; Wiley and Sons 2017) or Wiley (McLafferty 2020) databases, are commercially available, making identification of compounds much easier, especially when gas chromatographic retention indices are also employed. Interpretation of EI mass spectral fragmentation can be crucial in the structural elucidation of unknown compounds, especially when nuclear magnetic resonance (NMR) spectrometry is not an option due to insufficient amounts of sample to obtain meaningful spectra, or difficulties in obtaining pure samples in ~ microgram amounts or higher, for example, when trying to isolate trace components from complex mixtures.

Furthermore, the current trend towards open access data, including analytical data and spectra, becoming a requirement for publication, has created a need for permanent open access data repositories which maintain data in a computer-readable format. Deposition of data in such repositories is also increasingly required by funding agencies.

Discussion

Although the aforementioned NIST or Wiley databases are a good starting point, they can only provide matches with compounds that are in the database, i.e., recently identified

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novel structures or unusual structures are unlikely to be included in commercial databases. Although the mass spectra of unknown target compounds may be present in the literature in some form, they can be difficult to find. Furthermore, in many cases, the spectral data actually listed in the literature provides no help in terms of trying to identify an unknown structure. Literature databases such as SciFinder (American Chemical Society 2022) are structured to allow searching for names, but not for complete spectra, also making them more or less useless when trying to find proper reference spectra for comparison with that of an unknown. Whereas numerous spectra of new compounds not reported in the NIST database are published every year, there is no standard format; at best, they are presented as figures, or as a limited list of mass spectral fragments and their abundances, but again with no standardized criteria as to which fragments to list.

Research groups therefore tend to build their own databases with their own spectra to cope with these issues. Nevertheless, while spectra obtained from a group's own analyses can be easily added to custom databases, the integration of spectra published as figures or limited peak lists by other groups into such databases is difficult. Figures have to be transcribed manually or with the help of graphic analysis programs into a complete peak list that can then be integrated into the local data repository. This is time consuming and therefore rarely done.

Expanding a research group's own database could be made much more straightforward if spectra were available from an open access repository, in a standarized format for easy integration into individual spectral libraries. We therefore decided to start such an open access data repository of downloadable EI-mass spectra that we call "**Ma**ss Spectra for **C**hemical **E**cology"– MACE. MACE is intended to only include spectra which are not already present in the most common commercial databases NIST 17 or Wiley 7 at the time of integration. This will keep MACE relatively small, requiring limited resources to administer, and it will avoid redundancies in combined search routines. NIST 17 or Wiley 7 are not the newest versions of the respective databases, but one can assume widespread use among chemical ecologists. There are other important smaller libraries around, such as the Adams library (Adams 1995) or the dedicated terpene library Massfinder (König et al. 2005), but these are not as common as the large generic databases, and will not be used as references here.

The focus of the spectra in MACE is on compounds of interest in Chemical Ecology, such as pheromones, defensive compounds, plant volatiles, microbial volatiles, nonpolar lipids, and analogous biologically active signals and cues. We are aware of public mass spectral repositories, for example Massbank Europe (Schulze 2021) or GNPS (Global Natural Products Social Molecular Network) (Wang et al. 2016). Although Massbank allows single entries, and allows downloading the whole large database, relatively few entries are useful for chemical ecologists, and double entries within commercial databases occur. GNPS provides a large set of mass spectrometric tools and works in the cloud but requires a good working knowledge of of its software. Both seem to be used preferentially by users interested in metabolomics and related fields, but less so by users interested in the structural elucidation of unknown compounds. A large number of mass spectra relevant to chemical ecology can also be found in Pherobase (El-Sayed 2003–2022), or in case of fatty acids, in the Lipid Web (Christie 2022), but only as figures, which makes computer-based structural searches impossible.

