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Diagnostic fragmentation filtering for the global analysis of ergot alkaloids and indole–diterpenoids using LC–HRMS/MS in Norwegian and Canadian *Claviceps* species.

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Preface

This thesis was completed at the Norwegian University of Life Science NMBU, in collaboration with the Norwegian Veterinary Institute (NVI), during the period of August 2018 until May 2019. It represents 60 ECTS of a 120 ECTS master's degree in chemistry.

Analytic toxin chemistry and molecular biology are combined in this study. It has been challenging to work with this project, but also rewarding to gain knowledge of ergot and the chemistry behind. Knowing that the ergot issues relate to real concerns of farmers in Norway today and to the wildlife in forests, made this study particularly interesting.

I would like to thank all of the employees at the section of chemistry and toxicology who have been helping me with good advice and support throughout my time at the NVI, with a special attention to Hege Divon, Elin Rolén, and most importantly Silvio Uhlig who has been of an outstanding support in this study. I couldn't have asked for better supervisors. I would also kindly thank my supervisor Dag Ekeberg for great support.

Lastly, I would like to thank my parents, friends and boyfriend, all of whom have been a source of support and positive energy throughout my studies, from start to finish. I am very grateful. Additionally, I thank my coworker and friend Edvarda Wevling Matre for good support and advice.

Kari Anne Pauchon

Ås, May 14th, 2019

Sammendrag

Kunnskap om kornsykdommen som forårsakes av meldrøye, *Claviceps purpurea* (*C. purpurea)* er viktig med tanke på dyreliv og jordbruk ettersom meldrøyen produserer toksiner. Dataene består av 66 forskjellige prøver fra fem ulike geografiske lokasjoner: Eidsvoll, Larvik, Maridalen og Telemark (alle i Norge) og Saskatchewan i Canada. Genotype profelering av sklerotiene besto av 3 *Claviceps* arter: G1 (*C. purpurea sensu lato*), G2 (*C. humidiphila*) and G2a (*C. arundinis*). For skanning og gjenkjenning av allerede klassifiserte alkaloider og potensielt nye toksiner ble det brukt en diagnostic fragmentation filtering modul av ergot alkaloider og indole-diterpenoid på hele metabolomiske data fra høyt oppløsende masse spektrometrisk data. Principal component analysis og partial least squares avslørte art spesifikke alkaloid mønster. G2a ble funnet til å være vertsspesifikk.

Abstract

The understanding of the cereal disease caused by ergot (*C. purpurea*) is important with reference to wildlife and agriculture as ergot produces toxins. The sample set used in this study consisted of 66 *Claviceps* sclerotia from five distinct geographical locations: Eidsvoll, Larvik, Maridalen, Telemark (all in Norway) and Saskatchewan in Canada. Genotyping of the sclerotia revealed that the samples comprised of three *Claviceps* species: G1 (*C. purpurea sensu lato*), G2 (*C. humidiphila*) and G2a (*C. arundinis*). For screening and recognition of already classified and potentially novel toxins, diagnostic fragmentation filtering was applied for the extraction of the entire ergot alkaloid and indole-diterpenoid metabolome from the high-resolution mass spectrometry data. Principal component analysis and partial least squares revealed species-specific alkaloid patterns. G2a was found to be host specific.

Abbreviation

AP- Atmospheric Pressure

APCI- Atmospheric Pressure Chemical Ionization

CID- Collision-Induced Dissociation

DBE- Double Bond Equivalent

DFF- Diagnostic Fragmentation Filtering

EA- Ergot Alkaloid

EFSA- European Food Safety Association

ESI- Electrospray Ionization

FT- Fourier Transform

GGPP- Geranylgeranyl Pyrophosphate

HCD- High Energy induced Dissociation

HPLC- High performance Liquid Chromatography

HRMS- High Resolution Mass Spectrometry

ITS- Internal Transcribed Spacer

MS- Mass Spectrometry

MS/MS- Mass Spectrometry/ Mass Spectrometry

NRPS- Nonribosomal Peptide Synthetase

PCA- Principal Component Analysis

PLS- Principal Least Squares

RAPD- Randomly Amplified Polymorphic DNA

rDA- retro Diels Alder

RF- Radiofrequency

RT- Retention Time

tubB- beta-tubulin

UHPLC- Ultra High-performance Liquid Chromatography

VIP- Variable Importance in Projection

Table of content

1. Introduction

1.1 Background

Ergot is a plant parasitic fungus of the genus *Claviceps* and is a source of well-known bioactive alkaloids, as well as novel chemical compounds. This cosmopolitan species (complex) was previously known as *Claviceps purpurea*. However, modern molecular biology has shown that *C. purpurea* is rather a conglomerate of several species and lineages (Shun-Ichi, 1971) . The origin of the name Purpurea comes from the purple color exterior of the sclerotium.

The ergot fungi are known for their infection on wild and cultivated grasses (Dewick, 2011). The host range of ergot is very large. It includes about 400 plant species (Haarmann, 2009). These include forage grasses as well as cultivated plants such as rye, oat, barley and wheat, where rye is the most common.

Ergot forms a dried sclerotium and looks like a black oversized grain in its overwintering stage. The sclerotia contain a variety of poisonous ergot alkaloids (EA) and secondary metabolites. Ergot may be harvested together with the grain, and its toxins may then occur in flour or animal feed.

These alkaloids have caused diseases and several epidemic outbreaks in human history. Despite this, EA is widely used in medicine (De Grooth et al., 1998). Different EAs can have serious effects on the nervous system (Panaccione, 2005). They can lead to restricted blood flow in small terminal arteries, causing death of the tissue (Cowan et al., 2018). The development of gangrene is also called ergotism.

"Gangrenous ergotism has been variously called *ignis sacer*, the holy Fire or St Anthony´s fire, terms all referring to the accompanying burning sensations, often associated with feverish hallucinations of flames and devils."(Alm & Elvevåg, 2013).

Today, ergotism is rare in humans due to agricultural technology and safety instructions, but both farm and wild animals are still affected.

The European food safety authority (EFSA) has published a report on important EA in food and feed (Arcella et al., 2017). Therefore, it is important to investigate and improve the understanding of these chemical compounds and their distribution.

1.2 Hypothesis and research aim

The overall objectives of this study are (1) to test and apply novel mass spectrometry processing technology diagnostic fragmentation filtering (DFF) for the extraction of the entire ergot alkaloid and indole-diterpenoid metabolome from extracts based on UHPLC–HRMS/MS. (2) To combine the metabolomics data with genetic information using multivariate statistical analyses in order to reveal alkaloid patterns that are characteristic for different genotypes.

2. Theory:

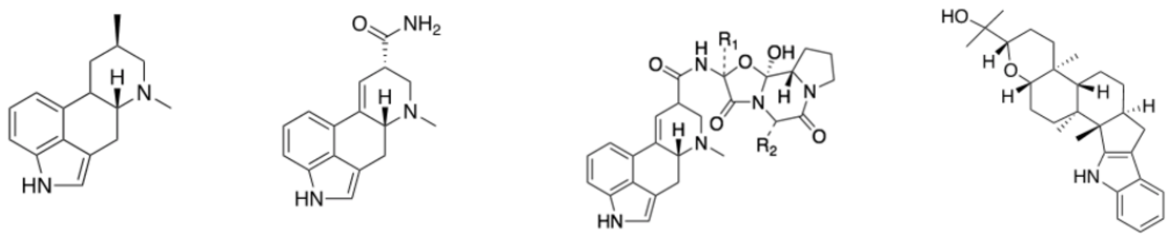
2.1 The life cycle of ergot

The life cycle of *C. purpurea* starts when windborne ascospores land on flowering wild and forage grasses during spring. The ascospores infect the ovary within a short period of time. In the infected ovary a special stroma grows, which produces a sticky honeydew containing fungal spores. The honeydew which contains millions of asexual spores attracts insect and in this way the disease is largely spread.

Additionally, the disease can be contaminated by head to head contact or even farming equipment. Honeydew production continues until the formation of sclerotia starts. The sclerotium then replace the seed grain and overwinter on the soil (Miedaner, 2015).

2.2 Structure and classification of Ergot Alkaloids and indole-diterpenoids

Ergot alkaloids can be divided into three major classes according to their structure as shown in (Figure 1). Clavins and simple lysergic acid amide derivatives (1), peptidic ergot alkaloids (2) and indole-diterpene alkaloids (3).



Clavines and simple lysergic acid derivatives (1) | Ergopeptines (2) | Indole-diterpenoids (3)

Figure 1: The main groups of Ergot Alkaloids

All of the above are indole derivatives (Kren & Cvak, 2003). All peptidic ergot alkaloids and many clavines contain ergoline (Figure 2) in their main structure. Nearly all the natural ergoline-derived alkaloids have a double bond in ring D of the tetracyclic ergoline ring system in Δ9,10 and the nitrogen in position 6 is always methylated.

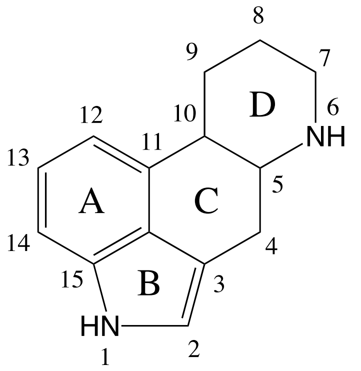


Figure 2: tetracyclic ergoline ring system.

2.2.1 Peptidic ergot alkaloids, ergopeptines and ergopeptams

The end product of EAs biosynthesis is the peptidic ergot alkaloid (2) in (Figure 1). This group can be classified as a tetrapeptidic or cyclol alkaloid by their closed ring structure. They are formed by lysergic acid that is esterified with a tripeptide moiety. Two of the amino acids are variable and thus the two residues R1 and R2 in (Figure 3) are variable. L-proline is the third amino acid of the peptidic moiety III. Which is highly conserved. All peptidic ergot alkaloids occur in two stereoisomeric forms, i.e 8-R and 8-S (Figure 3). However, it is the 8-R form that is the biosynthetic product, and also the biologically active isomers, while the 8-S from is the result of epimerization. The 8-S isomers are distinguished from the 8-R forms by adding a suffix to the trivial names of the individual alkaloids, e.g ergotamine is the 8-R, while ergotaminine is 8-S.

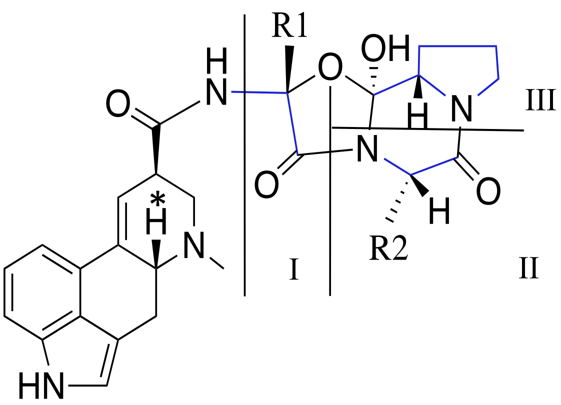


Figure 3: General structure of an ergopeptine with an R and S configuration with regard of the stereo genic center at C-8 (*) of the ergoline ring system. The different amid bonds are separated and forms the building block of the tripeptide moiety (I,II,III).

The different ergopeptines vary from each other with various amino acid substitution in position I and II (Figure 3). The amino acid in position III is always L-proline.
The amino acid in position I (and thus the substituent R1) has traditionally been used to sub-classify the ergot alkaloids into four subgroups (Table 1).

Table 1: Systematic arrangement of the ergopeptines adopted from (Dewick, 2011).

	Ergotamines	**Ergoxines**	**Ergotoxines**	**Ergoannine**
Position I / Position II	**Alanine**	**α-Amino butyric acid**	**Valine**	**Isoleucin**
Phenylalanine (CH2Ph)	Ergotamin	Ergostine	Ergocristine	Ergosedmine
Leucine (CH2CHMe2)	α-Ergosine	α-Ergoptine	α-Ergocryptine	
Isoleucine (CH(Me)Et)	β-Ergosine	β-Ergoptine	β-Ergocryptine	
Valine (CHMe2)	Ergovaline	Ergonine	Ergocornine	
α-Amino butyric acid (Et)	Ergobine	Ergobutine	Ergobutyrine	

2.2.2 Lactam ergot alkaloid, ergopeptams

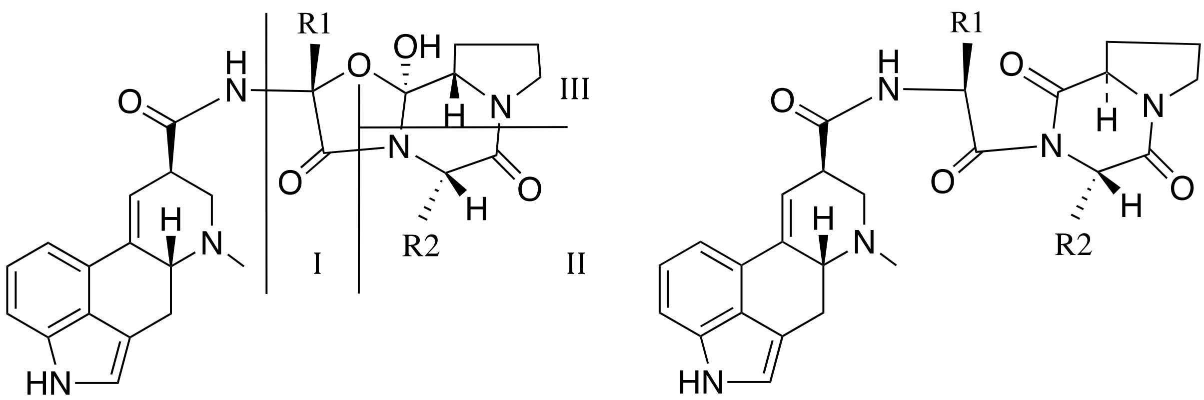


Figure 4: the general structure of ergopeptines and the general structure of the subgroups ergopeptames with an open ring moiety.

In contrast to the ergopeptine the ergopeptams have an open ring moiety between the first and the third amino acid. The ether bridge is missing, and the third amino acid is in D-configuration (Figure 4). The lactam group of natural product is a subgroup of the peptidic EA and its nomenclature ends with -am, e.g ergocristine where the lactam analogue is ergocristam (Kren & Cvak, 2003).

2.3 Structure and classification of indole-diterpenoids

The indole diterpenoids is a large class of secondary metabolites in *C. purpurea* (Figure 5).

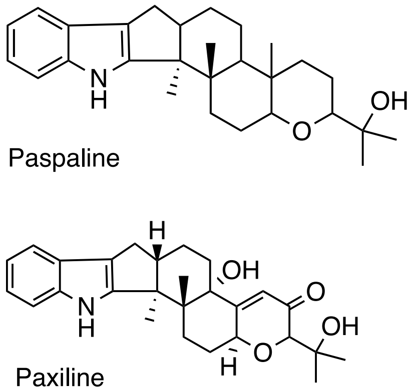


Figure 5: Is the structure of two Indole -diterpenoids.

They possess a common core structure consisting of a tetracyclic diterpene skeleton derived from geranylgeranyl pyrophosphate (GGPP) and an indole group derived from tryptophan or its intermediate precursor indole-3-glycerol phosphate (Mantle, 2009) .

Different metabolites are biosynthesized by additional prenylation, different ring substitutions and different ring stereochemistry, hence the structural diversity.

Paspaline has been shown to be a common biosynthetic precursor of fungal indole- diterpenoids (Saikia et al., 2006). The importance of these secondary metabolites relates to the serious effect some congeners have due to their neurotoxicity and tremorgenic syndromes, as a result of their ability to inhibit ion channels (Dowd et al., 1988) (Kozák et al., 2019). For example, the indole-diterpenoid are the cause of the “rye grass staggers” syndrome in livestock (Imlach et al., 2008).

2.4 Genetic variation within *Claviceps purpurea*

Genetic variability has been found in ergot within the species complex of *C. purpurea*. The variation was found with help of randomly amplified polymorphic DNA, (RAPD) (Pazoutova et al., 2000). Studies have shown that there are four main genetic groups or lineages. These were originally refered to as genotype: G1 (*C. purpurea sensu stricto*), G2 (*C. humidiphila*), G3 (*C. pastinae*) and G4 (*C. arundinis*) (Negard et al., 2015). G1 is found in dry locations, G2 in wet areas, G3 in saline habitats and G4 in very wet habitats. The genotypes reportedly show specific EA patterns, so-called chemoraces. The G4 is most closely related to G2, and they both produce indole-diterpene of paspaline type and other unidentified indole-diterpenoids. G4 was found to be very host specific (Negard et al., 2015). Another resent study recognized these 4 genotypes but labeled them differently: G1(*C. purpurea sensu stricto*), G2 (*C. humidiphila*), G2a (*C. arundinis*) and G3 (*C. pastinae)* (Shoukouhi et al., 2019). G2a corresponds to the previously labelled G4. The nomenclature G2a may seem more adequate as it illustrates the close relation of *C. humidiphila* and *C. arundinis* genotypes.

C. purpurea is different from other genera. The evolutionary adaptability of *C. purpurea* has been evident and is thought to be spread by humans (van Der Linde et al., 2016). In this matter the importance of diversity, host and geographical ranges should is of interest. The spread of the genus *Claviceps* is probably related to the ability ergot has to adapt to the cold winters and evolve on the soil.

2.5 Biosynthesis of peptide ergot alkaloids

The biosynthetic pathway for ergopeptines starts with isoprenylation of tryptophan yielding 4-dimethyltryptophan (DMAT). The second step is methylation of dimethylallyltryptophan (meDMAT). Followed by the tranformation is the formation of Chanoclavine-1-aldehyde formed by closure of ring C, oxidation by an alcohol dehydrogenase encoded by easD and moreover decarboxylation.

Chanoclavine-1-aldehyde is a common biosynthetic precursor of many EAs (Xie et al., 2011). The formation of agroclavine is then the result of methylation and closure of ring D (Liu & Jia, 2017). In the formation of both ring C and D the biosynthesis involves two cis-trans isomerization steps in the alkyl double bond (Floss, 2006).

Agroclavine can after a series of enzymatic reactions undergo a successive oxidation to form several clavine alkaloids such as elymoclavine, and lysergic acid (Figure 6).

The biosynthesis of the peptide part includes two nonribosomal peptide synthetase, (NRPS) genes, i.e. LPS1(A1-T1-C1-A2–T2–C2–A3–T3–Cyc) and LPS2 (A–T–C). D-lysergic acid is activated by the T domain in the LPS2.

Furthermore, LPS1 activates the different amino acids in the EA moiety alanine, phenyalanine and proline by the A1, A2, and A3 domains in LPS1.

The D-lysergic acid is then developed to a monopeptide, to a dipeptide and furthermore to a tripeptide moiety by LPS1 (Gu et al., 2013).

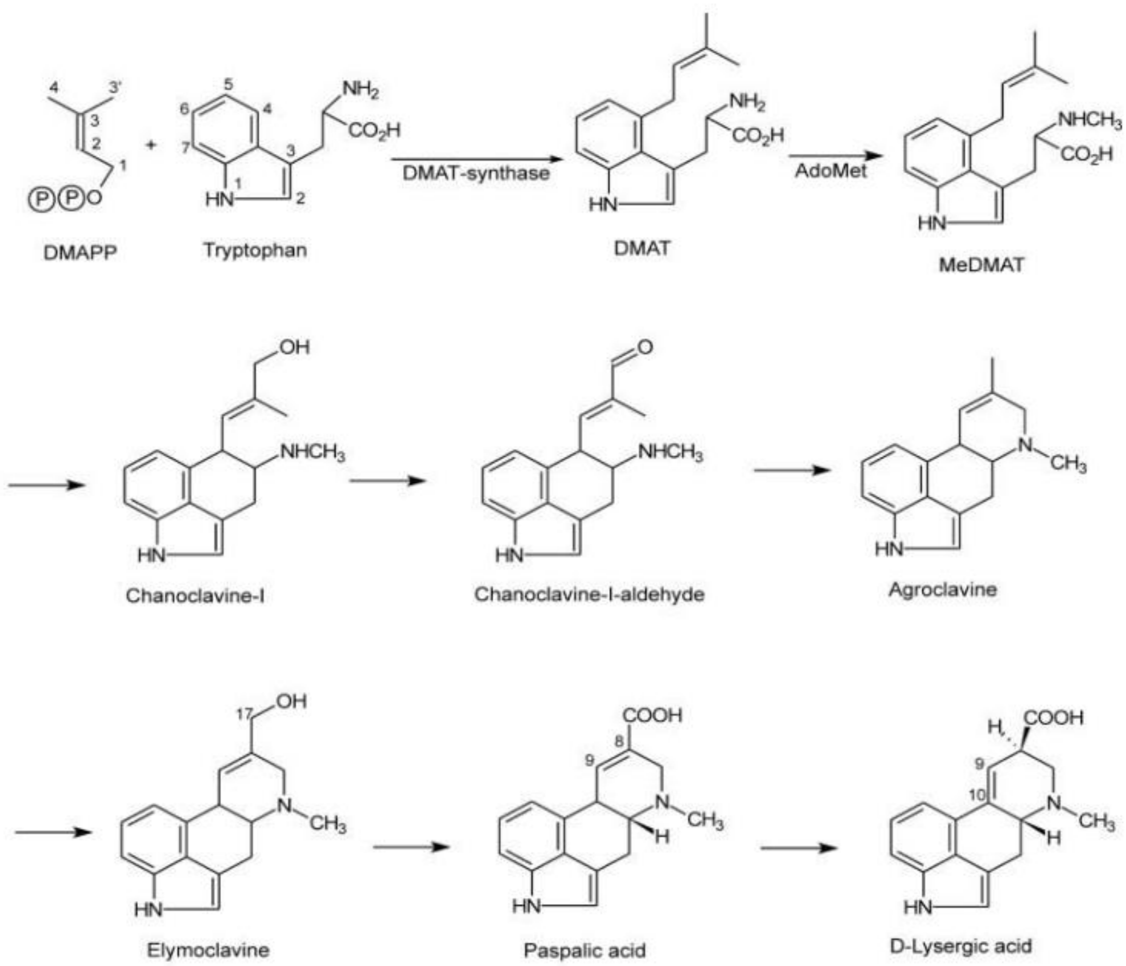


Figure 6: The pathway of lysergic acid biosynthesis is the first part of ergot alkaloid biosynthesis; adopted from (Correia et al., 2003).