The quality of a data repository correlates directly with the quality of the data. Therefore, only spectra of compounds with proven structure will be included in MACE. This is usually the case for published compounds and their derivatives, which have been synthesized, isolated, or for which the structures have been unequivocally elucidated. Typical derivatives might include hydrogenated compounds, methyl esters, dimethyldisulfide adducts of unsaturated compounds, and so on. Each entry is checked for spectral quality and whether it is already included in the generic reference databases before being selected for inclusion into MACE. The data in the repository will be stored as one simple text library file which can be easily integrated into individual mass spectral libraries. The focus is on local usage and integration into individual workflows, in contrast to cloud approaches like GNPS. A guiding principle is simple use and data structure to keep entry barriers, as well as maintenance, low. MACE will come with an open access CC-BY-SA license that allows distribution only under the same license terms if the original distributors are named, which will excludes the spectra being incorporated into commercial products. The data text file is stored permanently in the open access data repository of TU Braunschweig (Schulz and Möllerke 2022a). MACE will be continuously updated with revisions, with the current version being revision 2 (Schulz and Möllerke 2022c). The general concept of MACE, designed as a community effort, is shown in Fig. 1.

As a start, the spectra from the first revision originated from our group (Schulz et al. 1993; Wegener and Schulz 2002; Witte et al. 2009; Stamm et al. 2019, 2021; Ehlers et al. 2021; Gerbaulet et al. 2022) and older publications from the late Professor Meinwald's group (Meinwald and Meinwald 1966; Jain et al. 1983; Bell and Meinwald 1986) were included. However, the crucial prerequisite for a critical mass of spectra and widespread usability will be contributions from the chemical ecology community. For example, in the second release (Schulz and Möllerke 2022c), we have additions from the Ando group (Ando et al. 1993, 1995; Yamamoto et al. 2008; Yamakawa et al. 2009, 2011; Adachi et al. 2010; Muraki et al. 2014, 2017). The success