2.6 Liquid chromatography- mass spectrometry

Chromatography is a well-known separation tool in analytical chemistry. The compound of interest is often part of a complex mixture and the role of the chromatographic system is to provide separation (Ardrey, 2003). This tool can provide quantitative and or qualitative information of an analyte with use of a detector. Chromatography separates compounds with the use of two phases. These are commonly a stationary and a mobile phase. The polarity of both, the analyte and the two phases are an important factor when it comes to separation. The mobile phase moves along the stationary phase and the separation occurs depending on the affinity the compounds have to the different materials of the two phases.
There are several types of chromatographic systems. This experiment uses the Ultra High-Performance Liquid Chromatography (UHPLC) where the mobile phase is a liquid.

2.6.1 High Performance Liquid Chromatography (HPLC)

Basic HPLC instruments contain solvents/ eluents, vacuum pump/ chamber, an injector, a separation column and a detector (Figure 7).

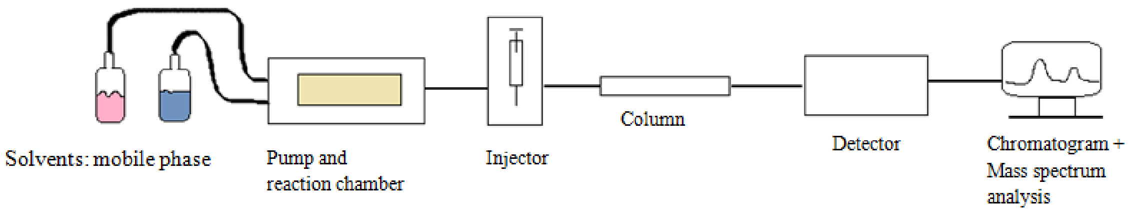


Figure 7: Schematic representation of an HPLC, with two eluents, a reaction chamber, an injector, a column, a detector and computer readout.

The reaction chamber pulls the mobile phase through a heater, so the gradient/eluents can mix together before entering the column. An injector inserts the liquid sample into the mobile phase. The chromatographic column provides the separation. In case of reversed-phase HPLC there is a stationary phase packed with non-polar material and a polar mobile phase that moves through the column. After separation on the column, the analytes reach the detector. The detector used in this study was a high-resolution mass spectrometer (HRMS). A mass spectrometer (MS) provides information about the structure. When linking the two, HPLC and MS, an important consideration is the use of an appropriate interface. The purpose of the interface is to remove the mobile phase and ionize analyte molecules.

2.6.2 Mass spectrometry

This detector separates ions according to their mass to charge ratio (*m/z*).
MS is used for quantitative and qualitative determination but more importantly, structure elucidation. The analyte is ionized by an ionization method, filtered or separated by a mass filter either “in space” or “in time”, and then detected to a readable format (Figure 8).

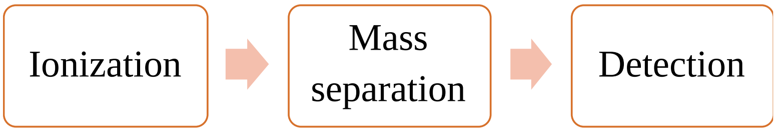


Figure 8: The basic sequence of a mass spectrometer.

2.6.2.1 Ion Source

In order to separate ions in the mass filter, the molecule has to be ionized with high energy. In HPLC an interface technology is required to remove the mobile phase from the analyte. Electrospray ionization (ESI) vaporizes the analyte-containing mobile phase into droplets and forms an aerosol (Figure 9). A high voltage is applied to the sample and results in migration of polarized ions to the solvent surface. A sufficient potential is then applied so the analyte is forced through a probe and the solvents evaporates. The analyte molecules can be positive or negatively charged according to the voltage applied in the ESI source. The analyte can then be introduced into the mass filter.

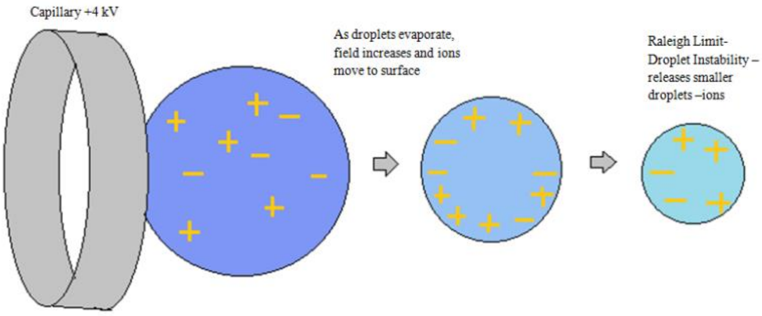


Figure 9: Schematic representation of an Electrospray Ionization. (ESI).

Another example of an ionization technique is the atmospheric pressure chemical ionization (APCI). Both the solvent and the sample become vaporized by traveling through the vaporizer heater. They enter a discharged needle where high voltage is applied.
Through a series of chemical reactions with the solvent, analyte ions are then formed when solvent reagent reacts with gas phase analyte molecules. Both of these ionization techniques occur under atmospheric pressure (AP).

2.6.2.2 Mass Filter

The quadrupole mass filter consists of 4 hyperbolic rods that are electrically connected. The radiofrequency (RF) applied to the rods is of constant frequency. An ion will be accelerated through the mass filter and get attracted to the rod which has the opposite charge. In this manner the ions will either collide with the rod or manage to reach the detector according to their mass to charge ratio (*m/z*).

In the orbitrap (Figure 10) the ions are trapped in an electromagnetic field both by a spindle and outer electrodes (Hu et al., 2005). The difficulty relies in introducing the ions into the orbitrap. This is done by the method of electrodynamic squeezing in the c-trap before entering the orbitrap mass filter (Michalski et al., 2011). The current induced in the split outer electrode is due to the oscillatory movement of the ions. The current frequency is proportional to the *m/z* of the analytes. The different frequencies are analyzed using Fourier Transform analysis (FT) in order to estimate the *m/z* of the fragments. The limited amount of ions held in the c-trap before entering the orbitrap is limited and this may affect the detection of minor ions (Greaves & Roboz, 2013).

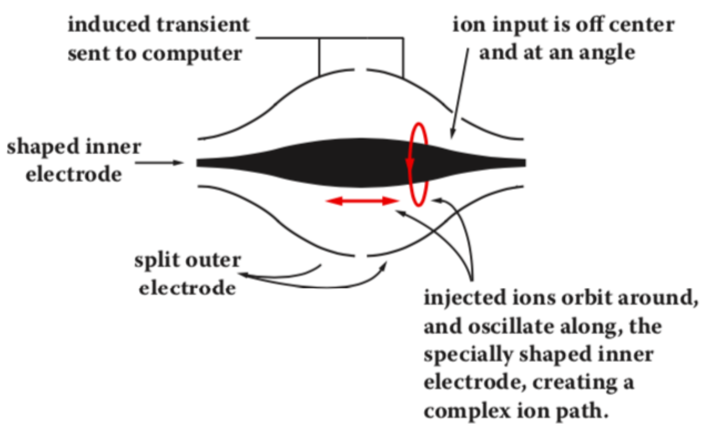


Figure 10: An illustration of the orbitrap mass filter (Greaves & Roboz, 2013).

2.6.2.3 Detector

A Photomultiplier is often used in mass spectrometry. The purpose is to enrich the signal of the ions and to further convert them to digital signal, providing readable information. Moreover, in this setup the orbitrap mass filter works as a detector as explained above.

2.7 Tandem mass spectrometry

The use of more than one mass filter is called tandem mass spectrometry or even mass spectrometry/mass spectrometry (MS/MS). The fundamental process of MS/MS is that a given precursor ion is decomposed into smaller product ions followed by the loss of natural fragments. Analysis of ions can be separated in space using sequential approach, where ions are separated in different hybrid instruments or in time within the same mass filter.

Before entering the second mass filter the ions are introduced into a collision cell. Translational energy has been added to the ions during the acceleration into the cell. They further collide with neutral atoms often Helium or Argon, with a high ionization potential and are maintained at a relatively high pressure (10^{-2}-10^{-3} mbar). When colliding, a part of the ions kinetic energy is converted into excess internal vibrational energy or electric energy. If the excess energy is adequate enough to break chemical bonds the ions are said to have undergone a Collision-induced dissociation (CID). (Greaves & Roboz, 2013)

There are other techniques that are utilized with the same purpose such as High energy induced dissociation (HCD) which occur in the orbitrap mass filter. Once in the cell the ions accumulate additional energy from collision with neutral gas atoms until they fragment into product ions. The fragmentation normally occurs in the breaking between a carbon and a neighboring cation, e.g., N, O, S and Si. The degree of fragmentation depends on the initial voltage applied for the acceleration of the ions. It depends also on the type of collision gas used (Greaves & Roboz, 2013).

2.8 Fragmentation

The retro diels alder (rDA) reaction is often observed in natural products, although any molecule that can formally be synthesized by Diels Alder is potentially a candidate for mass spectral rDA reactions. The rDA involves a cycloaddition reaction were a diene and a dienophile react and creates a new c-c bond (σ-bond) and two new π-bonds.
(Gross, 2011).

2.9 Diagnostic fragmentation filtering and other raw data processing

The software Mzmine was used as a tool to process the MS/MS data from the analysis on the UHPLC. The diagnostic fragmentation filtering (DFF) module was used to filter the desired *m/z* and neutral losses (Walsh et al., 2019). It outputs a plot showing the precursor ions on the x-axes vs. product ions on the y-axes. Additionally, it will output a file containing *m/z* and retention time RT of the filtered MS/MS scans. The analytical tool facilitates a class-targeted approach to rapidly identify known compounds and identify structural variants of a complex dataset.

2.10 Multivariate statistical modeling

Multivariate statistical modeling is an important tool to reveal relations among multiple variables at the same time. Mainly two modules or techniques were used to visualize the data and their relations.
A web-based tool, MetaboAnalyst 4.0 (Chong et al., 2018) was used to interpret the multivariate EAs and indole-diterpenoid data. This tool visualizes the data using e.g. principal component analysis, (PCA). PCA reduces the number of dimensions, without losing essential information of the dataset. PCA seeks linear combination of variables so most of the variability is explained.
Another important statistical method for the study of multivariate data is partial least squares (PLS), which is among the most often used classification method in metabolomics (Szymańska et al., 2012). It is a supervised method that uses multivariate regression techniques and extracts linear combination of variables to gain information that can predict class information. The goal is to test if the variables allow to discriminate groups in a studied population, and to visualize the observations on a 2- or 3-dimensional map. In addition, it interprets a distinct separation between the groups. It also allows datasets with few

observations and many variables. In this study, PLS was used in order to identify which alkaloids (i.e test variables) were responsible for any observed discrimination between the genotypes in *C. purpurea.*

2.11 EFSA opinions on ergot alkaloids

EFSA is an organization that provides independent scientific advice on food-related health risk (European Food Safety Authority, 2019). This information is used to define national rules and helps protect costumers from exposure to risk factors in the food chain. EFSA has been asked to estimate chronic and acute dietary exposure to EA in humans and animals in 2016.

3. Materials and Methods

3.1 Sampling

In total 66 sclerotia were analyzed; 50 from common grass hosts in the Norwegian forests in Maridalen, Telemark and Eidsvoll during autumn 2014-2017, 10 sclerotia randomly chosen from rye in Larvik, and 6 from Saskatchewan, Canada. The Canadian samples were sent by the Ministry of agriculture. The sclerotia was collected in their overwintering stage which consist of a hardened mycelium where the size differs from 0,5-2 cm. The sclerotia were cut in halves. One half was used for the genetic analysis. The other half was used for chemical analysis.

Table 2: An overview of the sample location, host name (in Norwegian and Latin) and sample ID.

Location	**Host**	**Nr. of samples**	**Sample ID**
Maridalen, Norway	Blåtopp (*Molinia caerulea)*	14	2,17-19,28,29,31-34,41-44
Telemark, Norway	Blåtopp (*Molinia caerulea)*	7	9,10,21,38,39,48,49
Telemark, Norway	Hundegress (raigras *Lolium perenne*)	4	35,37,45,47
Maridalen, Norway	Hundegress (raigras *Lolium perenne*)	3	3,16,27
Maridalen, Norway	Timotei (*Phleum pratense*)	3	4,15,26
Maridalen, Norway	Snerprørkvein (*Calamgagrostis arundinacea*)	6	1,7,12,20,23,30
Eidsvolld, Norway	Snerprørkvein (*Calamgagrostis arundinacea*)	6	5,6,13,14,24,25
Telemark, Norway	Strandrør (*Phalaris arundinacea*)	5	8,11,22,36,46
Maridalen, Norway	Kveke (*Elymus repens*)	2	40,50
Larvik, Norway	Rye (*Secale cereale*)	10	51-60
Saskatchewan, Canada	Wheat (*Triticum*)	3	1C,3C,5C
Saskatchewan, Canada	Barley (*Hordeum vulgare*)	1	2C
Saskatchewan, Canada	Oats (Avena sativa)	1	4C
Saskatchewan, Canada	Unknown	1	6C

3.2 Chemicals

The EA and the indole-diterpenoid reference standards had been purified earlier by a collaborating institutions, except lysergol, ergonovine maleate, α-ergocryptine, ergocornine, ergotamine tartarate and ergovaline that were from Sigma-Aldrich (St.Louis, MO, USA). Chemicals used for extraction and solvents for the analysis were acetonitrile of HPLC quality (Romil Ltd., Cambridge, UK).

3.3 Sample Preparation

3.3.1 Genetic analysis

The first half of the sclerotium was used for DNA extraction. The half sclerotia was introduced into small vials with small steel beads (Precellys MK28, Bertin Technologies, Tarnos, France) and 600 µL of Animal Tissue Lysis (ATL), buffer (Qiagen) was added. The buffer is used to destroy the cell and purify the nucleic acid.
The sample is then homogenized with a Percellys 24 (Bertin Technologies) during three sessions of 6500 rpm for 1 min with 2 min rest time between the sessions. The samples were stored in the freezer at -80°C. The samples were shock defrosted by incubation and mixing with an Agilent heat block at 56°C and 500 rpm. After melting and vortexing, 10 µL Proteinase K (20 mg/mL) was added to the sample before incubation at 56°C and 500 rpm, for 30-60 min. It was then centrifuged for 5 min at 12 000 g and 200 µL of the supernatant was transferred to Eppendorf tubes. The samples were stored in a freezer at -20°C. Further purification of DNA was done automatically with the Qiacube instrument.

Specific regions of the DNA which would be used for genotyping were amplified with Polymerase Chain Reaction (PCR). Two different genetic loci were used for genotyping; nuclear rDNA internal transcribed spacer region (ITS) and beta-tubulin (tubB). For amplification of the loci, primer pairs ITS1F- (5´CTTGGTCATTTAGAGGAAGTAA3´) and ITS4 (5´ TCCTCCGCTTATTGATATGC 3´) were used for ITS (White et al., 1990) and Bt3Neo_F: (5´-GCTCTAGACTGCTTTCTGGCAGACC-3´) and Bt3Neo_R: (5´-CGTCTAGAKGTRCCCATACCGGCA-3´) for tubB (Annis & Panaccione, 1998).
The PCR was done using a PuReTaq, Ready To Go PCR Beads in a plate kit adding a master mix consisting of 3µL forward primer (5µM), 3µL Reverse primer (5µM) and 17 µL MiliQ. 2-3 µL of extracted DNA was added, and the samples were set to a PCR program. The same procedure was carried out for each primer pair, but the PCR program varied (Table 3).

Table 3: The PCR prorgam of ITS and Bt3Neo primers. The bold section undergoes a cycle of 35 rounds.

PCR program for ITS primers:		
°C	**Time**	**mode**
95	5 min	Denaturation
95	**30 sek**	**Denaturation**
55	**20 sek**	**Annealing**
72	**30 sek**	**Elongation**
72	5 min	Elongation
8	∞	Storage

PCR program for Bt3Neo primers:		
°C	**Time**	**mode**
94	4 min	Denaturation
94	**30 sek**	**Denaturation**
66	**30 sek**	**Annealing**
72	**1 min**	**Elongation**
72	5 min	Elongation
8	∞	Storage

PCR products were verified using gel electrophoresis. To make 400 mL of 1,5% Agarose gel, 6 g of agarose was gently added to 400 mL of 1% TBE buffer. Further 40 µL Gel Red was added to visualize DNA. Gel Red binds the DNA and emits fluorescence when the sample is exposed to UV light. The solution was poured in a gel tray and rested for 30 min and became solid. Then 5 µL PCR product was mixed with 1µL loading dye and loaded onto the gel. For reference measurements 1µL (1Kb) ladder was used as a marker. Where PCR products were highly visible and with only single bands, the sample was sent for Sanger sequencing at Eurofins using the same primers as for PCR amplification, only in separated reactions.

3.3.2 Chemical analysis

One sclerotium-half was soaked in 0.5 mL of a solution of 80% acetonitrile and 20% water and stored at 3 °C over night. The purpose was to obtain moisted sclerotia so they easily could be smashed and homogenized. An Ultra-Turrax T25, (Janke and Kunkel, Staufen im Breisgau, Germany) was used to homogenize the sclerotia (Figure 11). This is a small and powerful device where speed adjustments can be made from, 5 000- 35 000 rpm. The instrument was rinsed between each sclerotium, with distilled water and 80% acetonitrile solution, to avoid carry-over. The homogenized solution was transferred into 2 mL Eppendorf tubes with 0.22 µm Nylon membrane filters (Corning Inc,Corning, NY, USA). The solution is then centrifuged during 5 min, at 20 000 rcf. The homogenized solution was transferred to HPLC- vials and stacked in the freezer at -34 °C until UHPLC-HRMS analyses.

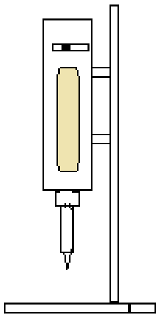


Figure 11: A sketch of the Pro Scientific, Ultra turax instrument.

3.4 Liquid chromatography –high resolution mass spectrometry

The instrument used to study the EA and the indole-diterpenoids was a vanquish Horizon ultrahigh-performance liquid chromatograph interfaced to a Q-Exactive high-resolution mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The mass spectrometer consists of an atmospheric pressure ionization API stack with an ESI interface, ion optics, and two mass analyzers- a quadrupole mass filter and an orbitrap mass analyzer. Important interface parameters included a source voltage of 3.2 kV, a capillary temperature of 270 °C, a shear gas flow of 35 units and an auxiliary gas flow of 10 units. The mass spectrometer was operated in positive mode. Ionization for the mass range for ergopeptines was *m/z* 200-700 and for the indole-diterpenoids *m/z* 350-550 for full MS. The molecular ion $[M+H]^+$ of the EAs were selected using an isolation width of *m/z* 2.0 and a normalized collision energy NCE of 30% . Chromatographic separation was achieved using an Accucore Vanquish C18+ column (100x 2.1 mm i.d., 1,5 µm particle size; Thermo Scientific).

The solvent used was 5mM ammonium acetate in water (A) and 5mM ammonium acetate in 95% acetonitrile and 5% water of LC–MS quality (B). Thermo Xcalibur Software version 2.3 was used for operation of the instrument, while version 4.2 was used for off-line data processing such as calculation of element formula. All the analysis were achieved with a resolution of 70 000 for full MS.