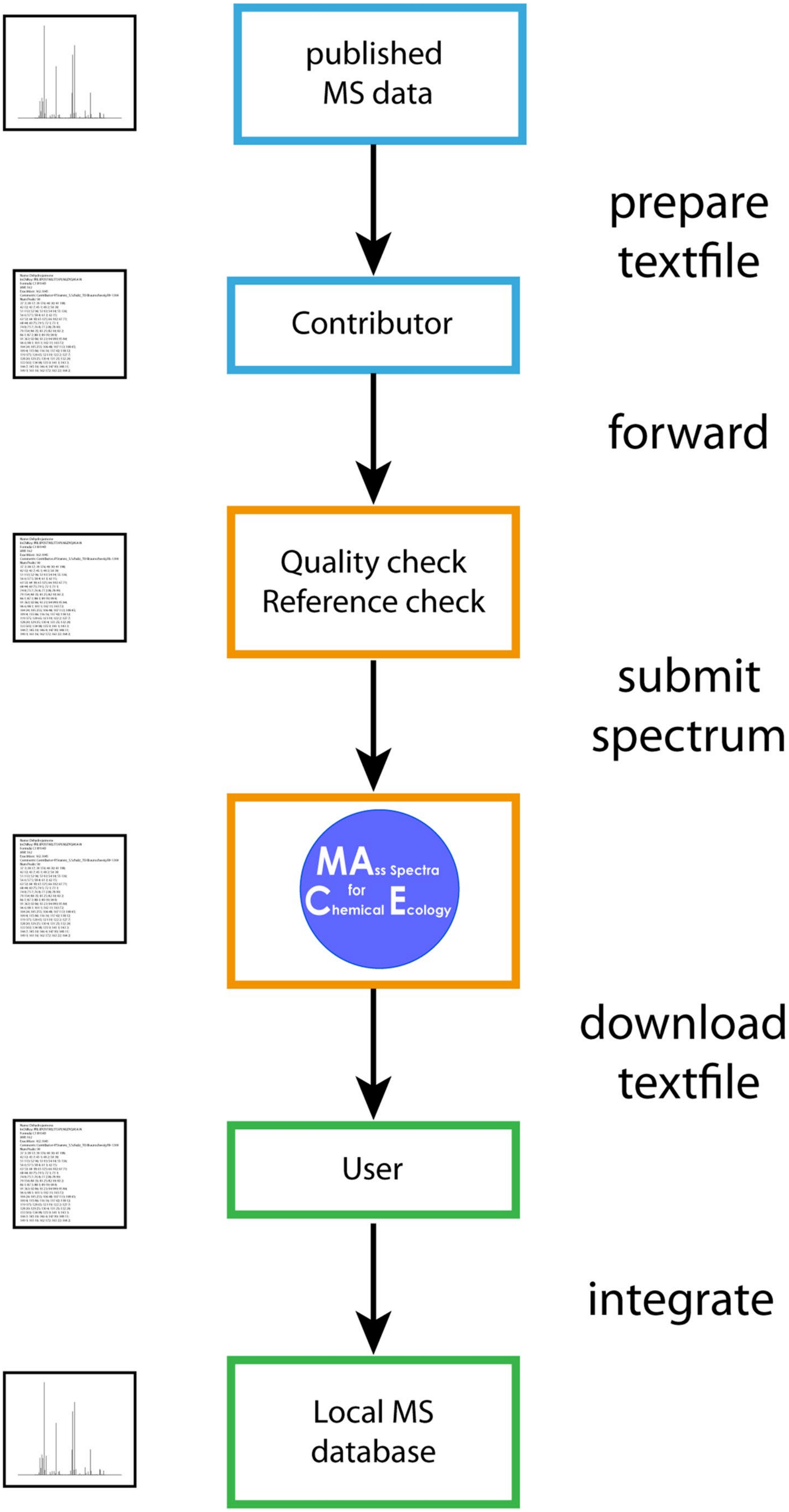


Fig. 1 Structure of MACE and flow of data. The contributors prepare text files of spectra from published work and submit them to MACE (blue). MACE maintenance checks spectral quality and whether they already occur in commercial databases, then integrates the data into the MACE database (orange). Users download the MACE text file for their own use and integrate the file into their individual databases (green)

of MACE as a community effort is critically dependent on contributions from as many groups as possible and we most strongly encourage such contributions, on an ongoing basis, to continuously expand MACE, and hence, expand its value to Chemical Ecology. Because the published data in the data repository cannot be altered, subsequent additions will be indexed by release numbers, starting with r01. Each release has its own DOI address, making it clearly identifiable and ensuring permanent, non-altered storage. This concept also decouples MACE from our own webpage, which currently provides a guide to MACE and additional useful details not included in this article (Schulz and Möllerke 2022b).

Data Organization

The MACE mass spectra are provided in a simple text file using the NIST.msp data format, which is readily importable into mass spectral databases via the NIST MS Search program (NIST 2008). Important information improving usability is integrated into various fields including the "Comments" field of each spectrum. Additional valuable information includes the retention index and the GC column used, the mass analyzer mode, the compound class of the molecule, the literature reference, the contributor of the spectrum, the SMILES (Weininger 1988) and InChIKey (Karol 2018) codes of the compound, an internal spectrum identifier, and license information. While we use the NIST search system, the data can also be imported into systems other than NIST. If MACE data are used in a publication, reference to MACE and to the original reference of the spectrum is required.

Data Structure

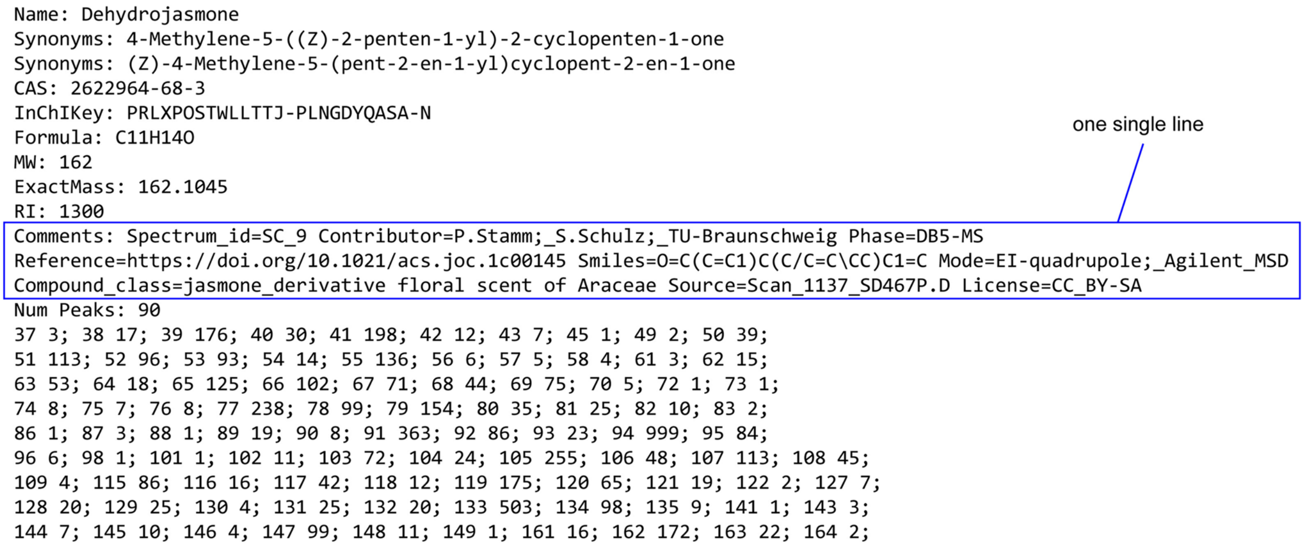
The MACE library is provided as a simple text file using the NIST data structure (NIST 2008), allowing users to import the file into their own databases. However, the extension of NIST data files is unfortunately .msp, which can lead to some difficulties in Windows systems. We therefore changed the extension to.mace to make the file distinct. It is important to note that being a text file, the extension is not important for functionality.

A sample entry according to the msp data structure is shown in Fig. 2. The spectrum always starts with the "**Name:**" field and ends with an empty line. Fields are always on one line and contain a descriptor ended by a ":" sign. This document structure must be followed exactly in order to successfully upload data to MACE.

The different fields are explained in detail in the following section. These fields should be completed by the contributor, if possible, to obtain the highest data quality. Nevertheless, only a few are really mandatory, as will be discussed below.

Name: Always begins the entry for a spectrum. Please use the trivial name here, if one is available for the compound. **Name** is a mandatory field.

Synonyms: Add proper chemical name here (e.g., IUPAC name), when a trivial name is used in **Name**. Several synonyms can be included, each one on a separate line. Please remove any stereo-descriptors that are associated with a single enantiomer because MS cannot differentiate enantiomers. The asterisk convention should be used instead if it becomes necessary to assign the relative configuration of compounds with more than one stereogenic center, according to IUPAC nomenclature, e. g. (3*R**,5*S**) (ACDLAbs 1993). This