Two different gradients were used on the UHPLC of the different EAs. Gradient 1 was used for the ergopeptines and gradient 2 was used for the indole-diterpenoids. The eluent flow rate was 0,3 mL/min for both. The mobile phase gradient profile (Gradient 1) was as follows (t in min): t_0, B=15%; $t_{0.2}$, B=15%; t_{14}, B=80%; $t_{17,19}$, B=100%; $t_{19.1}$, B=15%; ,t_{21}, B=15%; with a total run time 21,1 min. (Gradient 2) t_0, B=80%; $t_{0.2}$, B=80%; $t_{14,17}$ B=100%; $t_{17.1,20.1}$, B=80%, with a total run time of 20,1 min.

3.5 Diagnostic fragmentation filtering and other raw data processing.

After uploading the raw data into Mzmine the samples are manually visualized by DFF. An example of the settings used is showed in (Table 5). The different diagnostic fragment ions for ergopeptines was: *m/z* 208.0748 and 223.1230 as exact masses. These were set in the same diagnostic fragment for the ergopeptine, as the two fragments are the most abundant in the MS/MS data. For the indole-diterpene there were two separate fragments *m/z* 130.0651 and 146.0600, these fragments were done separately.

Tabell 5: Standard settings for the Mzmine processing The diagnostic ions differed.*

	Peak detection		
Mzmine processing parameters	**Mass detection**	**Targeted peak detection**	**Duplicate peak filter**
Retention time (min)	1.5-14.5		
precursor (m/z)	350-550		
m/z tolerance	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm
Diagnostic product *(m/z)*	130.0600 *		
Diagnostic neutral loss (Da)	0		
Minimum diagnostic ion intensity (% base peak)	3		
Intensity tolerance (%)		10	
Noise level		10E3	
Retention time tolerance (absolute, min)		2	0.1

	Peak Alignment and identification				
Mzmine processing parameters	**Clear peak list annotations**	**Custom database search**	**Join aligner**	**Adduct search**	**Gap filling**
m/z tolerance	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm	0.02 *m/z* or 5 ppm
Weight for *m/z*	20				
Retention time tolerance (absolute, min)	10	0.1			
Weight for RT (min)	20				
Adducts				ESI (+): Na, MeCN+NH4	

Secondly when potential EA was detected for each sample, under raw data methods and peak detection, targeted peak detection was done. The purpose was to obtain a single list of each samples where the different potential EA were listed. The settings were: Intensity was set to 10%, Noise level: 10E3, the m/z tolerance: 0.02 *m/z* or 5 ppm as the previous settings, and a RT tolerance of 2 min. This step was as the previous done manually for each sclerotium.

All the samples lists were selected and under peak list methods and filter, duplicate peak filter was performed so all the duplicate peaks were deleted. The settings for this parameter were: 0.02 *m/z* or 5 ppm and RT tolerance at 0.1 min.

Clear peak list annotations were done, under peak list method and filtering. This is a second filter and the parameters were set to: 0.02 *m/z* or 5 ppm, a weight for *m/z* 20, a RT tolerance to 10, and a weight for RT to 20.

Further a custom data base search with ID, *m/z*, RT, identity was done on samples as they all were marked. This tool was found under peak list method and identification. The settings were set to 0.02 *m/z* or 5 ppm and RT tolerance to 0.1.

The different samples lists were finally aligned to one list, join aligner. Additionally, an adduct search was done, so they could easily be identified and deleted. To finish, the samples were gap filled under the peak list method menu. This was done so EA with the same RT and same m/z were identified and set under the same ID.

The procedure above was done 3 times, with different diagnostic fragments. One for the ergopeptines and two times with different diagnostic fragments for the indole-diterpenoid.

The ID of the different potential EA is taken from the DFF module. The relative peak areas in % were adjusted by Thermo Xcalibur Software Quan browser version 4.2, as a verification of the detected peak of the MS/MS data showed in appendix 3A.

3.6 Bioinformatics and Statistical modeling

For phylogenetic analysis sequences of ITS and tubB were first aligned by MAFT (Katoh & Standley, 2013) in the software Geneious (Kearse et al., 2012). Sequences originating from a selection of 34 sclerotia where both ITS and tubB sequences had been generated. On the basis of the multiple alignment where ITS and tubB were concatenated a phylogenetic tree was constructed using the Neighbor-joining method. Five reference strains were included for the different genotypes of *Claviceps sensu lato*. (*C. purpurea sensu stricto* (G1) strain WFA, ITS: EU559017, tubB: EU558996; *C. humidiphila* (G2) strain WHS, ITS: EU559018, tubB: EU558997; *C. arundinis* (G2a) strain CCC480, ITS: EU344983, tubB: JX083420; *C. spartinae* (G3) strain ARG1, ITS: JX083542, tubB: JX083473; G3 strain CPE10, ITS: EU559007, tubB: EU558986. *C. grothii* CBS isolate 124.47, ITS: AJ133395, tubB: FJ711480, was used as the outgroup). Determination of the different references were preformed using NCBI nucleotide BLAST (basic Local Alignment Search Tool). Confidence of the tree topology was assessed using bootstrap analysis with 1000 iterations.

All multivariate analysis were conducted using MetaboAnalyst 4.0. The variation patterns of the potential EA were analyzed by PCA. Samples in rows by sample matrix containing relative peak intensity. The rows of the matrix were normalized by sum and log transformation was also used.

4. Results and discussion

4.1 Genetic affiliation of ergot samples

A phylogenetic analysis based on ITS and tubB from 34 sclerotia revealed four clades representing the 4 four main genotypes of the genus *C. purpurea sensu lato* (Figure 12). G1 forms a separate clade early and is highly supported with a 100% bootstrap support.
The G3 group is only represented by two representative sequences from GenBank. These separate from G2 and G2a with a bootstrap of 98.2%. G2 and G2a are more similar genetically, as the bootstrap is weaker with a value of 74.4%.

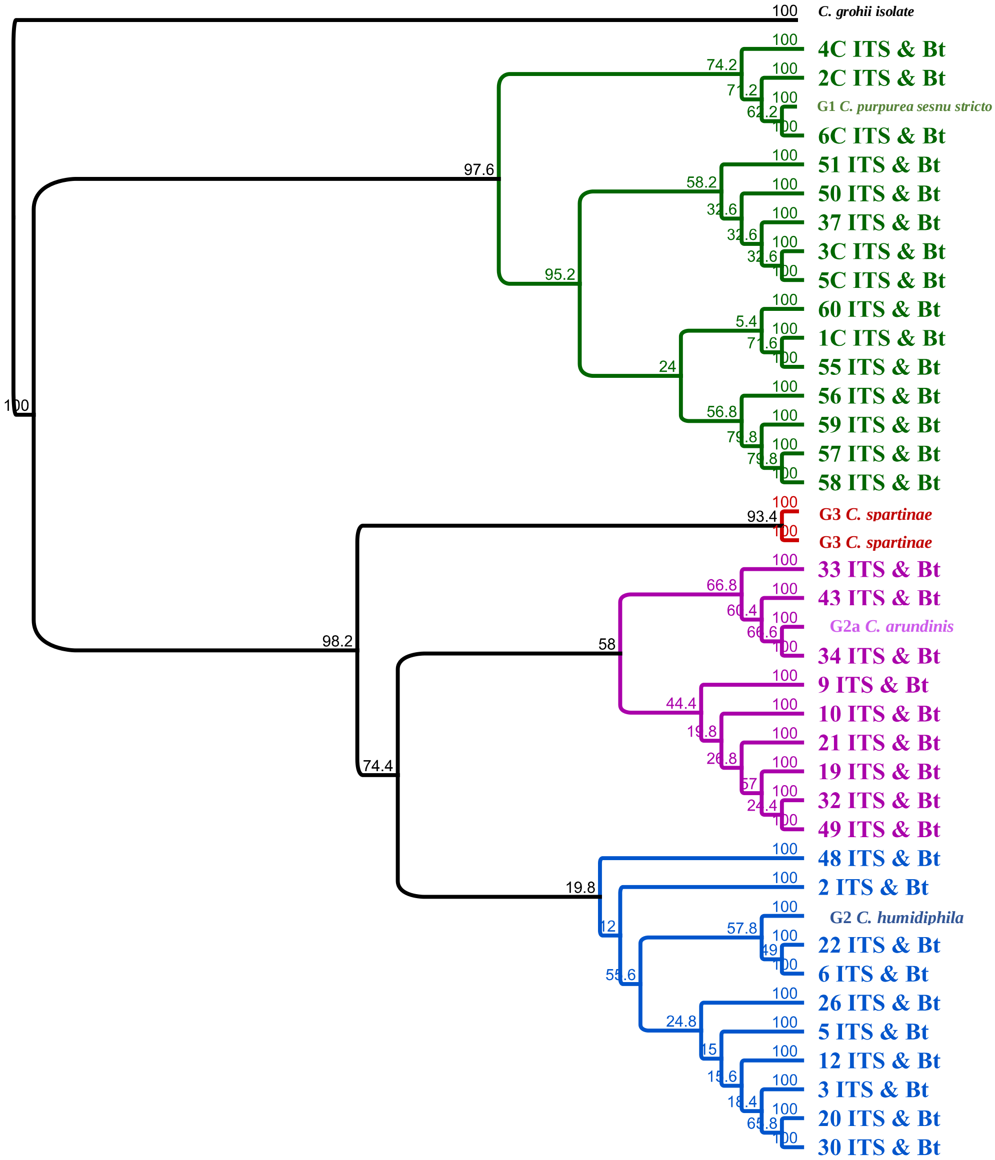


Figure 12: A phylogenetic tree of concatenated ITS and tubB sequences

G2a is host specific while G2 has a wider host range but is limited to grass species. G1 are of corn hosts in general, such as wheat, barley and oat both in Canada and Norway. There are some exceptions were G1 has been identified on grass species, three on “hundegress” (raigras *Lolium perenne*) and one “kveke“ (*Elymus repens*) (Table A1) in Appendix 1A.

4.2 Mass spectrometric fragmentation of Ergot alkaloids

The mass spectrometric fragmentation of EAs has been reported from a number of studies (Liu & Jia, 2017). They show that peptidic EAs all afford major product ions from the cleavage across the amide linkage between the ergoline and the peptide part (Figure 14). More specifically, series of product ions at *m/z* 208, 223, 251 and 268 is commonly observed for all peptide EAs (Figure 14). Since the *m/z* 208 and 223 product ions are common to all naturally-produced peptide EAs in the *Claviceps* species occurring in Norway and Canada, they were chosen for DFF of the full-MS/ddMS2 data set.

In previous research the product ion at *m/z* 208 was thought to be due to homolytical cleavage of the N-CH3 bond in the D-ring and hence explains the 15 amu difference between the abundant *m/z* 223 and 208 ions (Arroyo-Manzanares et al., 2014). However, accurate mass measurements in this study showed that the product ion at *m/z* 223.1226 is equivalent to ($C_{15}H_{15}N_2$; –1.59 ppm), while the product ion at *m/z* 208.0755 is equivalent to ($C_{14}H_{10}NO$; –0.91 ppm). Thus, the *m/z* 208 ion contain only one nitrogen atom and cannot arise from homolytic cleavage of the n-methyl group. The *m/z* 208 product ion is therefore likely to arise from a retro Diels-Alder (rDA) cleavage of the ergoline D-ring (Figure 13).

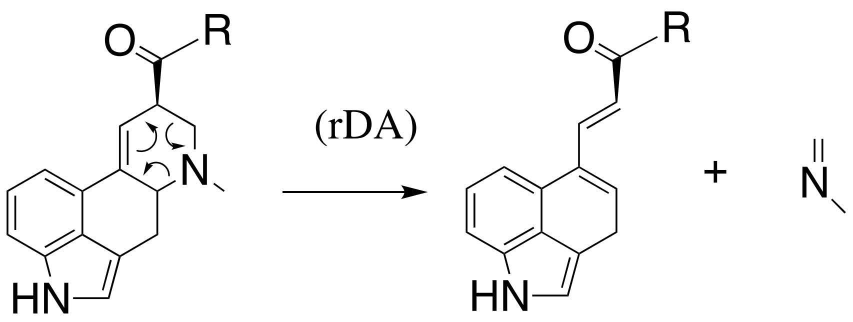


Figure 13: Mechanism for the retro-Diels-Alder (rDA) cleavage.

RDA involves a reorganization of bonds via a cyclic transition state, e.g between *m/z* 251.1174 ($C_{16}H_{15}N_2O$; –1.95 ppm) and 208.0755 ($C_{14}H_{10}NO$; –0.91 ppm). The mass difference between the product ions at *m/z* 348.1700 ($C_{21}H_{22}N_3O_2$; –1.76 ppm) and 305.1285 ($C_{19}H_{17}N_2O_2$; –1.71 ppm) may be explained by the same reaction. Furthermore, the product ion at *m/z* 277.1335 ($C_{18}H_{17}N_2O$; –1.406 ppm) may attributed to loss of CO (-28 Da) inform *m/z* 305 (Figure 14).

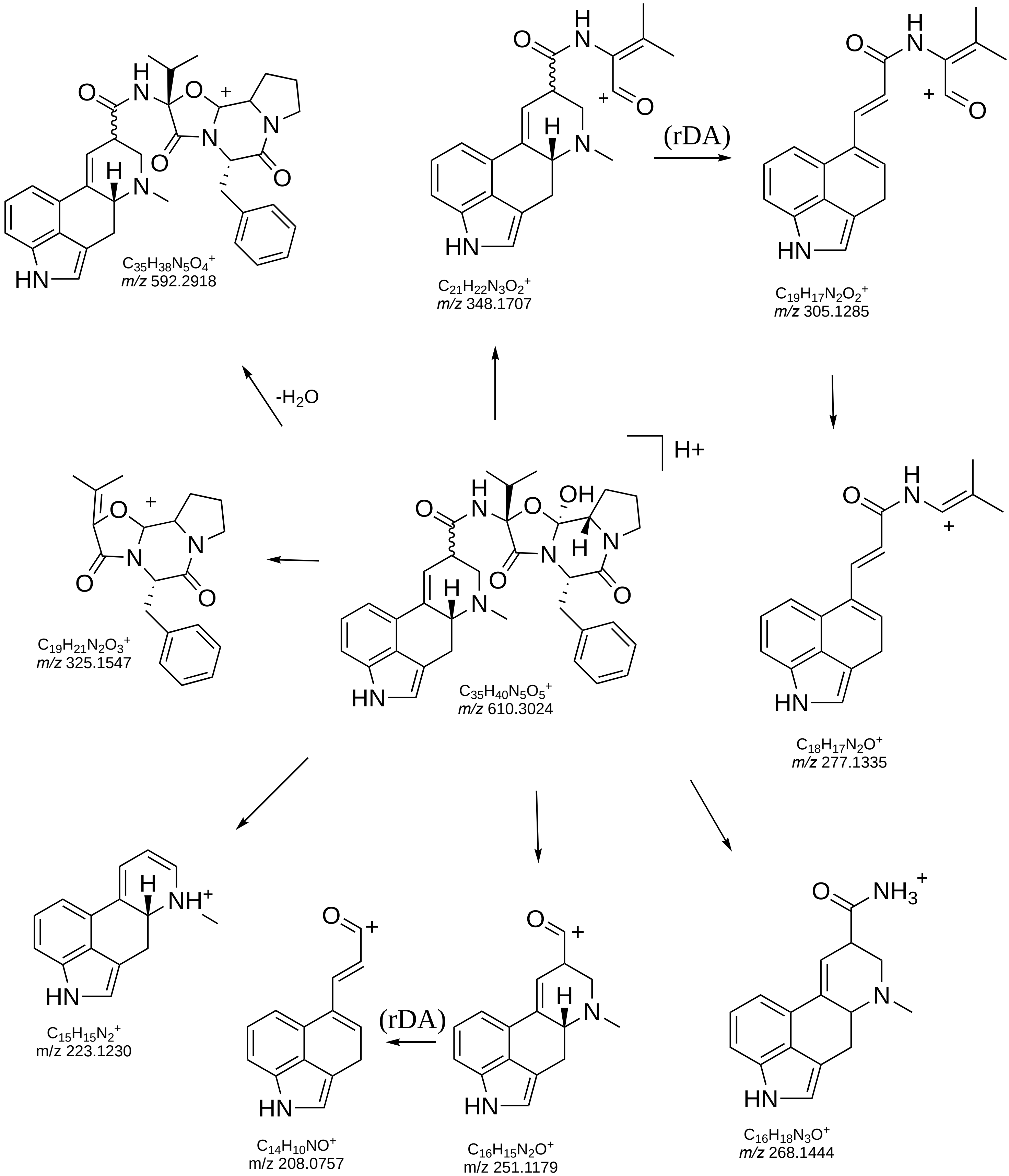


Figure 14: Major fragmentation pathway for the $[M+H]^+$ ions of ergocristine using higher-energy collision dissociation.

4.3 Mass spectrometric fragmentation of indole-diterpenoids

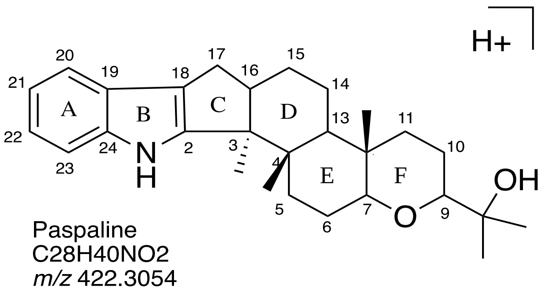


Figure 15: The structure of paspaline and its exact mass.

The mass spectrometric fragmentation *Claviceps*-related indole-diterpenoids has previously been reported (Uhlig et al., 2014). That study showed that indole-diterpenoids tend to fragment between the indole part of the molecule and the isoprene units, i.e. by cleavage across the C and the D-ring. These cleavages result in major product ions at *m/z* 130 and 182. Moreover, for some analogues the *m/z* 130 product ion is replaced by a product ion at m/z 146, which has been explained with a possible hydroxylation of the A-ring. Thus, both ions *m/z* 130.0651 and *m/z* 146.0600 were included in separate rounds of DFF.

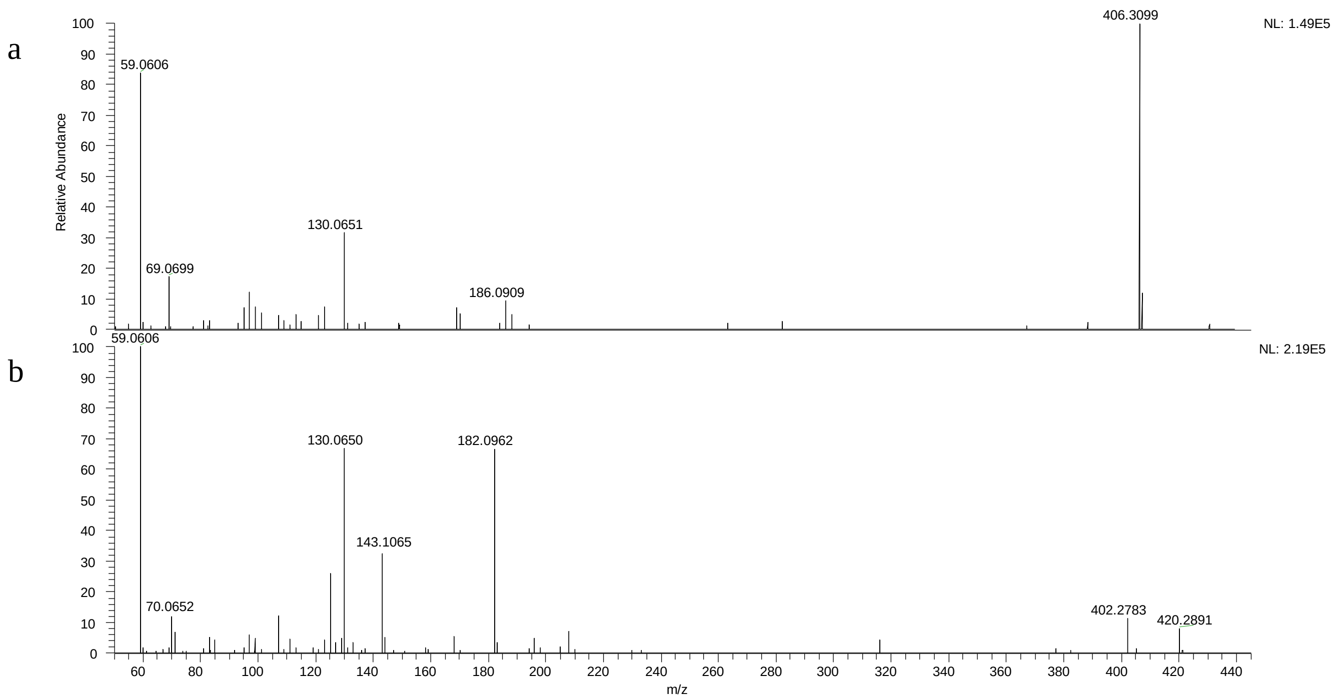


Figure 16: Representative HRMS/MS mass spectra of the putative [M+H]$^+$ ions of indole-diterpenoids observed at m/z 406 and m/z 420.

The product ion at m/z 59.0606 was observed in all the indole-diterpenoid mass spectra and is probably due to protonated acetone. The exact mass of protonated acetone is m/z 59.0491 and thus the observed accurate mass, was of relatively low mass accuracy (–193.337 ppm). However, cleavage of the isopropyl moiety of the F-ring (Figure 15), is most likely the explanation for the origin of the *m/z* 59.0606 ion.

4.4 Diagnostic fragmentation filtering of raw data

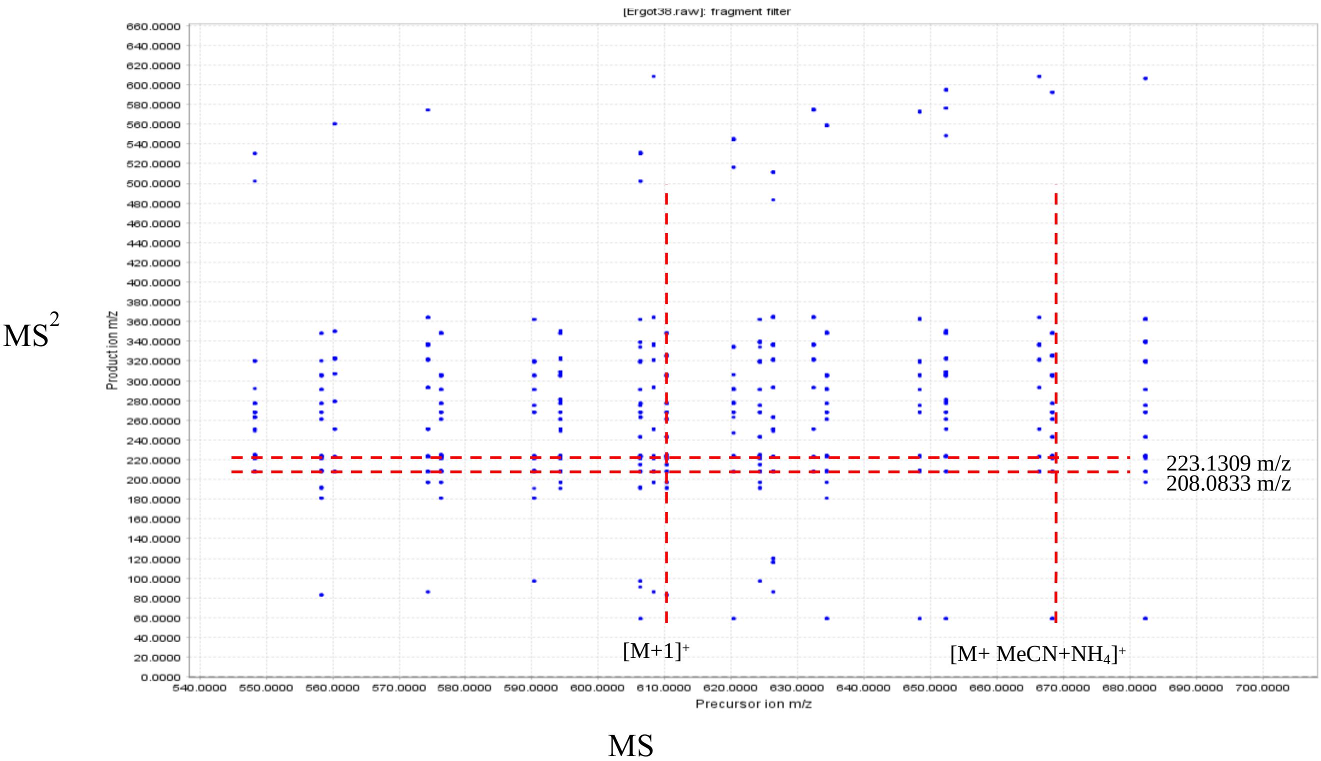


Figure 17: 2-D plot obtained from diagnostic fragment filtering of an ergot extract using m/z 208.0833 and m/z 223 for extraction of the ergot alkaloid metabolome. Precursor ion from potential ergot alkaloids are shown along the x-axis, and product ions along the y-axis. This has been exemplified for ergocristine.

The DFF module has been developed by colleagues at Agriculture Canada and has been included in the MZmine software (Figure 17). A total of 78 EAs and five indole-diterpenoids were detected with the help of DFF. Three clavines and the indole-diterpenoid paspaline were detected by comparison with reference standards. The relative concentration of paspaline in the samples was too low to trigger MS/MS during data-dependent scanning. The MS/MS mass spectra for each EA or indole-diterpenoid were carefully examined in order to ascertain their affiliation to these classes of compounds (Appendix 3A).

The DFF results of sample 38 (Figure 17) shows that the sclerotia contains relative high amounts of EAs and is among the sclerotia sampled in the Norwegian forest of the species family "blåtopp". This host was the only one identified as the G2a (C. arundinis) genotype. A similar result was accomplished in previous research, were G2a labeled G4 in the referred article, was found to have minor variation in host specificity (Negard et al., 2015).

4.5 Tentative identification of ergot alkaloids

The ergopeptines and lactam EAs are all structurally related and share a common skeleton, which makes it possible to use DFF for mining of the HRMS/MS raw data with the aim to extract the entire ergot metabolome. Peptide alkaloid analogues that could not be accounted for by comparison with reference standards were affiliated into their sub-groups, i.e. ergotamine, ergoxine, ergotoxine and ergoannine. The different subgroups can easily be distinguished by the product ion arising from cleavage across the amino acid next to the ergoline part. Thus, corresponding ion may be observed at *m/z* 320 in case of ergotamine, *m/z* 334 for ergoxines, *m/z* 348 for ergotoxines and *m/z* 362 for ergoannines (Figure 18). The equivalent strategy for screening and affiliation was done for the lactam analogues, which give corresponding product ions at *m/z* 322,336,350, and 364 (Figure 18).

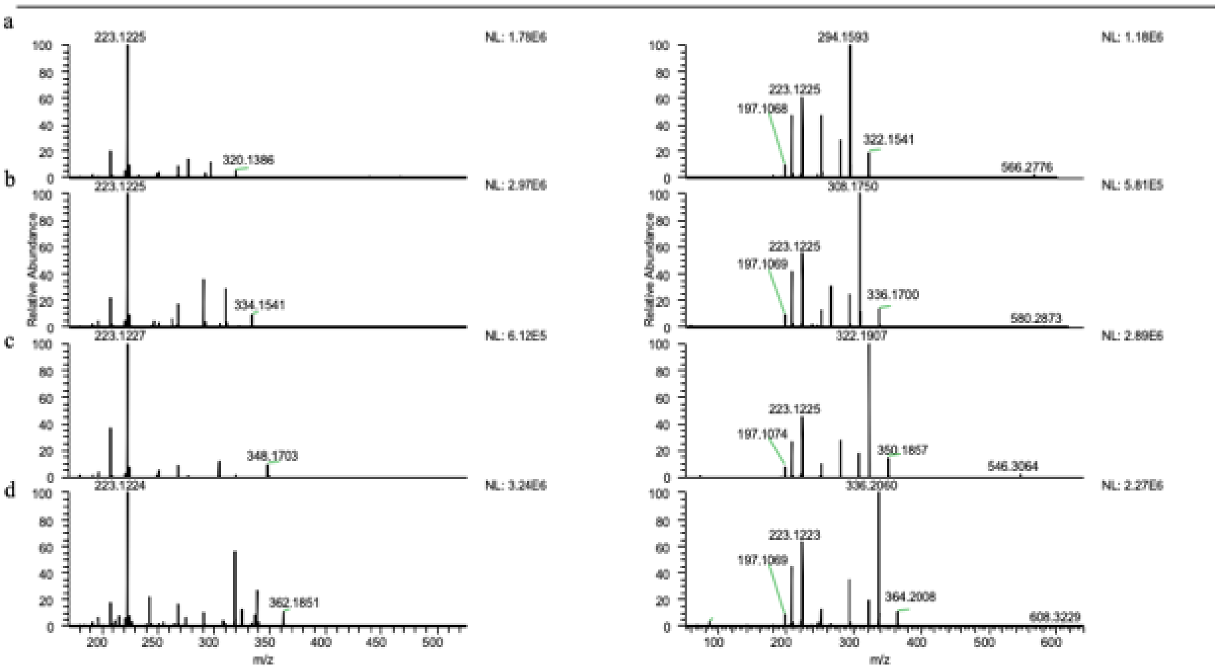


Figure 18: Representative example for HRMS/MS mass spectra of ergopeptines and lactam ergot alkaloids from the four different subgroups: ergotamine (a), ergoxine (b), ergotoxine (c) and ergoannine (d). Ergopeptines are shown on the left and lactams analogues on the right.

4.6 Tentative identification of indole diterpenoids

The indole-diterpene profiles were established using DFF based on the *m/z* 130.0651 or 146.0600 productions (Figure 19). The presence of a m/z 182.0962 product ion was used as further proof for an indole-diterpenoid molecule. The indole-fragments largely dominated the HRMS/MS mass spectra, and thus the spectra did not contain much structural information for individual analogues.

a

b

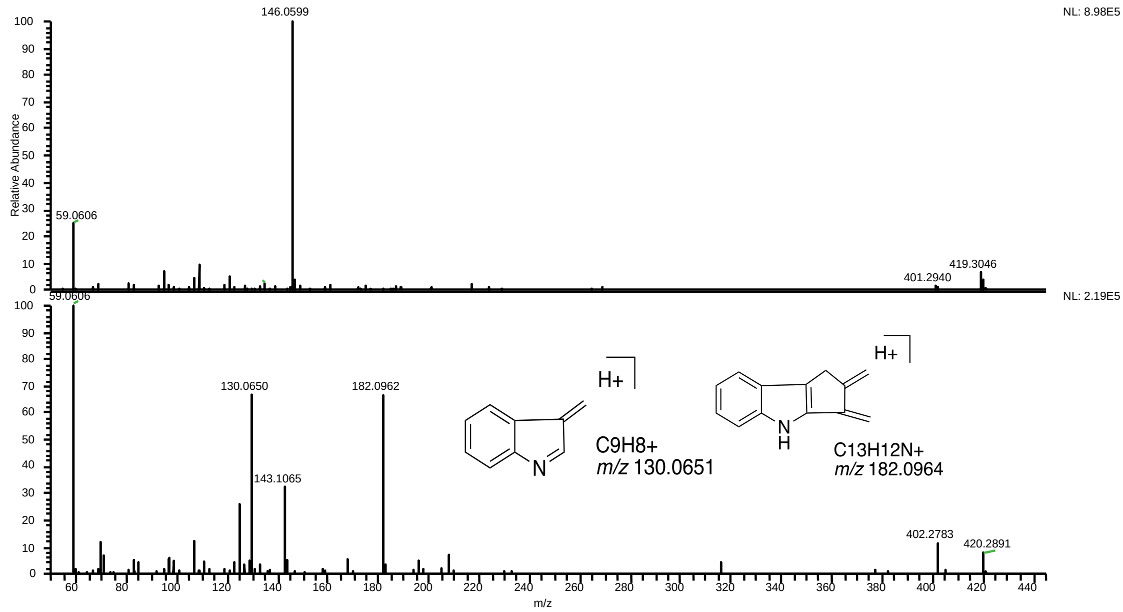


Figure 19: HRMS/MS spectra for two indole-diterpenes observed at m/z 420. The mass spectrum of the analogue shown in the upper trace indicates hydroxylation of the indole moiety.

The product ion at *m/z* 146.0599 ($C_9H_8NO^+$; –1.098 ppm) in mass spectra (a) (Figure 19) tentatively comes from the indole as the suggested molecule consist of a nitrogen and has a degree of unsaturation of 7 double bond equivalent (DBE). The fragment at *m/z* 143.1065 ($C_8H_{15}O_2^+$; –1.162 ppm) in mass spectra (b) (Figure 19) is tentatively from the isoprenoid unit part of the molecular ion *m/z* 420 since the suggested formula consists of two oxygen and has a DBE of 2. Moreover, a tentative structure of the fragments *m/z* 130 and 182 coming from the indole are illustrated in (Figure 19).

4.7 Multivariate data analysis

The PCA model (Figure 20) visualizes the total EA and indole-diterpenoid variation of the data set. Using relative alkaloid profiles, the G1genotype sclerotia formed a distinct cluster in the 3-D PCA scores plot, while the G2 and G2a sclerotia largely overlapped (Figure 20). This is in-line with an earlier study that showed that alkaloid profiles in G2 and G2a are rather similar (Negard et al., 2015). The Canadian ergot sclerotia were identified as G1. They formed a separate cluster in the PCA scores plot indicating some differences in the EA and indole-diterpenoid profiles relative to the Norwegian G1 (Figure 20).

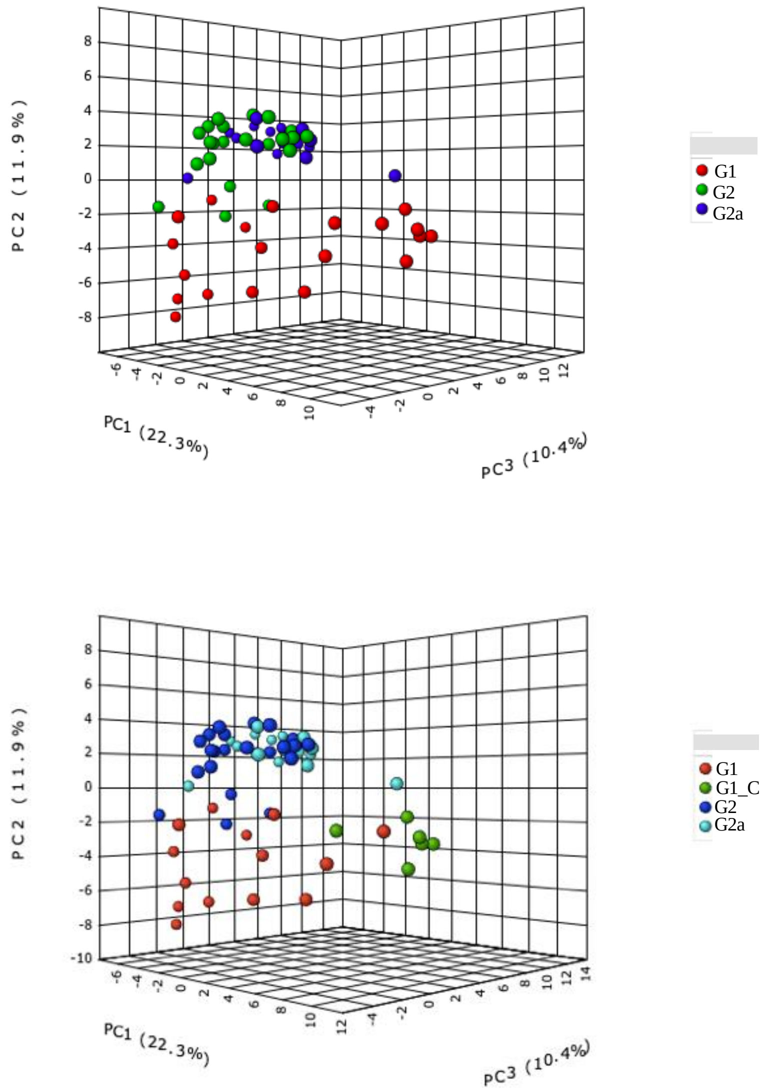


Figure 20: Scores plot from principal component analysis (PCA) based on the ergot alkaloid and indole-diterpenoid profiles in the Claviceps sclerotia. The three PCA components explain 44% of the variability of the alkaloid data. In the bellow scores plot the Canadian are marked separately in green.

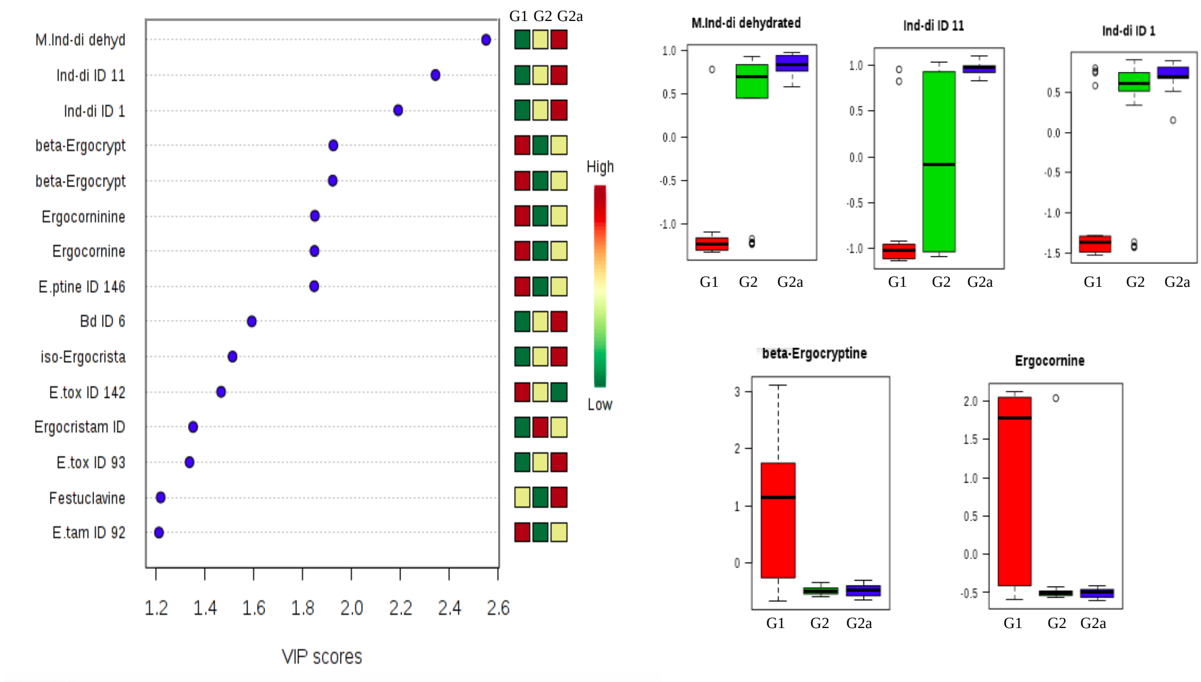


Figure 21: The ten most important features indicated by PLS. The colored boxes on the right indicate the relative concentrations of the corresponding metabolites in each group under study. The corresponding boxplot of the five most important features are shown to the right.

Partial least square (PLS) is a supervised method (i.e contains group information) that uses multivariate regression techniques to extract, via linear combination of original variables (here EA and indole-diterpenoid profiles), the information that can predict the class membership (affiliation to the different *C. purpurea* genotypes). The variable importance in projection (VIP) is a weighted sum of squares of the PLS loadings taking into account the amount of explained Y-variation in each dimension. Thus, the VIP parameter may be used to assess the contribution of a variable (i.e. an alkaloid) to the observed group separation. According to the VIP scores plot, three indole-diterpenoids contributed most to the observed group separation (Figure 21). As can be seen from the boxplots in figure 21, the production of the three indole-diterpenoids was rather similar in G2 and G2a *Claviceps*, while they were practically absent in G1 *Claviceps*. This is in accordance to an earlier study on alkaloid production in different *Claviceps* species (Negard et al., 2015). It has also been suggested that G1 *Claviceps* produces a larger variety of different EAs, which was supported in this study. Thus, only G1 *Claviceps* sclerotia contained β-ergocryptine and ergocornine (Figure 21).

4.8 Ergot alkaloids evaluated by EFSA.

In their recent opinions, EFSA presented 7 EA to be of major importance. These are: ergonovine, ergotamine, ergosine, ergocristine, α- and β-ergocryptine, and ergocornine, including their 8-S epimers (-inine forms) (Arcella et al., 2017). However, we found that the seven EAs in some sclerotia only account for a fraction of the entire EA complex (Figure 22). Figure 22 exemplifies this for sclerotia from host plants that are of special importance as they are either sources of grain for human consumption (oats, rye, barley), or are important feed plants (timothy).

In several of the Norwegian sclerotia from rye, no or very low amounts of EA were found. However, the seven EA assigned as the "most important" by EFSA accounted for 56-80% of the total EAs (based on the HRMS peak areas) in Norwegian rye sclerotia that contained EAs (Figure 22). In the Canadian rye sclerotium, the seven EAs accounted for 51% of the total EAs. These data emphasize the difficulties connected with the establishment of legal limits for the toxins in food and feed.