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Name: Dehydrojasmone
Synonyms: 4-Methylene-5-((Z)-2-penten-1-yl)-2-cyclopenten-1-one
Synonyms: (Z)-4-Methylene-5-(pent-2-en-1-yl)cyclopent-2-en-1-one
CAS: 2622964-68-3
InChIKey: PRLXPOSTWLLTTJ-PLNGDYQASA-N
Formula: C11H14O
MW: 162
ExactMass: 162.1045
RI: 1300
Comments: Spectrum_id=SC_9 Contributor=P.Stamm;_S.Schulz;_TU-Braunschweig Phase=DB5-MS
Reference=https://doi.org/10.1021/acs.joc.1c00145 Smiles=O=C(C=C1)C(C/C=C\CC)C1=C Mode=EI-quadrupole;_Agilent_MSD
Compound_class=jasmone_derivative floral scent of Araceae Source=Scan_1137_SD467P.D License=CC_BY-SA
Num Peaks: 90
37 3; 38 17; 39 176; 40 30; 41 198; 42 12; 43 7; 45 1; 49 2; 50 39;
51 113; 52 96; 53 93; 54 14; 55 136; 56 6; 57 5; 58 4; 61 3; 62 15;
63 53; 64 18; 65 125; 66 102; 67 71; 68 44; 69 75; 70 5; 72 1; 73 1;
74 8; 75 7; 76 8; 77 238; 78 99; 79 154; 80 35; 81 25; 82 10; 83 2;
86 1; 87 3; 88 1; 89 19; 90 8; 91 363; 92 86; 93 23; 94 999; 95 84;
96 6; 98 1; 101 1; 102 11; 103 72; 104 24; 105 255; 106 48; 107 113; 108 45;
109 4; 115 86; 116 16; 117 42; 118 12; 119 175; 120 65; 121 19; 122 2; 127 7;
128 20; 129 25; 130 4; 131 25; 132 20; 133 503; 134 98; 135 9; 141 1; 143 3;
144 7; 145 10; 146 4; 147 99; 148 11; 149 1; 161 16; 162 172; 163 22; 164 2;
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Fig. 2 MACE entry in.msp format. The entries should be entered in a simple text editor without line breaks, except for the actual mass spectrometric data at the end. Note that the comment field, with multiple possible entries, is one single line procedure will avoid claims of enantiomers being identified via mass spectral matches by inexperienced users.

InChIKey: This structure description key is used in many web and other applications. MSSearch allows direct connection to PubChem by clicking this key. PubChem provides various types of information about a compound. InChIKey keys can be generated with different chemical drawing programs, e.g. with ChemDraw using the "Copy As" tool. Additionally, free structure drawing software such as ChemSketch or online tools such as http://www.cheminfo.org/Chemistry/Cheminformatics/Generate_InChI/index.html can be used to generate InChIKey codes.

CAS: CAS number if known. The number can be easily obtained by importing the Smiles code into SciFinder and performing a structure search, or simply drawing the structure in Scifinder and searching. Some double bond or other stereochemical formatting may be necessary in SciFinder before searching, to ensure that the search will bring up the CAS number for the correct stereoisomer.

Molecular Formula (MF), Molecular Weight (MW), and **Exact Mass**: Add the respective data here. The "Molecular Weight" field must be filled in, otherwise mass spectral search programs will likely not work. Be aware that MW is the nominal mass in MS. For example, $C_{35}H_{72}$ has an exact mass of 492.5634, but a nominal mass of 492. The exact mass is the monoisotopic molecular mass, not the molecular weight more commonly used in Chemistry. Again, these data can be obtained from most chemical drawing programs.

RI: Retention index of the compound. Semi-standard non-polar retention indices are preferred, but other data from other phases are also welcome. RI values can be calculated according to van den Dool and Kratz (1963).

Comments: As with all the other fields, the "Comments" field is only a single line, but it can contain a number of user defined tags. These tags can improve usability and a number of them are defined in MACE. None of them are mandatory. These tags have names that are followed by a "=" and the following term must not have spaces. The tags are separated with empty spaces. Any other text outside the tags will occur in the output under **Comments**, the rest in appropriate fields. The data are only clearly visible when the database is configured to show these tags (see below), otherwise the data will be found in the comment line output. Spaces in tag entries are not allowed. Thus, we recommend that words in tags be connected by a connecting character, such as an underscore. An example showing the use of underscores and empty spaces is illustrated in Fig. 2, where the blue box indicates one single line. The following tags are used.

Spectrum = This entry is an internal number given by MACE. It should be left blank and will be assigned when the compound/spectrum is added to MACE.

Contributor = Submitters and laboratory contributing the spectrum

Phase = Specifies the GC column(s) used for retention index (RI) calculation(s). We usually use semi-standard non-polar phases such as HP5-MS, but if RIs are measured on more than one column, they can be provided.

Mode = Specifies what type of mass analyzer was used (e.g. quadrupole, sector field, ion trap or time-of-flight), and the instrument manufacturer. Spectra may differ according to the type of mass analyzer used.