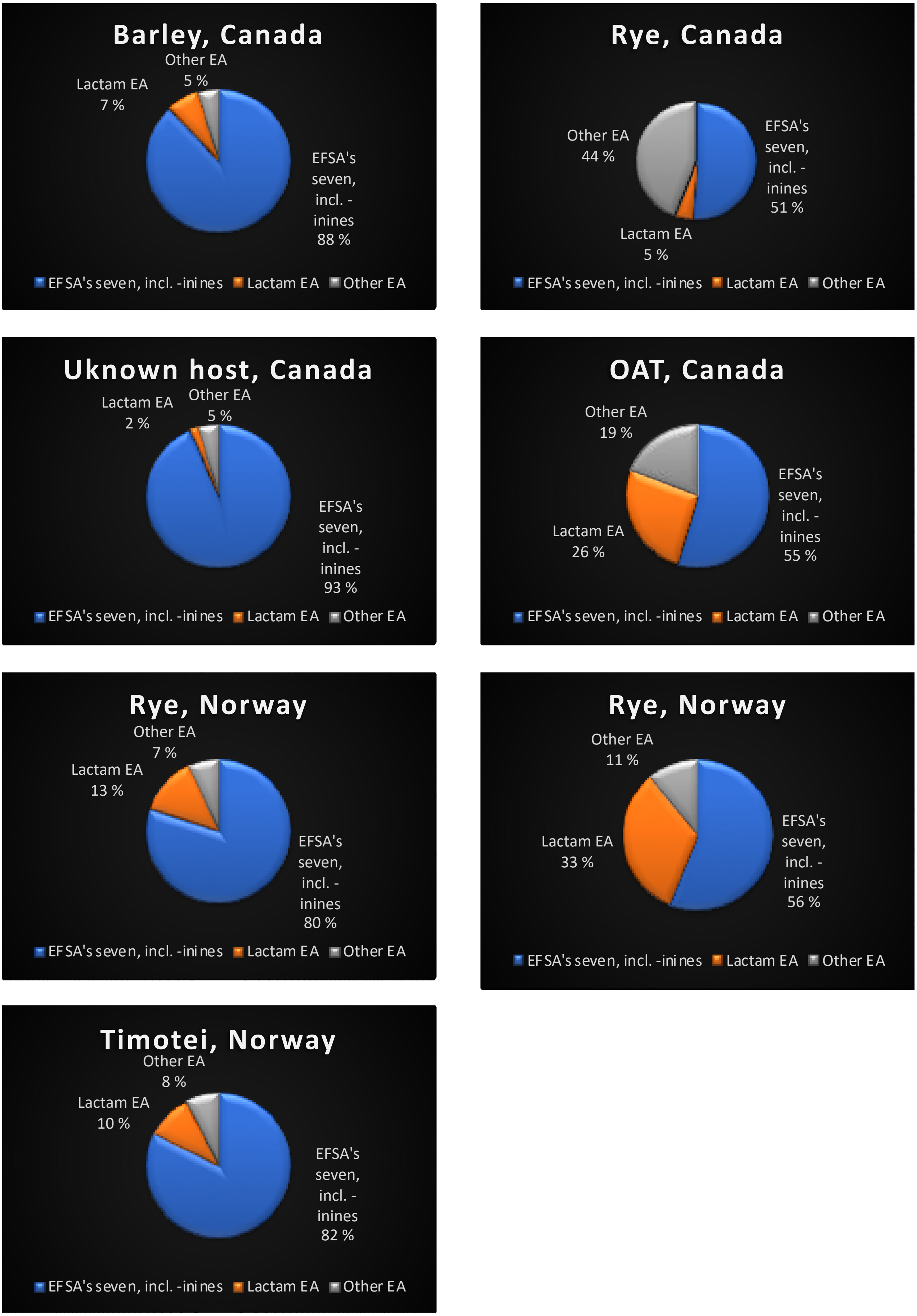


Figure 22: visualizes 7 different samples of Ergot. Each diagram shows the relative amount in % of EA and include the seven EAs EFSA consider of major importance.

5. Conclusion

66 sclerotia originating from different geographical and host sources were analyzed by UHPLC– HRMS/MS and processed by DFF. Genetic analysis was conducted to establish the genotype profile of the samples so the chemistry and the biology of the metabolomics data could be combined. A phylogenetic tree was established to understand the genetic variation between the various samples and establishing the different genotypes: G1 (*C. purpurea sensu lato*), G2 (*C. humidiphila*) and G2a (*C. arundinis*).

In the given PCA model, the metabolomics data strongly support a correlation between the genotype and the profile of the toxins produced by ergot. The PCA underlines the chemical similarities between samples that are genetically close to one another. The indole diterpenoids show a special impact on the G2a genotype. Additionally, the data matrix of the metabolomics data show host specific patterns of the genotype profiles. G1 is generally found in samples from corn such as oats, rye and barley both in Canada and Norway. G2a is host specific and grows on "blåtopp" (*Molinia caerulea),* while G2 has a wider host range of grass species.

A major part of this study was to verify and apply the use of the DFF module to establish a screening and potential novel EAs. The DFF module allowed the identification of 78 EAs, three clavines and five indole-diterpenoids. These are shown in appendix 3A.

EFSA established a classification of EA in terms of safety. In several of the Norwegian sclerotia from rye, no or very low amounts of EAs were found. However, the seven EAs assigned as the "most important" by EFSA accounted for 56-80% of the total EAs in Norwegian rye sclerotia that contained EAs. In the Canadian rye sclerotium, the seven EAs accounted for 51% of the total EAs. These data emphasize the difficulties in establishing legal limits for the toxins in food and feed.

Further studies can be conducted on the analysis of the lactam analogues and the toxicity of these EAs. Additionally, there might be an interest in doing research on the differences in alkaloid composition of the G2 and the G2a genotypes, since these are shown to have a strong correlation.

6. References

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7. List of figures

8. Appendix

Appendix: 1 Genetic analysis

Table 1A: An overview of the sample ID, host species name (in Norwegian and latin), genotype and location.

Sample ID	**Species (Norwegian)**	**Genotype**	**Location**
2,17,18,19,28,29,31,32,33,34,41,42,43,44	Blåtopp (*Molinia caerulea)*	G2a	Maridalen, Norway
9,10,21,38,39,48,49	Blåtopp (*Molinia caerulea)*	G2a	Telemark, Norway
35,37,45,47	Hundegress *(raigras Lolium perenne)*	G2, (G1)	Telemark, Norway
3,16,27	Hundegress *(raigras Lolium perenne)*	G2	Maridalen, Norway
4,15,26	Timotei (*Phleum pratense*)	G2	Maridalen, Norway
1,7,12,20,23,30	Snerprørkvein (*Calamgagrostis arundinacea*)	G2	Maridalen, Norway
5,6,13,14,24,25	Snerprørkvein (*Calamgagrostis arundinacea*)	G2	Eidsvoll, Norway
8,11,22,36,46	Strandrør (*Phalaris arundinacea*)	G2	Telemark, Norway
40,50	Kveke (*Elymus repens*)	G1	Maridalen, Norway
51-60	Rug (*Secale cereale*)	G1	Larvik, Norway
1C,3C,5C	Wheat (*Triticum*)	G1	Saskatchewan, Canada
2C	Barley (*Hordeum vulgare*)	G1	Saskatchewan, Canada
4C	Oats (Avena sativa)	G1	Saskatchewan, Canada
6C	Unknown	G1	Saskatchewan, Canada

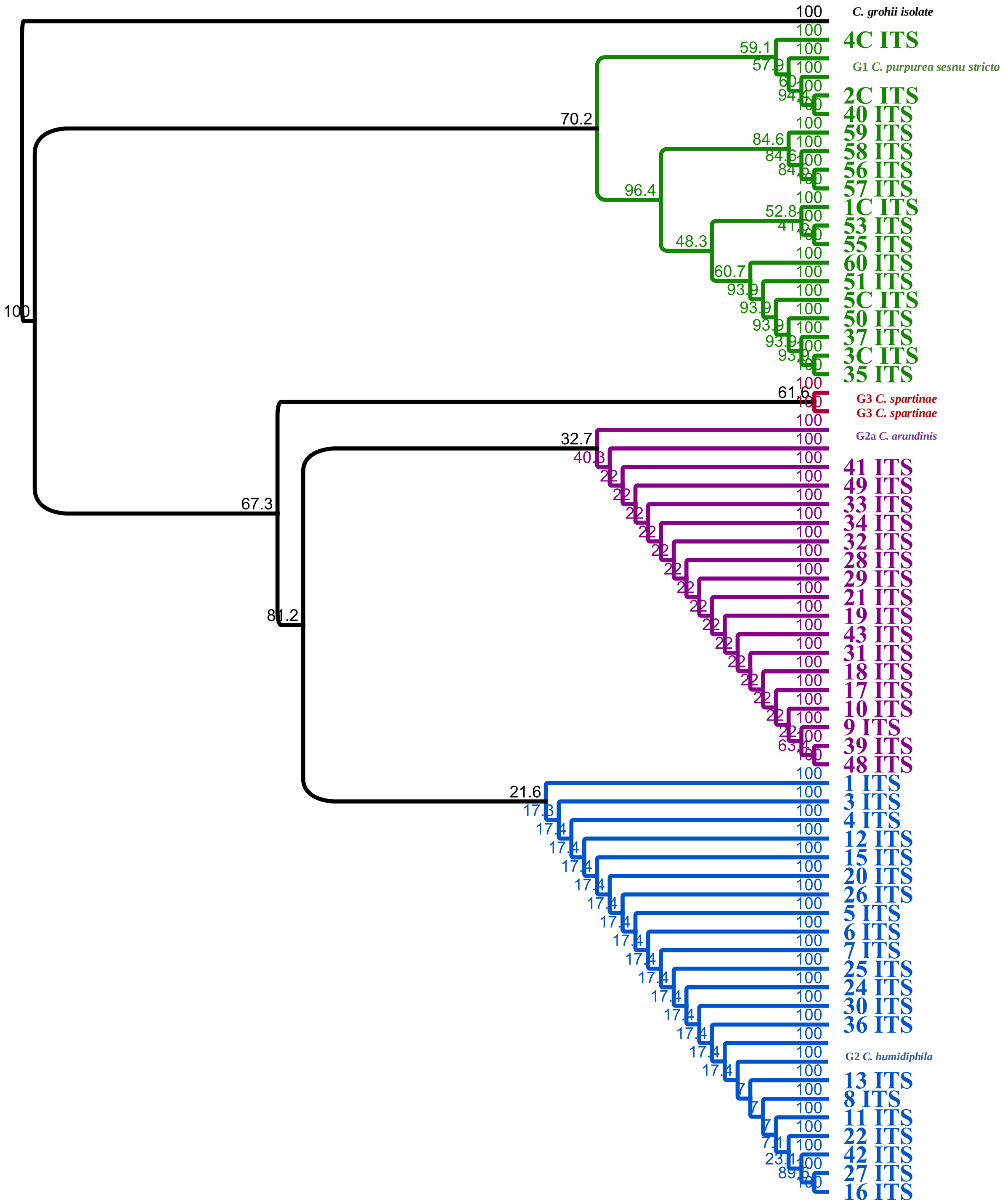

Figure 1A: A phylogenetic tree of concatenated ITS sequence.

Appendix 2: Multivariate statistics

R Command History

[1] "mSet<-InitDataObjects(\"pktable\", \"stat\", FALSE)"
[2] "mSet<-Read.TextData(mSet, \"Replacing_with_your_file_path\", \"rowu\", \"disc\");"
[3] "mSet<-SanityCheckData(mSet)"
[4] "mSet<-RemoveMissingPercent(mSet, percent=0.5)"
[5] "mSet<-ImputeVar(mSet, method=\"min\")"
[6] "mSet<-FilterVariable(mSet, \"none\", \"F\", 25)"
[7] "mSet<-PreparePrenormData(mSet)"
[8] "mSet<-Normalization(mSet, \"SumNorm\", \"LogNorm\", \"AutoNorm\", ratio=FALSE, ratioNum=20)" [9] "mSet<-PlotNormSummary(mSet, \"norm_0_\", \"png\", 72, width=NA)"

[10] "mSet<-PlotSampleNormSummary(mSet, \"snorm_0_\", \"png\", 72, width=NA)" [11] "mSet<-PCA.Anal(mSet)"
[12] "mSet<-PlotPCAPairSummary(mSet, \"pca_pair_0_\", \"png\", 72, width=NA, 5)" [13] "mSet<-PlotPCAScree(mSet, \"pca_scree_0_\", \"png\", 72, width=NA, 5)"

[14] "mSet<-PlotPCA2DScore(mSet, \"pca_score2d_0_\", \"png\", 72, width=NA, 1,2,0.95,0,0)" [15] "mSet<-PlotPCALoading(mSet, \"pca_loading_0_\", \"png\", 72, width=NA, 1,2);"
[16] "mSet<-PlotPCABiplot(mSet, \"pca_biplot_0_\", \"png\", 72, width=NA, 1,2)"
[17] "mSet<-PlotPCA3DScoreImg(mSet, \"pca_score3d_0_\", \"png\", 72, width=NA, 1,2,3, 40)" [18] "mSet<-PLSR.Anal(mSet, reg=TRUE)"

[19] "mSet<-PlotPLSPairSummary(mSet, \"pls_pair_0_\", \"png\", 72, width=NA, 5)"
[20] "mSet<-PlotPLS2DScore(mSet, \"pls_score2d_0_\", \"png\", 72, width=NA, 1,2,0.95,0,0)"
[21] "mSet<-PlotPLS3DScoreImg(mSet, \"pls_score3d_0_\", \"png\", 72, width=NA, 1,2,3, 40)"
[22] "mSet<-PlotPLSLoading(mSet, \"pls_loading_0_\", \"png\", 72, width=NA, 1, 2);"
[23] "mSet<-PLSDA.CV(mSet, \"T\",5, \"Q2\")"
[24] "mSet<-PlotPLS.Classification(mSet, \"pls_cv_0_\", \"png\", 72, width=NA)"
[25] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_0_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\",
[26] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_1_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\",
[27] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_2_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\",
[28] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_3_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\",
[29] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_4_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\",
[30] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_5_\", \"png\", 72, width=NA, \"coef\", \"G4\", 10,FALSE)" [31] "mSet<-PlotPLS.Imp(mSet, \"pls_imp_6_\", \"png\", 72, width=NA, \"vip\", \"Comp. 1\", 10,FALSE)" [32] "mSet<-PlotPCA3DScoreImg(mSet, \"pca_score3d_1_\", \"png\", 72, width=NA, 1,2,3, 40)"
[33] "mSet<-PlotHCTree(mSet, \"tree_0_\", \"png\", 72, width=NA, \"euclidean\", \"ward.D\")"
[34] "mSet<-SaveTransformedData(mSet)"
[35] "mSet<-PreparePDFReport(mSet, \"guest7453549218475969215\")\n"

———————————–
The report was generated on Wed Mar 27 09:13:58 2019 with R version 3.5.1 (2018-07-02).

Appendix 3: Data matrix of metabolomics data

Table 3A: An overview of the metabolomics data. 66 Samples in columns and 87 toxins in rows. ID, m/z, RT taken from Mzmine. Element composition was established by Thermo Xcalibur Software version 2.3.

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot01	Ergot02	Ergot03	Ergot04	Ergot05	Ergot06	Ergot07	Ergot08	Ergot09	Ergot10
								G2	G4	G2	G2	G2	G2	G2	G2	G4	G4
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	20507	1348498	11782	2267	4845	26289	7189	0	103138	12399
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		7244	2426418	21517	6003	81868	121986	21756	16834	137563	128580
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	1196	412002	0	0	0	15040	0	0	19492	4837
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	194838	5035109	17465	0	270357	332241	543954	267042	1168128	0
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	9627	740259	0	0	14622	108400	71732	48050	122916	0
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	9739	0	0	0	0	0	0	0	0
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		0	53796	0	0	0	0	0	4612	13813	0
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	45640	7761141	18203	689028	165959	253163	120955	348449	2292269	1536674
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	28465	0	0	0	0	0	0	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	366439	13773206	140762	5992043	978272	562888	209118	1396111	13615002	1663471
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	4282	14425	3895	2654	71026	8156	6672	167346	0	0
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	2227	8550	1355	1859	33256	9279	4559	134044	0	0
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	11386	67192392	217563	170191	586397	18642	19189	22976	37375096	5891431
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	0	16374661	15970	10090	56877	8033	0	56528	4460752	1919067
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	0	1961496	88750	34749	115162	1488987	6566	4075	74029	27410
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		0	91638	0	0	0	203896	0	0	0	0
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		0	86693	175474	154491	1542	135742	0	22705	43468	0
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		0	230227	117299	0	0	353130	14371	0	130623	65948
Indole-diterpenoid, hydroxyl	1	420,2895	2,03	C28H38NO2	11	-0,5		0	818334	262334	36411	43060	1509397	102023	71247	128508	327350
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	0	9617	0	3491	0	0	0	0	0	0
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		0	0	0	1324	0	0	0	0	0	0
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		0	7512	0	0	0	0	0	0	0	0
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		1218	14344	0	1616	0	0	0	0	0	0
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		6203	4982	84235	0	14328	167122	0	342	0	0
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	7766	99687	6535	0	62257	106322	0	0	0	0
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	0	65671	15766	0	0	39907	0	0	0	0
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	3820	127530	26818	0	0	74986	0	0	0	0
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		0	0	0	0	0	1104	0	0	0	0
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso* -Ergocornam*	0	2270	0	0	0	0	0	0	0	0
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	1089	134335	0	0	42737	12276	0	0	17489	3596
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		8014	5324	14250	0	21570	52638	0	0	0	0
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		5324	24066	6796	0	7933	18416	8338	0	0	0
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		3401	17203	0	0	0	15655	0	0	0	0
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		20354	11498	16974	0	36843	72252	0	0	0	0
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		3824	27070	7189	0	3389	15370	5206	0	0	0
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	839702	1197753	7533239	20119	1494889	14434118	84054	72017	0	0
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	4221788	2591678	14330109	44318	3333530	26428013	237980	231688	0	0
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		2095	174258	2455	4461	41446	572604	362017	11152	0	0
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso-* alpha-Ergocryptam*	5805	6047335	5034	41466	876897	2733317	511413	41168	390617	101114
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		0	256564	0	0	14000	158987	8692	0	0	3517
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	181	249918	0	0	2311	0	0	0	52658	17085
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	5805	6047335	5034	41466	876897	2733317	511413	40672	390617	101114