Reference = The DOI reference to the publication of the original spectrum, preferably from a known authentic standard. This is helpful for users because it allows easy access to the original publications and makes citation in publications easier.

Smiles = A character code for drawing structures easily. Copying this code into drawing programs or databases such as Scifinder will automatically generate the structure. The Smiles code can be obtained as described above for the InChIKey code.

License = Should not be altered. It allows usage by individuals, but not the use of the spectrum in a commercial product without a license.

Class = Specifies the compound class. This can possibly be vague, but defining the class can be helpful in some cases, for example, terpenoids, fatty acids, steroids, etc.

Source = Local file name and scan number of the data from the submitter. This entry allows the spectrum to be traced back to its origin.

The data are most valuable when all tags are filled. Nevertheless, submitters can send data with some incomplete fields.

Num Peaks: Number of peaks to follow. Absolutely necessary for correct function of the file. Without this, searching will not work. Usually already in the data when a mass spectrum is exported into a text file.

The actual data of the spectrum follow. Line breaks are acceptable here. Several slightly different formats are allowed in the .msp format (NIST 2008). The spectrum entry is ended by an empty line. The MACE library can be converted into other formats using converters such as Lib2NIST (Stein 2012) and others. If other such converters exist, please let us know and we will add them to the MACE website.

Contributing to MACE

Any published compound whose identity has been unequivocally proven can be added to MACE if it broadly fits the general chemical ecology theme of the database. All spectra should be submitted as a single text file to mace@tu-braunschweig.de via email. If formats other than .msp formats are used, they should be first converted using converters such as Lib2NIST (Stein 2012). An especially easy way to convert files to the proper format is to use the OpenChrome software (Lablicate 2022) that accepts as input a wide range of mass spectral data formats. Export of a peak in .msp format can then be easily performed.

After submission, the spectra will be checked for quality, for presence in the NIST 17 and Wiley 7 databases, and then added to MACE. All newly added spectra will be published together with the older spectra as a complete new revision from time to time. New revisions will be announced on the website and elsewhere.

Mass Spectra of the First Revision

The spectra were chosen to cover a wide variety of compounds to show the inclusive character of the collection. The respective structures are shown in Fig. 3. Included are examnples of arthropod cuticular lipids, moth and butterfly pheromones, flower volatiles, bacterial volatiles, and defense compounds. Furthermore, examples of derivatization products such as methyl esters or dimethyldisulfide adducts have also been included.

A few comments are appropriate. For example the spectra of the *syn*- and *anti*-dimethylheptadecanoates, SC-1/2 and SC-3/4 (Gerbaulet et al. 2022), are almost identical, but they have different RI values which allow them to be reliably distinguished. They serve as an example that stereoisomers should be defined, if possible. In cases where the relative configuration is not known, as is often the case with arthropod cuticular hydrocarbons such as 11,15-dimethylhentriacontane SC-5, single entries are also acceptable, especially with linear compounds with alkyl branches. Although SC-5 was not synthesized, its diagnostic mass spectral fragments (Pomonis et al. 1989) in combination with its RI provided an unequivocal identification, allowing its inclusion into MACE. In the case of danaidal (Krasnoff et al. 1987) a spectrum was published in the Wiley 7 database under its IUPAC name (Fig. 4B), but the spectrum is of low quality, and contains spurious peaks (*m/z* 85, 120). Therefore, danaidal (Fig. 4A) was included as entry SC-34. The related compounds SC-13, SC-17, and