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot01	Ergot02	Ergot03	Ergot04	Ergot05	Ergot06	Ergot07	Ergot08	Ergot09	Ergot10
								G2	G4	G2	G2	G2	G2	G2	G2	G4	G4
Ergotoxine	Ergocorninine	562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	0	0	0	0	0	0	0	0	0	0
Ergotoxine	Ergocornine	562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	0	0	0	0	0	0	0	0	0	0
Ergotoxine	33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	514975	214230	894506	0	376280	1367551	98952	40331	0	0
Ergotoxine	146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	0	0	0	0	0	0	0	0	0	0
Ergotamine	88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	392751	2452	3444	6277	2626	0	0	0	0
Ergotamine	75	564,2582	12,36	C33 H34N5O4	20	-4,13		0	878662	0	2913	10538	6477	0	0	0	0
Ergotamine	81	566,2417	10,94	C32 H32N5O5	20	3,36		0	10207	25128	0	2821	35671	0	0	0	0
Lactam-ergotamin	108	566,2768	10,73	C33 H36N5O4	19	1,09		0	11540	0	0	0	0	0	0	0	0
Lactam-ergotamin	24	566,2768	9,04	C33 H36N5O4	19	1,09		0	2794199	2156	5272	17264	0	0	0	2107	0
Lactam-ergotamin	95	566,2770	11,43	C33 H36N5O4	19	1,45		0	49259	0	0	0	0	0	0	0	0
Lactam-ergotamin	46	574,3377	12,92	C33 H44N5O4	15	-1,88		0	745615	0	0	18004	5499	2876	0	20650	29987
Lactam-ergoannine	13	574,3378	10,95	C33 H44N5O4	15	-1,71		0	11111291	4927	1339	1880890	196605	185426	341506	1348836	422334
Lactam-ergoannine	57	574,3378	11,45	C33 H44N5O4	15	-1,71		0	878261	0	0	0	2925	3238	0	105341	25507
Ergotoxine	145	576,3171	9,00	C32 H42N5O5	15	-1,64		0	7002	0	0	2111	16256	19022	0	0	0
Ergotoxine	61	576,3174	13,50	C32 H42N5O5	15	-1,12		0	68813	0	0	0	9672	3243	3095	0	0
Ergotoxine	Alpha-Ergocryptine	576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	350351	17835049	309052	586593	3927618	62031037	36732714	1134547	13594	13954
Ergotoxine	Alpha-Ergocryptinine	576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	52667	5065589	109944	159505	1037264	43276715	16094657	240913	1362	1546
Ergotoxine	Beta-Ergocryptine	576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine	Berta-Ergocryptinine	576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine	141	576,3199	13,30	C32 H42N5O5	15	3,22		0	4042	0	0	0	9132	0	0	0	0
Lactam-ergotoxin	140	576,3201	9,71	C32 H42N5O5	15	3,56		0	35004	0	0	7450	55565	27888	0	0	0
Ergoxine	96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	2189	0	0	491	0	0	0	0	0
Lactam-ergoxine	99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	47350	0	0	4059	0	0	0	1492	0
Ergotamine	105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	33250	0	0	0	0	0	0	0	0
Ergotamine	92	582,2712	8,18	C33 H36N5O5	19	0,18		0	184919	0	0	0	0	0	0	0	0
Ergotamine	Ergotamine	582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	183215	34204948	304496	433446	693348	372751	467	117704	0	0
Ergotamine	Ergotaminine	582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	25848	22560879	113086	117671	289559	192287	0	28179	0	0
Ergotoxine	35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	0	84631	0	0	16803	876244	1198887	10202	0	0
Ergotoxine	27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	16691	701943	5206	864	152115	2154937	5051936	112923	0	0
Ergotoxine	38	594,2750	13,22	C34 H36N5O5	20	6,57		0	10622	0	0	11317	67506	64784	0	0	0
Lactam-ergotoxine	45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso*-Ergocristam*	0	998635	2917	40777	66003	105039	0	7885	35038	43990
Lactam-ergotoxine	76	594,3083	12,91	C35 H40N5O4	19	1,38		0	555855	0	0	22220	10249	0	0	14766	3977
Lactam-ergotoxine	7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	472370	56834410	278309	1011659	6539940	2490048	1081	566696	7764229	1767486
Ergoxine	72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	29828	215677	91667	25405	184277	39253	0	21222	0	0
Ergoxine	71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	2054	104276	40058	6637	62556	33984	0	4683	0	0
Lactame-ergoannine	5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	22621	203230634	141806	43029	195346	64995	0	17161	31404182	8787597
Ergotoxine	Ergocristine	610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	16511599	743823	19342806	15744947	79444748	54687003	389758	17615066	87392	9218
Lactam-ergotoxine	93	610,3030	9,88	C35 H40N5O5	19	0,99		6294	258578	4381	124339	103969	36089	0	13580	73772	17203
Ergotoxine	91	610,3035	9,27	C35 H40N5O5	19	1,81		25043	145278	27202	16522	252805	54619	0	29919	51171	9234
Ergotoxine	Ergocristinine	610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	2210872	195496	9140082	4678803	32182293	36441149	92380	4972902	13666	908
Ergotoxine	73	610,3038	13,74	C35 H40N5O5	19	2,30		9837	0	54013	20645	345330	225520	0	39277	0	0
Ergoannine	87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	34674	70259	87408	53004	234569	327397	0	53106	5339	12315
Ergotoxine	129	624,3188	13,11	C36 H42N5O5	19	1,21		0	17179	0	0	5159	0	0	0	0	0
Ergoannine	31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	2109	0	23700	11867	29869	69158	0	8811	0	0

Alkaloid Group	ID		row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot11	Ergot12	Ergot13	Ergot14	Ergot15	Ergot16	Ergot17	Ergot18	Ergot19	Ergot20
									G2	G2	G2	G2	G2	G2	G4	G4	G4	G2
Clavine		1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	12448	3728	21894	58871	1187	4083	395661	35360	3768732	49580
Clavine		2	241,1699	6,56	C16 H21 N2	8	0,0		128269	40984	100141	6745	0	733662	687364	70556	147659	3769
Clavine		3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	19436	0	39212	0	0	16646	89772	19606	204014	0
Simple lysergic derivative	Ergonovine		326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	0	865250	2084969	293751	1957	24050	1484287	2305	0	33993
Simple lysergic derivative	Ergonovinine		326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	0	158149	524745	0	0	12549	596955	0	0	0
Simple lysergic derivative		119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	0	2189	0	0	0	0	0	4697	0
Simple lysergic derivative		112	342,1816	2,39	C19H24N3O3	10	1,12		0	10129	157414	0	0	0	83158	0	0	0
Breakdown product?		15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	139932	192631	210236	33069	105259	103119	1015905	48158	1479338	73985
Breakdown product?		120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	3365	0	0	0	0
Breakdown product?		113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?		9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	1345129	650338	558079	722564	116137	87439	1022595	19411	7994868	182040
Breakdown product?		98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	7663	6796	8554	3214	853	2450	28296	0	2751	0
Breakdown product?		94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	5126	7117	6189	0	1032	4490	35473	0	2598	1063
Breakdown product?		6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	49031	41440	31411	32399	5460	4203	4552171	26631	29118982	56666
Breakdown product?		12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	0	0	0	0	4442	25135	2655019	50543	2354003	0
Indole-diterpenoid		1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	0	0	26643	0	62205	428860	234644	4743	5803	19412
Indole-diterpenoid		22	406,3099	8,43	C28H40NO	10	-1,2		0	0	0	0	0	56446	5830	0	0	0
Indole-diterpenoid		23	406,3099	6,53	C28H40NO	10	-1,2		0	0	24711	0	229305	43250	1603	0	0	56079
Indole-diterpenoid		11	420,2891	3,19	C28H38NO2	11	-1,5		0	0	0	0	3212	7409	82551	21399	22270	36935
Indole-diterpenoid, hydroxyl		1	420,2895	2,03	C28H38NO2	11	-0,5		0	0	101498	90573	306327	774344	802009	30767	101786	123658
Indole-diterpenoid		24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	0	600	0	0	1306	0	1025	629	1132	556
Lactam-ergotoxine		117	471,2742	9,91	C29 H35N4O2	15	-2,66		0	0	0	0	0	0	0	0	0	0
Lactame-ergoannine		122	485,2900	10,68	C30 H37N4O2	15	-2,27		0	0	0	0	0	0	0	0	2962	915
Lactam-ergotoxine		123	515,2660	5,99	C30 H35N4O4	16	1,39		0	0	0	0	0	0	0	0	0	0
Ergotamine		79	530,2726	11,73	C30H36N5O4	12	0,83		37680	0	0	16649	10564	449924	135489	0	0	4648
Lactam-ergotamine		69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	43072	0	0	220531	19195	13151	238981	0	5286	7847
Ergotamine	Ergovalinine		534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	0	0	0	3983	0	41863	7729	0	0	0
Ergotamine	Ergovaline		534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	9541	0	0	25237	0	30199	12307	0	0	0
Ergotoxine		142	544,2901	10,69	C31 H38N5O4	16	-3,18		0	1145	2425	0	0	0	0	0	0	0
Lactam-ergotoxine		136	546,3075	11,38	C31H40N5O4	15	0,03	*iso*-Ergocornam*	0	0	0	0	0	0	0	0	0	0
Lactam-ergotoxine		66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	2673	0	3708	12363	1540	0	9768	0	59830	0
Ergoxine		116	548,2867	8,82	C30 H38N5O5	15	-0,08		18877	0	0	3960	0	68566	34394	0	0	0
Ergotamine		77	548,2867	10,07	C30 H38N5O5	15	-0,08		13910	15971	5517	33809	8614	42916	60776	0	0	1907
Ergotamine		83	548,2868	7,81	C30H38N5O5	15	0,10		10730	0	0	32592	0	34614	44457	0	0	0
Ergotoxine		121	548,2870	7,35	C30 H38N5O5	15	0,46		48892	0	0	24025	3067	52216	44366	0	0	6571
Ergoxine		64	548,2870	12,26	C30H38N5O5	15	0,46		7176	5165	2982	15705	6841	139837	105406	0	0	0
Ergotamine	Ergosinine		548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	3914681	49205	164055	1897234	1412092	41989439	14779899	74488	47470	737638
Ergotamine	Ergosin		548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	13231681	180372	458282	10386687	3944209	42848281	21279728	131114	71229	2129596
Ergotoxine		135	558,3062	11,31	C32 H40N5O4	16	-2,30		3518	288012	713579	1978	3197	14325	20992	0	0	1898
Lactam-ergotoxine		132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso*- alpha-Ergocryptam*	29792	591270	5071927	17759	22924	9332	154192	0	1376262	7877
Lactam-ergoannine		50	560,3236	12,20	C32 H42N5O4	15	0,84		0	7988	159754	0	0	2119	17559	0	27745	0
Lactam-ergotoxin		42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	0	0	9890	0	0	0	33021	0	158252	0
Lactam-ergotoxin		17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	29792	591270	5070841	17759	22924	9332	154924	0	1377659	8201

Alkaloid Group	ID	row	m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot11	Ergot12	Ergot13	Ergot14	Ergot15	Ergot16	Ergot17	Ergot18	Ergot19	Ergot20
									G2	G2	G2	G2	G2	G2	G4	G4	G4	G2
Ergotoxine	Ergocorninine		562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	0	0	0	0	0	0	0	0	0	0
Ergotoxine	Ergocornine		562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	0	0	0	0	0	0	0	0	0	0
Ergotoxine		33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	939388	44890	150326	946762	337712	2280168	644687	1118	0	201310
Ergotoxine		146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	0	0	0	0	0	0	0	0	0	0
Ergotamine		88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	0	0	0	0	0	2522	0	0	1014
Ergotamine		75	564,2582	12,36	C33 H34N5O4	20	-4,13		0	0	0	0	0	13814	5727	606	0	0
Ergotamine		81	566,2417	10,94	C32 H32N5O5	20	3,36		4576	0	0	20751	0	57763	30725	0	0	0
Lactam-ergotamin		108	566,2768	10,73	C33 H36N5O4	19	1,09		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin		24	566,2768	9,04	C33 H36N5O4	19	1,09		0	0	0	0	0	0	7928	0	0	0
Lactam-ergotamin		95	566,2770	11,43	C33 H36N5O4	19	1,45		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin		46	574,3377	12,92	C33 H44N5O4	15	-1,88		0	0	8062	0	0	0	111553	0	162000	0
Lactam-ergoannine		13	574,3378	10,95	C33 H44N5O4	15	-1,71		0	127386	546949	0	0	0	1166547	0	4988823	10865
Lactam-ergoannine		57	574,3378	11,45	C33 H44N5O4	15	-1,71		0	2629	10106	0	0	0	56246	0	412321	0
Ergotoxine		145	576,3171	9,00	C32 H42N5O5	15	-1,64		0	15205	39563	0	0	0	441	0	0	0
Ergotoxine		61	576,3174	13,50	C32 H42N5O5	15	-1,12		0	0	458717	0	0	28646	12670	0	0	0
Ergotoxine	Alpha-Ergocryptine		576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	520559	29050878	74811922	494229	389911	1613197	2558999	7830	0	245838
Ergotoxine	Alpha-Ergocryptinine		576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	87963	8577547	43372692	62566	118012	2511772	1771813	4596	0	61686
Ergotoxine	Beta-Ergocryptine		576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine	Berta-Ergocryptinine		576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine		141	576,3199	13,30	C32 H42N5O5	15	3,22		0	0	9580	0	0	0	0	0	0	0
Lactam-ergotoxin		140	576,3201	9,71	C32 H42N5O5	15	3,56		0	21850	88969	0	0	0	0	0	8802	0
Ergoxine		96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	0	0	0	0	2956	0	0	0	0
Lactam-ergoxine		99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	0	0	0	0	0	0	0	7616	0
Ergotamine		105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	0	0	0	0	0	0	0	0	0
Ergotamine		92	582,2712	8,18	C33 H36N5O5	19	0,18		0	0	0	0	0	0	0	0	0	0
Ergotamine	Ergotamine		582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	98120	0	3373	65127	45483	439892	423287	0	0	121825
Ergotamine	Ergotaminine		582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	17785	0	0	7206	14195	356032	241666	0	0	30983
Ergotoxine		35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	0	431679	1228178	0	0	18711	351530	0	0	0
Ergotoxine		27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	10766	2649338	4287888	18411	9205	28969	10818	0	5199	4480
Ergotoxine		38	594,2750	13,22	C34 H36N5O5	20	6,57		0	99032	64906	0	0	12699	34832	0	0	0
Lactam-ergotoxine		45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso* -Ergocristam*	6983	0	0	0	11923	36888	135310	0	213490	5662
Lactam-ergotoxine		76	594,3083	12,91	C35 H40N5O4	19	1,38		0	0	0	0	0	0	20626	0	69963	2278
Lactam-ergotoxine		7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	807288	2570	1961	536265	663332	304771	4581584	12416	20008999	1184344
Ergoxine		72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	9856	2039	0	18829	11462	118076	103131	0	0	39200
Ergoxine		71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	0	0	0	0	3604	160283	71475	0	0	10100
Lactame-ergoannine		5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	39221	0	0	20269	20703	6478	21734773	55738	97529263	262671
Ergotoxine	Ergocristine		610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	10570302	178694	934271	5635936	9899112	50265284	32209781	217858	100285	20949446
Lactam-ergotoxine		93	610,3030	9,88	C35 H40N5O5	19	0,99		11446	0	0	0	3880	0	38590	0	204243	14111
Ergotoxine		91	610,3035	9,27	C35 H40N5O5	19	1,81		12229	0	0	1956	17229	95060	41109	0	113246	38362
Ergotoxine	Ergocristinine		610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	2105956	25125	295012	411735	4093497	112453231	32240860	199013	127578	7761349
Ergotoxine		73	610,3038	13,74	C35 H40N5O5	19	2,30		8446	0	0	0	33042	1341470	261556	0	0	72049
Ergoannine		87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	22444	0	0	21760	30453	152480	11389734	29900	55355	46251
Ergotoxine		129	624,3188	13,11	C36 H42N5O5	19	1,21		0	0	0	0	0	0	4917	0	18310	0
Ergoannine		31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	3065	0	0	0	10104	237648	6180038	12649	0	10152

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot21	Ergot22	Ergot23	Ergot24	Ergot25	Ergot26	Ergot27	Ergot28	Ergot29	Ergot30
								G4	G2	-	G2	G2	G2	G2	G4	G4	G2
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	602955	1836320	22411	38586	17797	108445	85796	1153606	2701659	9001
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		380199	570823	80269	2034037	29697	343733	1235154	329448	240737	0
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	56740	301283	2932	161396	0	86210	21150	192288	108702	0
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	2195491	1748	458380	711963	329737	30872	83456	2520797	0	25300
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	28892	0	5463	255375	0	0	20771	222619	0	0
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	0	0	0	0	0	0	0	0	0
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		30816	0	0	63229	0	0	0	24836	0	0
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	1006835	783831	133497	1446194	92805	358972	33475	4916554	2577746	0
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	5186839	2399983	197025	1015855	773686	1787315	164911	16228691	6341719	20018
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	1725	52921	15529	30551	17270	13191	21035	1868	2800	0
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	0	32015	14280	49657	5270	3112	19809	1988	0	0
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	28746542	149251	34809	69361	70424	95380	3607	62982462	44328885	41088
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	1773992	7472	0	35832	0	3729	1730	8292884	5005458	0
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	83194	113862	7289	551451	13709	200551	388077	289143	20731	0
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		43400	1214	0	137981	0	187672	60547	32306	0	0
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		161695	10341	0	0	32240	333770	253998	230696	0	0
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		26656	0	0	60777	0	119493	344679	206890	40225	0
Indole-diterpenoid, hydroxy	1	420,2895	2,03	C28H38NO2	11	-0,5		210521	149593	41456	1129498	110590	168436	364008	602381	190160	0
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	0	0	0	0	0	14784	1264	0	0	0
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		8192	0	0	2294	0	0	0	14165	17144	0
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		31895	1019	0	0	0	0	0	38298	101013	0
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		25091	7409	0	0	2800	60351	1423	127126	16437	0
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		0	254270	0	492265	0	84082	1014053	0	0	0
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	2617	308408	0	50534	0	1014551	164324	53785	12673	0
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	0	27286	0	126269	0	3351	185086	0	0	0
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	0	101974	1016	114886	0	34235	250305	0	0	0
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		0	0	1807	7439	0	0	0	0	0	0
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso* -Ergocornam*	0	0	0	0	0	0	0	3317	0	0
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	35822	21300	2746	7992	0	48660	2105	360175	99275	0
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		0	113316	0	84816	0	34305	286654	0	0	0
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		0	100435	36769	42984	22354	79876	213325	0	0	0
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		0	98220	0	18562	0	93357	142419	0	0	0
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		0	339732	0	70804	0	162564	278106	2348	0	0
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		0	59915	16285	145991	0	30124	270565	0	0	0
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	22116	22627409	180826	44910024	80480	9247774	86590626	100088	33415	153629
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	53908	63081051	580400	41871930	161516	37790506	109163512	212136	69867	520327
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		0	35638	797691	1499050	29332	10925	23356	0	0	0
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso-* alpha-Ergocryptam*	614259	223535	1778812	5312134	53674	232712	36644	3797524	2323336	0
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		0	0	29698	797216	0	0	0	70386	36307	0
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	135532	0	0	0	0	0	0	658491	302614	0
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	614259	223535	1778812	5312134	54020	235775	36644	3797524	2323336	0

Alkaloid Group	ID		row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot21	Ergot22	Ergot23	Ergot24	Ergot25	Ergot26	Ergot27	Ergot28	Ergot29	Ergot30
									G4	G2	-	G2	G2	G2	G2	G4	G4	G2
Ergotoxine	Ergocorninine		562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	0	3365	0	0	0	0	0	0	0	0
Ergotoxine	Ergocornine		562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	0	3968	0	0	0	0	0	0	0	0
Ergotoxine		33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	0	5192646	238513	3962488	12606	2206175	2112587	0	0	81351
Ergotoxine		146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	0	3968	0	0	0	0	0	0	0	0
Ergotamine		88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	5385	0	7151	6354	0	1926	0	0	0
Ergotamine		75	564,2582	12,36	C33 H34N5O4	20	-4,13		0	3111	0	61431	0	0	17418	0	0	0
Ergotamine		81	566,2417	10,94	C32 H32N5O5	20	3,36		0	146621	0	229066	0	39878	453384	0	0	0
Lactam-ergotamin		108	566,2768	10,73	C33 H36N5O4	19	1,09		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin		24	566,2768	9,04	C33 H36N5O4	19	1,09		3371	4774	0	0	1245	3438	0	17566	4748	0
Lactam-ergotamin		95	566,2770	11,43	C33 H36N5O4	19	1,45		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin		46	574,3377	12,92	C33 H44N5O4	15	-1,88		16426	0	8068	117658	0	0	0	201110	186685	0
Lactam-ergoannine		13	574,3378	10,95	C33 H44N5O4	15	-1,71		2531627	29578	764154	900227	12084	6943	479	9420509	10691117	7916
Lactam-ergoannine		57	574,3378	11,45	C33 H44N5O4	15	-1,71		312746	0	30340	0	0	0	0	796864	1161416	0
Ergotoxine		145	576,3171	9,00	C32 H42N5O5	15	-1,64		0	0	69857	21286	0	0	0	21515	0	0
Ergotoxine		61	576,3174	13,50	C32 H42N5O5	15	-1,12		0	4985	492308	1111843	1646	0	16265	0	0	0
Ergotoxine	Alpha-Ergocryptine		576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	0	3729764	83088863	159291844	2987159	1352045	2479989	31313	4454	40046
Ergotoxine	Alpha-Ergocryptinine		576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	0	631370	37971824	257304372	600402	104665	1489867	8440	2186	7106
Ergotoxine	Beta-Ergocryptine		576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine	Berta-Ergocryptinine		576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	0	0	0	0	0	0	0
Ergotoxine		141	576,3199	13,30	C32 H42N5O5	15	3,22		0	0	18857	55249	0	0	0	0	0	0
Lactam-ergotoxin		140	576,3201	9,71	C32 H42N5O5	15	3,56		0	0	65377	59377	0	0	0	10256	9675	0
Ergoxine		96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	0	0	12392	0	0	5597	0	0	0
Lactam-ergoxine		99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	0	0	0	0	2290	0	20915	10562	0
Ergotamine		105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	0	0	0	0	0	0	0	0	0
Ergotamine		92	582,2712	8,18	C33 H36N5O5	19	0,18		0	0	0	0	0	0	0	0	0	0
Ergotamine	Ergotamine		582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	0	652380	0	1200494	680564	167644	1056682	3386	0	14914
Ergotamine	Ergotaminine		582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	0	157676	0	1238748	82882	24846	618881	0	0	2575
Ergotoxine		35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	0	8237	3822253	17190923	19837	0	5058	0	0	0
Ergotoxine		27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	0	111479	14566492	15182305	173665	16224	24109	8044	8989	3806
Ergotoxine		38	594,2750	13,22	C34 H36N5O5	20	6,57		0	13551	566490	3173307	11500	0	38621	0	0	0
Lactam-ergotoxine		45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso*-Ergocristam*	29376	53846	0	521112	8177	11676	59780	217501	206468	0
Lactam-ergotoxine		76	594,3083	12,91	C35 H40N5O4	19	1,38		30542	24138	0	21223	5684	15834	14459	94880	78189	0
Lactam-ergotoxine		7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	11727409	8080971	25146	4449097	2679143	6664284	2471700	37796809	27099490	94096
Ergoxine		72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	0	77455	0	211804	179964	54901	262387	0	0	2389
Ergoxine		71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	0	14950	0	374912	18855	5843	178655	0	0	0
Lactame-ergoannine		5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	56735369	434407	971	33009	224233	92553	75951	122583103	147155120	113774
Ergotoxine	Ergocristine		610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	92619	50633689	631365	118795940	42468568	19791189	74577205	139368	49246	4545404
Lactam-ergotoxine		93	610,3030	9,88	C35 H40N5O5	19	0,99		54159	69141	0	30376	37055	30713	35345	206066	159409	0
Ergotoxine		91	610,3035	9,27	C35 H40N5O5	19	1,81		83839	108014	0	87755	25772	38395	152775	226734	129891	8908
Ergotoxine	Ergocristinine		610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	81898	13578434	157003	188568167	5342722	1926743	75007738	143255	37105	1213390
Ergotoxine		73	610,3038	13,74	C35 H40N5O5	19	2,30		0	123590	0	1034084	14865	7101	760387	0	0	13002
Ergoannine		87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	4116	164329	0	549752	374298	8607	264422	18628	33656	9332
Ergotoxine		129	624,3188	13,11	C36 H42N5O5	19	1,21		2512	23899	0	0	0	0	0	5590	11071	0
Ergoannine		31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	0	18248	0	428046	19984	0	131577	0	0	1300

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot31	Ergot32	Ergot33	Ergot34	Ergot35	Ergot36	Ergot37	Ergot38	Ergot39	Ergot40
								G4	G4	G4	G4	G1	G2	G1	G4*	G4	G1
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	15994	10239	82319	376002	2816	4642	0	7933683	46584	25661
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		59686	129744	195128	650160	7609	56739	54868	29233464	222820	1134587
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	13849	11847	25998	79475	0	63071	0	2922732	12815	19923
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	0	1183685	48875	0	0	73540	24770	79790	961140	246634
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	0	635179	19454	0	0	46788	24452	125449	514879	239430
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	3703	0	0	0	0	0	0	0	0
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		0	17298	0	0	0	0	0	40575	14232	54242
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	41615	360569	206841	1530285	0	265027	5489457	359882	79687	474833
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	93324	568892	625893	2838316	3547	184031	2435455	184298	221065	138519
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	0	2222	98103	9902	0	2523	0	10981	76331	0
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	0	0	14837	2672	0	2448	0	31491	22903	0
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	1279409	5680678	4144578	15765377	40013	12047	0	1455241	955726	27607
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	256278	1352407	490879	2278792	38961	5180	82588	1257836	174099	33981
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	71979	228794	57093	4315320	0	176572	0	7083933	1857066	280521
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		0	0	30488	336813	9162	35248	0	2436873	144743	2473588
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		11202	0	0	51927	109230	0	918	117319	83551	666326
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		80698	61709	24645	4736369	0	90167	0	5675627	611726	42773
Indole-diterpenoid, hydroxyl	1	420,2895	2,03	C28H38NO2	11	-0,5		421320	894891	238389	5699710	0	542243	0	4202432	3361086	377524
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	0	0	0	8437	1037	0	1035	331534	0	105846
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		0	3263	982	3067	0	0	2199	0	0	2417
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		0	3308	0	26602	1880	0	2958	7489	0	14421
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		0	0	0	0	0	0	0	0	0	0
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		0	0	168665	0	0	0	0	278750	246590	8504
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	0	0	84566	2771	0	0	77045	447113	267903	1542
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	0	0	30045	0	0	0	0	16279	43728	0
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	0	0	63578	0	0	0	0	8321	71886	0
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		0	0	0	0	0	1715	0	8728	27300	3417
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso*-Ergocornam*	0	0	0	0	0	0	17172	33280	3073	0
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	0	11599	8633	49185	0	1967	342723	41655	122025	6934
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		0	0	41724	0	0	0	0	3488	48730	0
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		0	0	46312	0	0	0	0	342963	137024	0
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		0	0	27817	0	0	0	0	173007	62038	0
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		0	0	84558	0	0	0	0	8127	53263	0
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		0	0	43712	0	0	4425	0	1075622	152091	11769
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	1154	8840	15463195	48426	5171	47290	1420	22681047	21530435	905312
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	5616	19746	33559784	116327	12471	84743	3707	12189092	33419728	675509
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		0	0	25111	0	0	305413	0	694922	149907	16937
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso*- alpha-Ergocryptam*	36797	408136	87973	1809192	1242	1368684	1205703	1781316	1161414	14838
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		2265	27175	0	81295	0	74025	291524	2500284	59107	3537
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	2770	43805	30034	234062	0	0	4710901	0	0	4917
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	36797	407973	87973	1809192	1242	1368684	1205703	1779465	1161414	14838

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot31	Ergot32	Ergot33	Ergot34	Ergot35	Ergot36	Ergot37	Ergot38	Ergot39	Ergot40
								G4	G4	G4	G4	G1	G2	G1	G4*	G4	G1
Ergotoxine	Ergocorninine	562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	0	0	0	0	0	0	0	0	0	3918
Ergotoxine	Ergocornine	562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	0	0	0	0	0	0	0	0	0	5072
Ergotoxine	33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	0	0	2412346	0	0	35161	0	805712	2048754	131548
Ergotoxine	146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	0	0	0	0	0	0	0	0	0	5080
Ergotamine	88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	0	0	0	0	0	0	0	1904	0
Ergotamine	75	564,2582	12,36	C33 H34N5O4	20	-4,13		0	0	0	0	2068	0	0	47662	0	9401
Ergotamine	81	566,2417	10,94	C32 H32N5O5	20	3,36		0	0	4484	0	0	0	0	111535	34853	0
Lactam-ergotamin	108	566,2768	10,73	C33 H36N5O4	19	1,09		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin	24	566,2768	9,04	C33 H36N5O4	19	1,09		0	0	0	9850	0	0	0	0	1352	0
Lactam-ergotamin	95	566,2770	11,43	C33 H36N5O4	19	1,45		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin	46	574,3377	12,92	C33 H44N5O4	15	-1,88		18231	299254	14786	599523	0	35214	36682	4589678	61159	0
Lactam-ergoannine	13	574,3378	10,95	C33 H44N5O4	15	-1,71		160735	3009028	452517	9210877	7452	595958	485137	3575659	739070	24143
Lactam-ergoannine	57	574,3378	11,45	C33 H44N5O4	15	-1,71		0	109650	21664	408341	0	5083	0	5226	33568	0
Ergotoxine	145	576,3171	9,00	C32 H42N5O5	15	-1,64		0	0	0	0	0	6135	2957	15922	5332	2971
Ergotoxine	61	576,3174	13,50	C32 H42N5O5	15	-1,12		0	0	0	0	0	17988	0	2147997	155487	1099838
Ergotoxine	Alpha-Ergocryptine	576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	0	10557	2501032	36725	0	30394080	32306	69939893	15077461	1554589
Ergotoxine	Alpha-Ergocryptinine	576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	0	5046	658749	20655	0	43707306	23050	283152295	8666507	8694343
Ergotoxine	Beta-Ergocryptine	576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	0	0	0	0	0	0	545344
Ergotoxine	Berta-Ergocryptinine	576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	0	0	0	0	0	0	2268425
Ergotoxine	141	576,3199	13,30	C32 H42N5O5	15	3,22		0	0	0	0	0	14968	0	455609	5602	1097414
Lactam-ergotoxin	140	576,3201	9,71	C32 H42N5O5	15	3,56		0	2268	0	11332	0	33458	12210	0	0	0
Ergoxine	96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	0	0	0	0	0	0	0	0	0
Lactam-ergoxine	99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	0	0	10147	0	0	0	0	0	0
Ergotamine	105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	0	0	0	0	0	0	0	0	0
Ergotamine	92	582,2712	8,18	C33 H36N5O5	19	0,18		0	0	0	0	0	0	0	0	0	0
Ergotamine	Ergotamine	582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	0	0	214779	0	1918	52117	0	15068	218718	32757
Ergotamine	Ergotaminine	582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	0	0	61159	0	0	32524	0	22237	110098	43041
Ergotoxine	35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	0	0	122903	0	0	9733934	0	10168434	355255	154188
Ergotoxine	27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	0	4673	655926	11950	0	9014256	12311	2090365	777315	43449
Ergotoxine	38	594,2750	13,22	C34 H36N5O5	20	6,57		0	0	0	0	0	54465	0	3029300	42374	0
Lactam-ergotoxine	45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso*-Ergocristam*	40918	302610	25624	496839	0	20807	0	6064499	212044	5432
Lactam-ergotoxine	76	594,3083	12,91	C35 H40N5O4	19	1,38		0	23732	3582	55528	0	4680	0	76336	26726	0
Lactam-ergotoxine	7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	770470	5845534	1952743	18682629	20543	531649	4542	5432184	5692618	62196
Ergoxine	72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	0	0	64186	0	0	13347	0	8066	71660	4970
Ergoxine	71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	0	0	19006	0	0	15212	0	32428	42203	42948
Lactame-ergoannine	5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	5977160	39903148	12002263	116313255	129660	13755	20928	43767890	23287527	457801
Ergotoxine	Ergocristine	610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	8448	22984	23923342	75507	12212	27080821	33047	11208976	38355403	13564807
Lactam-ergotoxine	93	610,3030	9,88	C35 H40N5O5	19	0,99		9315	56059	27607	206516	0	9355	0	0	45138	0
Ergotoxine	91	610,3035	9,27	C35 H40N5O5	19	1,81		0	0	28255	0	0	27862	0	12086	105534	4399
Ergotoxine	Ergocristinine	610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	5084	14885	8343351	60360	4886	35239146	30820	39074418	25323230	67522816
Ergotoxine	73	610,3038	13,74	C35 H40N5O5	19	2,30		0	0	46284	0	0	197839	0	495065	413544	272886
Ergoannine	87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	30518	149639	6883284	241928	0	152142	0	9550822	16560247	192371
Ergotoxine	129	624,3188	13,11	C36 H42N5O5	19	1,21		0	7764	0	22249	0	0	0	9423	4879	0
Ergoannine	31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	0	0	1560232	3546	0	203356	0	39838557	6664509	142336

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot41	Ergot42	Ergot43	Ergot44	Ergot45	Ergot46	Ergot47	Ergot48	Ergot49	Ergot50
								G4	G2	G4	-	-	-	G1*	G4	G4	G1
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	100654	605817	290128	1357	163438	156034	0	48245	0	2765
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		1391909	1158435	854977	24979	6793856	4793746	48065	1482186	18355	1760899
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	54010	432211	92195	2586	261502	242631	0	82787	0	73351
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	0	37738	0	0	10507010	353476	0	0	0	6732595
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	0	9091	0	0	17478594	587907	5523	1454	13856	11506621
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	0	19835	0	53484	0	0	0	0	6802
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		0	0	0	0	4109273	47279	0	0	0	41855
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	4142788	618346	7677612	33672	8720	50451	0	98727	104903	4489594
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	0	0	0
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	0	0	0	0	0	0	2486	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	1118202	3334704	14757010	142411	0	23878	0	44532	127839	775314
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	0	155376	10401	0	3642	65427	0	9081	1400	12817
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	0	60777	5434	0	1174	159140	1229	13408	0	35917
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	9441570	362033	52616260	1531417	0	267534	0	0	1441643	92372
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	17832501	35595	18889189	129057	26732	159050	45594	6800	354816	265870
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	685744	123356	2528030	52442	0	657688	0	1346074	904446	0
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		110970	17263	106004	0	134848	228089	115467	504374	69734	13791
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		0	853889	195028	0	32888	323836	315127	6556	82337	6758
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		305942	208405	479689	68339	7212	153953	0	405298	412856	18808
Indole-diterpenoid, hydroxyl	1	420,2895	2,03	C28H38NO2	11	-0,5		333665	315681	2229623	309063	0	1180686	0	1056013	1622914	6038
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	0	6210	11105	0	1925	2995	0	0	1480	1107
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		0	3990	1857	0	7476	0	0	0	0	9578
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		0	0	15058	0	0	0	0	0	0	0
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		0	50983	12662	0	4550	0	0	0	0	0
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		0	686027	0	0	9052	105039	0	775250	0	1371840
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	0	490050	39532	0	0	36626	0	30697	469674	131399
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	0	87960	0	0	0	77994	0	93585	0	2971383
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	0	226316	0	0	7584	64862	0	54361	0	1699019
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		0	5283	0	0	0	264497	0	0	0	2114776
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso*-Ergocornam*	0	0	6686	0	0	187635	0	0	0	1378170
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	3757	45802	315911	0	0	759672	0	0	139710	3797413
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		0	144018	0	0	0	64967	0	85433	0	510469
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		0	150965	0	0	0	167625	0	55478	0	2067172
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		0	71892	0	0	0	0	0	25030	5335	647691
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		0	356966	0	0	0	36373	0	45205	5497	263067
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		0	83462	0	0	0	817616	0	212601	0	10886301
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	5020	56478686	133457	2162	896739	9876904	13065	61586227	6974	113078317
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	12031	142391494	456333	9162	1022865	8425197	15270	41708559	13269	74234271
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		0	102711	0	0	823	5548	0	61565	0	1528272
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso*- alpha-Ergocryptam*	353416	467041	6062478	30932	0	11765	0	84091	78371	5040403
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		132206	5149	170566	0	0	2611	0	32296	0	4056975
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	18696	0	1292794	6431	0	5080	0	0	11173	2636034
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	352041	467041	6062478	30932	0	11765	0	84091	78371	5018672

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Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot41	Ergot42	Ergot43	Ergot44	Ergot45	Ergot46	Ergot47	Ergot48	Ergot49	Ergot50
								G4	G2	G4	-	-	-	G1*	G4	G4	G1
Ergotoxine	Ergocorninine	562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	0	0	0	0	0	17742	0	0	0	1236948
Ergotoxine	Ergocornine	562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	0	0	0	0	0	17742	0	0	0	1235806
Ergotoxine	33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	0	11454917	5439	0	2451414	2623968	2404	2237162	2156	7502383
Ergotoxine	146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	0	0	0	0	0	17742	0	0	0	1232789
Ergotamine	88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	3821	0	0	0	0	0	8535	0	0
Ergotamine	75	564,2582	12,36	C33 H34N5O4	20	-4,13		4054	0	0	0	0	10994	0	2143	0	8325
Ergotamine	81	566,2417	10,94	C32 H32N5O5	20	3,36		0	157941	0	0	0	28500	0	191059	0	309921
Lactam-ergotamin	108	566,2768	10,73	C33 H36N5O4	19	1,09		0	0	0	0	0	0	0	0	0	668595
Lactam-ergotamin	24	566,2768	9,04	C33 H36N5O4	19	1,09		0	0	17777	0	0	0	0	0	0	0
Lactam-ergotamin	95	566,2770	11,43	C33 H36N5O4	19	1,45		0	0	0	0	0	0	0	0	0	0
Lactam-ergotamin	46	574,3377	12,92	C33 H44N5O4	15	-1,88		869623	0	1274770	11718	0	15535	0	0	32239	1577810
Lactam-ergoannine	13	574,3378	10,95	C33 H44N5O4	15	-1,71		1640865	32962	29168611	268383	2775	52926	0	2738	244113	1321535
Lactam-ergoannine	57	574,3378	11,45	C33 H44N5O4	15	-1,71		9558	0	2869268	3669	0	0	0	0	3329	0
Ergotoxine	145	576,3171	9,00	C32 H42N5O5	15	-1,64		1975	2511	0	0	0	0	0	0	0	467654
Ergotoxine	61	576,3174	13,50	C32 H42N5O5	15	-1,12		0	19567	0	0	0	44953	0	216694	0	59415793
Ergotoxine	Alpha-Ergocryptine	576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	10273	9761735	23419	0	235288	553334	0	5950076	0	164180165
Ergotoxine	Alpha-Ergocryptinine	576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	17952	1906401	17271	1911	692233	2411100	1117	14645420	0	474796220
Ergotoxine	Beta-Ergocryptine	576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	0	0	219335	0	0	0	120782352
Ergotoxine	Berta-Ergocryptinine	576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	0	0	1036649	0	0	0	391002795
Ergotoxine	141	576,3199	13,30	C32 H42N5O5	15	3,22		0	0	0	0	0	42746	0	3274	0	59415793
Lactam-ergotoxin	140	576,3201	9,71	C32 H42N5O5	15	3,56		0	0	32573	0	0	0	0	0	0	64070
Ergoxine	96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	1613	0	0	0	0	0	0	0	0
Lactam-ergoxine	99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	0	28074	0	0	0	0	0	0	0
Ergotamine	105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	0	0	0	0	0	0	0	0	0
Ergotamine	92	582,2712	8,18	C33 H36N5O5	19	0,18		0	0	0	0	0	0	0	0	0	0
Ergotamine	Ergotamine	582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	1733	737285	0	0	72792	23965	0	159913	0	197976
Ergotamine	Ergotaminine	582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	0	213273	0	0	0	28252	0	255106	0	345502
Ergotoxine	35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	0	14019	0	0	235630	1868783	0	54500	0	29580652
Ergotoxine	27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	0	213576	26302	0	75453	839271	0	52993	0	13873728
Ergotoxine	38	594,2750	13,22	C34 H36N5O5	20	6,57		0	39873	0	0	0	8269	0	421344	0	981120
Lactam-ergotoxine	45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso* -Ergocristam*	1767644	104215	875818	9880	0	123750	0	472875	41450	0
Lactam-ergotoxine	76	594,3083	12,91	C35 H40N5O4	19	1,38		21371	41673	221972	0	0	0	0	10582	0	0
Lactam-ergotoxine	7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	3812289	12390090	60474038	338496	2724	623582	0	1523631	563247	7034
Ergoxine	72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	0	333331	822	0	0	10301	0	72874	0	3635
Ergoxine	71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	0	83951	0	0	0	26324	0	147465	0	10950
Lactame-ergoannine	5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	24382996	1201116	277413180	3932050	23211	4747290	7579	40956	5966647	0
Ergotoxine	Ergocristine	610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	28984	122373729	487756	13022	235780	20083895	33903	68248638	27639	3159716
Lactam-ergotoxine	93	610,3030	9,88	C35 H40N5O5	19	0,99		28920	166873	559015	0	0	0	0	0	6177	0
Ergotoxine	91	610,3035	9,27	C35 H40N5O5	19	1,81		0	189625	0	0	0	18630	0	90566	0	0
Ergotoxine	Ergocristinine	610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	52945	36297682	99541	5407	52855	51660689	55953	194105254	40582	8746311
Ergotoxine	73	610,3038	13,74	C35 H40N5O5	19	2,30		0	234232	0	0	0	454858	0	2057506	0	53591
Ergoannine	87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	134781	1045240	105097	21489	0	56075349	98443	193555	63673	3760
Ergotoxine	129	624,3188	13,11	C36 H42N5O5	19	1,21		4762	0	34122	0	0	16671	0	0	0	0
Ergoannine	31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	0	143820	1956	0	0	119548806	120573	406457	93361	15093

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot51	Ergot52	Ergot53	Ergot54	Ergot55	Ergot56	Ergot57	Ergot58	Ergot59	Ergot60
								G1	-	G1	G1*	G1	G1	G1	G1	G1	G1
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	0	0	2862239	2402	12947	0	340857	1512	0	0
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		9462	0	14736524	30128	27983	5702	458232	1281	0	0
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	0	0	906061	0	0	0	127054	0	0	0
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	38933	2054	153589	0	1625275	3842	17386	0	1654	44788
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	61686	6522	46067	0	360813	0	5926	0	0	9905
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	0	0	0	0	0	5294	0	0	0	0
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		0	0	0	0	0	0	0	0	0	0
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	3142	0	6342847	7680	64011	0	1195195	0	0	0
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	2220	0	0	0	0	0	0	0	0	0
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	0	0	37707	0	0	0	0	0	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	2409	0	12308018	18961	104164	0	2178056	0	0	0
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	0	0	226616	0	1966	0	61601	1065	0	0
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	0	1034	169052	3324	0	0	64190	3240	0	0
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	0	0	1497557	0	0	0	103981	0	0	0
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	59085	39744	781968	52702	8683	32702	102831	39348	30773	30696
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	0	0	0	0	0	0	0	0	0	0
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		37613	0	0	0	16995	0	2303	0	0	23678
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		75709	0	541119	0	177734	7895	1309	0	48254	170394
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		0	0	0	0	0	0	0	0	0	0
Indole-diterpenoid, hydroxyl	1	420,2895	2,03	C28H38NO2	11	-0,5		0	0	743	0	0	0	0	0	0	0
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	65680	4483	187109	1016	8723	1402	0	0	6831	0
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		0	0	41288	0	0	2055	22302	0	6087	9691
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		0	0	8148	0	0	3329	0	1527	10314	2236
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		0	0	214390	0	0	0	0	0	0	0
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		3977	0	3588160	2925	0	0	59792	0	0	0
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	0	0	22125965	25063	96955	6338	53442	0	0	0
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	7467	0	1334944	0	0	0	2482358	4526	0	0
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	4255	0	841695	0	0	0	2812808	5325	0	0
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		5798	0	0	0	2042	0	965522	1955	0	0
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso*-Ergocornam*	2966	0	68855	0	4497	0	83449	0	0	0
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	12697	0	1994574	0	347641	0	3946110	7822	0	0
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		0	0	2034574	0	0	0	35259	0	0	0
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		5777	0	3747636	6354	2396	0	911122	0	0	0
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		0	0	2792484	2633	1671	0	10845	0	0	0
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		0	0	1634531	1292	0	0	40355	0	0	0
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		10672	9121	7646963	17555	5852	0	713106	0	16995	0
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	554309	24623	284569835	356876	170348	139563	6953346	17907	4552	0
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	297790	27826	230263780	521500	248089	109237	9721880	24408	4441	1461
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		13989	0	20641	0	11091	0	680690	2011	0	0
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso*- alpha-Ergocryptam*	20362	4855	1066046	0	681337	0	2540262	5043	0	0
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		24583	0	61835	0	19202	0	71284	0	0	0
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	0	0	1068751	0	252328	0	2039945	4780	0	0
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	19430	2810	1065236	0	680236	0	2538549	0	0	0