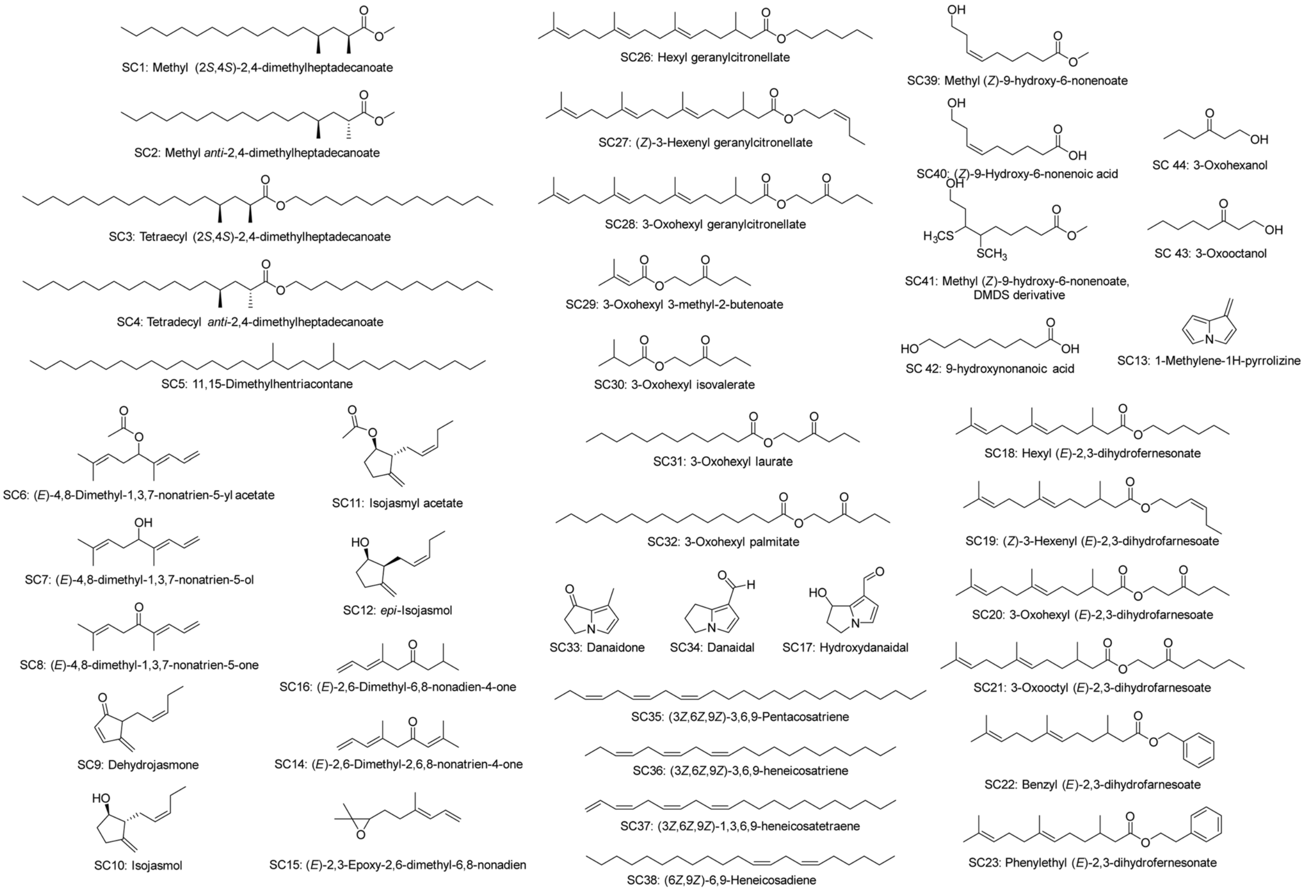

Fig. 3 Compounds included in MACE revision 1. Structures included in the current revision 2 can be found on the MACE website (Schulz and Möllerke 2022b)