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot51	Ergot52	Ergot53	Ergot54	Ergot55	Ergot56	Ergot57	Ergot58	Ergot59	Ergot60
								G1	-	G1	G1*	G1	G1	G1	G1	G1	G1
Ergotoxine	Ergocorninine	562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	5535	0	170286	0	12036	0	394191	0	0	0
Ergotoxine	Ergocornine	562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	5535	0	171769	0	12369	0	393916	0	0	0
Ergotoxine	33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	19115	0	18779203	20523	11835	5306	350275	0	0	0
Ergotoxine	146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	5535	0	166361	0	12369	0	393750	0	0	0
Ergotamine	88	564,2579	9,94	C33 H34N5O4	20	-4,66		0	0	1597417	3830	0	0	0	0	0	0
Ergotamine	75	564,2582	12,36	C33 H34N5O4	20	-4,13		0	0	5590007	5291	0	2886	0	0	0	0
Ergotamine	81	566,2417	10,94	C32 H32N5O5	20	3,36		0	0	3101775	1184	0	0	20219	0	0	0
Lactam-ergotamin	108	566,2768	10,73	C33 H36N5O4	19	1,09		0	0	435131	0	0	0	0	0	0	0
Lactam-ergotamin	24	566,2768	9,04	C33 H36N5O4	19	1,09		0	0	16230833	17837	2517	4368	0	0	0	0
Lactam-ergotamin	95	566,2770	11,43	C33 H36N5O4	19	1,45		0	0	947932	0	0	0	0	0	0	0
Lactam-ergotamin	46	574,3377	12,92	C33 H44N5O4	15	-1,88		0	0	0	0	0	0	9715	5470	9121	0
Lactam-ergoannine	13	574,3378	10,95	C33 H44N5O4	15	-1,71		9963	0	193025	0	47843	0	348095	0	0	0
Lactam-ergoannine	57	574,3378	11,45	C33 H44N5O4	15	-1,71		0	2833	0	0	3833	2473	5028	3152	3181	0
Ergotoxine	145	576,3171	9,00	C32 H42N5O5	15	-1,64		1830	0	12466	0	5995	0	333559	0	0	0
Ergotoxine	61	576,3174	13,50	C32 H42N5O5	15	-1,12		164382	12591	0	0	0	0	768165	0	0	0
Ergotoxine	Alpha-Ergocryptine	576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	1212779	100848	3259216	22192	1066787	15880	70696043	406170	96416	16867
Ergotoxine	Alpha-Ergocryptinine	576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	4499806	366539	3210994	83031	387562	54813	47454076	357579	65101	9112
Ergotoxine	Beta-Ergocryptine	576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	748601	65858	120042	10315	295096	10237	49510196	268331	74554	13323
Ergotoxine	Berta-Ergocryptinine	576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	1960565	158876	107059	35936	100902	20381	45653777	167046	54089	12520
Ergotoxine	141	576,3199	13,30	C32 H42N5O5	15	3,22		164380	12105	0	0	0	0	768165	0	0	0
Lactam-ergotoxin	140	576,3201	9,71	C32 H42N5O5	15	3,56		0	0	0	0	7674	0	68618	0	0	0
Ergoxine	96	578,2759	13,39	C34 H36N5O4	20	-0,49		0	0	470965	0	0	0	0	0	0	0
Lactam-ergoxine	99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	0	0	946511	0	0	0	0	0	0	0
Ergotamine	105	582,2709	9,07	C33 H36N5O5	19	-0,34		0	0	338198	0	0	0	0	0	0	0
Ergotamine	92	582,2712	8,18	C33 H36N5O5	19	0,18		0	0	1039038	0	0	0	0	0	0	0
Ergotamine	Ergotamine	582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	0	0	142431393	319831	66839	77343	14391	913	0	0
Ergotamine	Ergotaminine	582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	0	0	181132944	253272	59700	93808	12472	0	3153	0
Ergotoxine	35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	52765	0	29074	0	0	0	1523681	0	0	0
Ergotoxine	27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	8234	4922	90670	3245	2116	3674	4275908	49423	8642	3796
Ergotoxine	38	594,2750	13,22	C34 H36N5O5	20	6,57		2091	2379	76624	0	0	0	41390	0	0	527
Lactam-ergotoxine	45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso*-Ergocristam*	0	0	2643056	0	0	0	0	0	0	0
Lactam-ergotoxine	76	594,3083	12,91	C35 H40N5O4	19	1,38		0	0	4505134	0	0	0	0	4818	19779	0
Lactam-ergotoxine	7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	0	0	170333002	184271	41879	49869	0	0	0	0
Ergoxine	72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	0	0	10834807	12531	3058	0	2692	0	0	0
Ergoxine	71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	0	0	11857745	5745	1212	0	0	0	0	0
Lactame-ergoannine	5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	6727	0	23866545	21941	3935	10251	0	0	0	0
Ergotoxine	Ergocristine	610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	43347	4050	321606637	1116646	281510	445044	26070	2453	298	1223
Lactam-ergotoxine	93	610,3030	9,88	C35 H40N5O5	19	0,99		0	0	2103319	0	0	0	0	0	0	0
Ergotoxine	91	610,3035	9,27	C35 H40N5O5	19	1,81		0	0	1551508	0	0	0	0	0	0	0
Ergotoxine	Ergocristinine	610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	74516	7660	356437536	584801	157625	222981	11171	2042	275	875
Ergotoxine	73	610,3038	13,74	C35 H40N5O5	19	2,30		0	0	6468013	2472	0	0	0	0	0	0
Ergoannine	87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	3091	4752	4515779	4058	4652	0	0	0	17203	0
Ergotoxine	129	624,3188	13,11	C36 H42N5O5	19	1,21		0	0	40675	0	0	0	3888	0	0	0
Ergoannine	31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	5017	0	3096906	0	0	0	0	0	0	0

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot1C	Ergot2C	Ergot3C	Ergot4C	Ergot5C	Ergot6C
								G1	G1	G1	G1	G1	G1
Clavine	1	239,1543	5,99	C16 H19 N2	9	0,0	Agroclavine	3344073	7620420	3028365	678339	924277	217817
Clavine	2	241,1699	6,56	C16 H21 N2	8	0,0		6985357	26574136	17996047	3985981	8266743	3002166
Clavine	3	241,1699	5,23	C16 H21 N2	8	0,0	Festuclavine	1510108	8273251	3228355	584384	580771770	7981036
Simple lysergic derivative	Ergonovine	326,1859	4,15	C19H24N3O3	10	-1,24	Ergonovine	416264156	1089575882	695153252	21692385	4328669	266692980
Simple lysergic derivative	Ergonovinine	326,1859	5,17	C19H24N3O2	10	-1,24	Ergonovinine	200557796	475120984	334223431	8078049	1319803	183695826
Simple lysergic derivative	119	340,2015	4,98	C20H26N3O2	10	-1,33	Methylergonovine*	1233084	2951311	2100732	21523	0	755308
Simple lysergic derivative	112	342,1816	2,39	C19H24N3O3	10	1,12		2235679	8316493	4397524	26725	0	1286478
Breakdown product?	15	368,1960	4,38	C21H26N3O3	11	-2,36	Breakdown product?	4895505	7415591	9035850	10469293	71111	1291346
Breakdown product?	120	368,1960	6,30	C21H26N3O3	11	-2,36	Breakdown product?	908719	2991180	662502	0	0	772544
Breakdown product?	113	368,1960	7,17	C21H26N3O3	11	-2,36	Breakdown product?	6703	58753	58023	7575	0	0
Breakdown product?	9	368,1977	3,14	C21H26N3O3	11	2,26	Breakdown product?	11209126	22598754	18265885	10637863	97709	1046223
Breakdown product?	98	380,1964	6,94	C22 H26N3O3	12	-1,23	Breakdown product?	5741841	5504689	1302517	1015482	26187	1083401
Breakdown product?	94	380,1967	8,19	C22 H26N3O3	12	-0,44	Breakdown product?	5280359	5473579	2346163	1539079	38333	1153929
Breakdown product?	6	382,2119	4,24	C22 H28N3O3	11	-1,62	Breakdown product?	7889146	13844335	3051625	2009998	4201	187275
Breakdown product?	12	382,2119	5,22	C22 H28N3O3	11	-1,62	Breakdown product?	1432868	2230742	1072065	1373232	2625	267966
Indole-diterpenoid	1	404,2965	7,58	C28H38NO	11	-0,9	Major C. purpurea indole-diterpenoid	0	0	0	0	0	0
Indole-diterpenoid	22	406,3099	8,43	C28H40NO	10	-1,2		0	60485	0	18646	13329	8762
Indole-diterpenoid	23	406,3099	6,53	C28H40NO	10	-1,2		113630	176288	1869	33351	43883	62647
Indole-diterpenoid	11	420,2891	3,19	C28H38NO2	11	-1,5		0	0	0	0	0	0
Indole-diterpenoid, hydroxyl	1	420,2895	2,03	C28H38NO2	11	-0,5		0	0	0	1589	0	0
Indole-diterpenoid	24	422,3045	5,73	C28H40NO2	10	-1,9	Paspaline	20681	2506	0	2220	0	0
Lactam-ergotoxine	117	471,2742	9,91	C29 H35N4O2	15	-2,66		582226	3983703	712225	261959	11610	324541
Lactame-ergoannine	122	485,2900	10,68	C30 H37N4O2	15	-2,27		280948	2441670	128850	31689	4700	161732
Lactam-ergotoxine	123	515,2660	5,99	C30 H35N4O4	16	1,39		952547	2182184	724281	5264	0	86765
Ergotamine	79	530,2726	11,73	C30H36N5O4	12	0,83		586953	4268339	252702	1270114	15548	26403
Lactam-ergotamine	69	532,2920	8,65	C30 H38N5O4	15	0,32	Ergosine-lactam*	2368283	10108541	745841	4242618	89775	12625
Ergotamine	Ergovalinine	534,2720	10,90	C29 H36N5O5	15	1,69	Ergovalinine	607561	223136	393475	36647542	383606	85459
Ergotamine	Ergovaline	534,2722	8,75	C29 H36N5O5	15	2,07	Ergovaline	423148	172457	351341	32838667	262687	61834
Ergotoxine	142	544,2901	10,69	C31 H38N5O4	16	-3,18		11932	5157	8535	3740358	63013	8307
Lactam-ergotoxine	136	546,3075	11,38	C31H40N5O4	15	0,03	*iso* -Ergocornam*	0	7154	7634	6633144	60242	3005
Lactam-ergotoxine	66	546,3077	9,30	C31H40N5O4	15	0,40	Ergocornam*	311887	129197	139348	133343335	1684437	119920
Ergoxine	116	548,2867	8,82	C30 H38N5O5	15	-0,08		325102	3924190	118424	1704521	9241	11850
Ergotamine	77	548,2867	10,07	C30 H38N5O5	15	-0,08		407307	8800639	641383	3147756	42156	19013
Ergotamine	83	548,2868	7,81	C30H38N5O5	15	0,10		280211	5555785	443236	1400109	8964	10643
Ergotoxine	121	548,2870	7,35	C30 H38N5O5	15	0,46		132539	2571347	113117	657916	4482	9068
Ergoxine	64	548,2870	12,26	C30H38N5O5	15	0,46		903530	16254387	1118876	7415079	118045	46479
Ergotamine	Ergosinine	548,2874	11,74	C30 H38N5O5	15	1,19	Ergosinine	45927453	361827220	21667945	105301626	1540405	3019869
Ergotamine	Ergosin	548,2878	9,51	C30 H38N5O5	15	1,92	Ergosine	38087272	353226415	25315278	119459147	1231702	2908252
Ergotoxine	135	558,3062	11,31	C32 H40N5O4	16	-2,30		929688	871983	684916	7154942	236180	229726
Lactam-ergotoxine	132	560,3235	10,40	C32 H42N5O4	15	0,66	*iso-* alpha-Ergocryptam*	11227453	12125707	13171343	262097034	5132660	710263
Lactam-ergoannine	50	560,3236	12,20	C32 H42N5O4	15	0,84		618915	835856	931552	22418373	218925	66108
Lactam-ergotoxin	42	560,3240	10,03	C32 H42N5O4	15	1,55	alpha-Ergocryptam*	0	0	0	53176880	770925	38022
Lactam-ergotoxin	17	560,3240	10,26	C32 H42N5O4	15	1,55	beta-Ergocryptam*	11226458	12125707	13171343	262106820	5125008	710263

Alkaloid Group	ID	row m/z	RT (min)	Element comp.	RDB	Error (ppm)	Identity	Ergot1C	Ergot2C	Ergot3C	Ergot4C	Ergot5C	Ergot6C
								G1	G1	G1	G1	G1	G1
Ergotoxine	Ergocorninine	562,3011	13,17	C31 H40N5O5	15	-2,30	Ergocorninine	5138	57048	9775	3771001	55019	0
Ergotoxine	Ergocornine	562,3015	10,70	C31 H40N5O5	15	-1,59	Ergocornine	7797	56211	9775	3771001	55019	0
Ergotoxine	33	562,3036	10,26	C31 H40N5O5	15	2,14	Ergoptinine*	3169762	6754223	1698634	53283787	593685	212408
Ergotoxine	146	562,3040	8,45	C31 H40N5O5	15	2,85	Ergoptine*	7356	14453	9775	3727649	52411	0
Ergotamine	88	564,2579	9,94	C33 H34N5O4	20	-4,66		8997776	4391417	6939865	71276	19859	3235441
Ergotamine	75	564,2582	12,36	C33 H34N5O4	20	-4,13		27291765	11254466	13693230	189279	63727	8853107
Ergotamine	81	566,2417	10,94	C32 H32N5O5	20	3,36		423898	220641	374361	70836	0	4228
Lactam-ergotamin	108	566,2768	10,73	C33 H36N5O4	19	1,09		2285489	349570	0	0	0	25743
Lactam-ergotamin	24	566,2768	9,04	C33 H36N5O4	19	1,09		87613423	16992183	49111816	295810	64231	1867321
Lactam-ergotamin	95	566,2770	11,43	C33 H36N5O4	19	1,45		4721545	757840	1708122	5416	0	80051
Lactam-ergotamin	46	574,3377	12,92	C33 H44N5O4	15	-1,88		156381	164173	121585	2137349	8750	36191
Lactam-ergoannine	13	574,3378	10,95	C33 H44N5O4	15	-1,71		3289139	3351197	1407939	23740437	399148	96707
Lactam-ergoannine	57	574,3378	11,45	C33 H44N5O4	15	-1,71		14217	14895	23570	284393	11465	6084
Ergotoxine	145	576,3171	9,00	C32 H42N5O5	15	-1,64		136334	201901	158054	3092001	23118	18302
Ergotoxine	61	576,3174	13,50	C32 H42N5O5	15	-1,12		3562243	3642311	2943332	63229414	594560	536732
Ergotoxine	Alpha-Ergocryptine	576,3177	11,32	C32 H42N5O5	15	-0,60	alpha-Ergocryptine	93457002	92070074	77694929	851108749	20110793	22641553
Ergotoxine	Alpha-Ergocryptinine	576,3179	13,84	C32 H42N5O5	15	-0,25	alpha-Ergocryptinine	96157138	61226254	44975170	861425945	14972784	18795879
Ergotoxine	Beta-Ergocryptine	576,3179	11,46	C32 H42N5O6	15	-0,25	beta-Ergocryptine*	0	0	0	224575850	4291850	0
Ergotoxine	Berta-Ergocryptinine	576,3179	13,91	C32 H42N5O7	15	-0,25	beta-Ergocryptinine*	0	0	0	188593808	2143211	0
Ergotoxine	141	576,3199	13,30	C32 H42N5O5	15	3,22		96692	115275	85506	33461388	273072	49002
Lactam-ergotoxin	140	576,3201	9,71	C32 H42N5O5	15	3,56		283106	156588	170913	4982147	46862	14578
Ergoxine	96	578,2759	13,39	C34 H36N5O4	20	-0,49		4867241	1162308	1517462	0	0	1118876
Lactam-ergoxine	99	580,2933	9,73	C34 H38N5O4	19	2,53	Ergostinam*	3902930	741713	1727557	0	0	89712
Ergotamine	105	582,2709	9,07	C33 H36N5O5	19	-0,34		3170489	830925	1854110	11250	0	473491
Ergotamine	92	582,2712	8,18	C33 H36N5O5	19	0,18		6569958	4261803	17653728	81337	11917	645230
Ergotamine	Ergotamine	582,2715	9,96	C33 H36N5O5	19	0,69	Ergotamine	890933833	412369635	652632466	7359189	1810424	291823917
Ergotamine	Ergotaminine	582,2716	12,41	C33 H36N5O5	19	0,87	Ergotaminine	1036570950	396018655	498002257	6343508	1703911	306134679
Ergotoxine	35	590,3333	14,64	C33 H44N5O5	15	-0,67	Ergogalinine*	506843	319516	622674	7468395	36165	114854
Ergotoxine	27	590,3338	11,98	C33 H44N5O5	15	0,18	Ergogaline*	1340373	1668866	2775575	10546269	28161	597762
Ergotoxine	38	594,2750	13,22	C34 H36N5O5	20	6,57		670081	195178	818467	839519	0	59832
Lactam-ergotoxine	45	594,3083	12,42	C35 H40N5O4	19	1,38	*iso* -Ergocristam*	3057114	4927281	6131826	10067	18419	788287
Lactam-ergotoxine	76	594,3083	12,91	C35 H40N5O4	19	1,38		13105241	6607558	7220008	23470	0	927335
Lactam-ergotoxine	7	594,3088	10,41	C35 H40N5O4	19	2,22	Ergocristam*	287488413	275190889	329595857	3003994	1260962	31576730
Ergoxine	72	596,2853	10,60	C34 H38N5O5	19	-2,43	Ergostine*	66626649	22370601	33736255	214748	69390	18773648
Ergoxine	71	596,2855	13,43	C34 H38N5O5	19	-2,09	Ergostinine*	118742063	27724779	35031442	234189	54407	25249191
Lactame-ergoannine	5	608,3214	11,22	C36 H42N5O4	19	-2,85	Ergosedmine-lactam*	71843246	90371124	53218727	0	91489	10594432
Ergotoxine	Ergocristine	610,3004	11,58	C35 H40N5O5	19	-3,27	Ergocristine	1217130043	1391056484	1133351540	22319671	7598021	702379628
Lactam-ergotoxine	93	610,3030	9,88	C35 H40N5O5	19	0,99		6594850	5965103	4743294	16654	7414	1042229
Ergotoxine	91	610,3035	9,27	C35 H40N5O5	19	1,81		6719663	9295170	10111356	19229	12249	2658173
Ergotoxine	Ergocristinine	610,3038	14,23	C35 H40N5O5	19	2,30	Ergocristinine	1474162882	1073024159	764463371	12879099	4307861	677297276
Ergotoxine	73	610,3038	13,74	C35 H40N5O5	19	2,30		37408565	35357623	37242843	202233	42312	13975099
Ergoannine	87	624,3188	12,47	C36 H42N5O5	19	1,21	Ergosedmine*	11301446	14480903	10434940	61170	35192	13632190
Ergotoxine	129	624,3188	13,11	C36 H42N5O5	19	1,21		74258	227084	3184765	61798	0	388088
Ergoannine	31	624,3195	14,87	C36 H42N5O5	19	2,33	Ergosedminine*	18698977	9391244	5783539	31494	8796	11252189

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