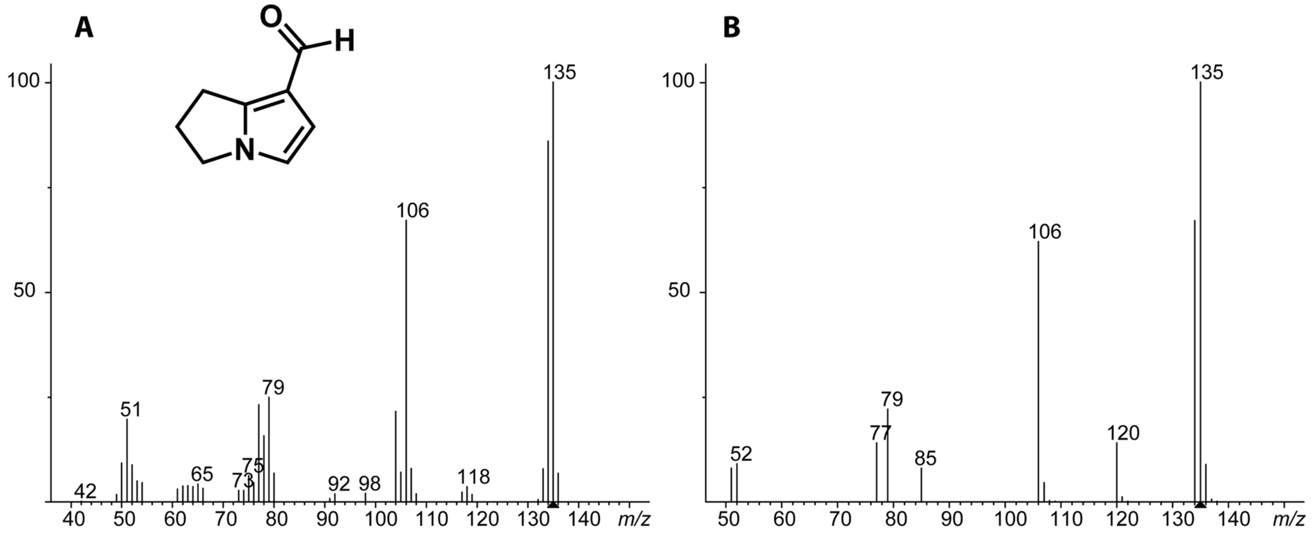

Fig. 4 Mass spectrum of danaidal (SC-34) published in MACE (**A**) and the Wiley 7 database entry (**B**)

SC-33 are reported in many publications as pheromones of male Lepidoptera (Meinwald and Meinwald 1966; Bell and Meinwald 1986).

The homomonoterpenes SC-6—SC-8 and SC-14—SC16 are useful for plant volatiles research (Wegener and Schulz 2002; Stamm et al. 2021), as are the jasmone derivatives SC-9—SC-12 (Stamm et al. 2021). Polyenes SC-35—SC-38 (Bell and Meinwald 1986; Witte et al. 2009) are parent compounds of the class II moth pheromones (Ando and Yamamoto 2020), but are also present in insect cuticular hydrocarbons, and rather surprisingly, are not found in reference databases. A whole set of spectra of related compounds is found in revision 2. The rest of the spectra originate from recent work in our group on butterfly semiochemicals (Stamm et al. 2019; Ehlers et al. 2021).

User and Contributor Benefits

The benefit of MACE for the user is evident, because users obtain a dedicated add-on for their own mass spectral libraries. The benefit for the contributor may be less obvious, and we recognize that the small time commitment needed to transfer spectra to MACE may hinder spectra submission. However by submitting spectra to MACE, contributors will increase the visibility of their own research, potentially leading to further citations if their spectra are used in a publication, due to the license requirements. Contribution to MACE and other open access databases would likely become easier as journals begin publishing mass spectra in computer-readable formats in supporting material or data repositories, as is already required by some journals for NMR data of new compounds.

Conclusion

In summary, MACE is a free mass spectral repository that can be used with many MS systems and is relatively easy to maintain and expand, with long-term data storage, availability, and data integrity being built into the system. Expanding the database with contributions from the chemical ecology community will increase its usability and dissemination. MACE data contained in revisions 1 and 2 can be found in an open access data repository with a DOI number (Schulz and Möllerke 2022a, c), while the MACE website (Schulz and Möllerke 2022b) is maintained at http://www.oc.tu-bs.de/schulz/html/MACE.html. We appreciate contributions and encourage submitters to obtain more information and contribution forms by visiting the MACE website (Schulz and Möllerke 2022b) and the MACE data repository (Schulz and Möllerke 2022c).

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Declarations

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

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